DIGGING DEEPER

VOLUME 2
DIGGING DEEPER

Edited by

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VOLUME 2
The 9th Biennial SGA Meeting is organized by the Irish Association for Economic Geology with assistance from the Society of Economic Geologists

Cover Design: Woodcut showing methods of deepening mines in the 16th Century.
From Georgius Agricola (1556) "De Re Metallica"

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Published and distributed by the Irish Association for Economic Geology

ISBN [0-950989-4-4] set of two volumes
ISBN [0-950989-4-4] Volume 1

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Preface

In 2003 the Council of the Society for Geology Applied to Mineral Deposits (SGA) decided to accept the offer from the Irish Association for Economic Geology (IAEG) to organize its’ 9th Biennial Meeting. The title proposed was “Digging Deeper”, not meant in the this literal sense (although this is partly true in some ore districts) but metaphorically in terms of using more scientific applications and methodologies to understand mineral deposits and also to use advanced techniques in mineral exploration. The IAEG believed that this would have a broad interest to industry which is presently booming and would, we believed, still be in the throws of this boom in 2007.

The IAEG is Ireland’s most influential geological association and has been in existence since 1973 and has hosted several international conferences and published a number of major thematic volumes. However the 9th Biennial SGA Meeting will be the largest geological conference ever held in the country and an event that the IAEG is proud to be associated with.

Although the minerals industry has traditionally been “boom and bust”, the current strong upsurge in metal prices (hitting historic record levels for several commodities), and the resultant boom for the exploration and mining industry has been coupled with a major problem in that limited experienced geological professionals are available for the industry’s demands. This is an issue that must be addressed, and urgently.

Of particular interest has been the massive upsurge in recent times of exploration for uranium, coupled not only with the substantive price rise, but also with the world-wide demand to deal with perceived global-warning. Clearly in an energy driven world fossil fuels are not only now perceived as damaging but also are clearly finite and hence the newly perceived “green credentials” of nuclear power. This interest was underlined by the strong interest in the thematic session on uranium at the conference.

Closer to home the Irish minerals industry continues, and enjoys good profitability at last, and the zinc mines at Navan, Lisheen and Galmoy prosper and a new phase of exploration in the Irish midlands has began to flourish and Ireland’s first gold mine achieved producer status in 2007.

Twenty two thematic sessions were agreed by the SGA and the call for presentations brought 409 extended abstracts for review from authors based in 49 different countries. The Society of Economic Geologists kindly organized a thematic session entitled Compressional Tectonics, Expanding Resources: Exploration Advances in the Tethyan Belt.

The team of 46 Conveners completed their tasks of review and the result of this effort is the volumes to which this note is the preface and which includes 394 presentations. I would like to thank all of these individuals for the sterling effort they put in, not only as reviewers but also as solicitors for additional papers. The presentations were made over four days in four parallel oral sessions with additional poster display sessions.
Eight short courses were offered over the weekend prior to the conference - Orogenic Lode Gold Deposits, Granite related Gold Deposits, Sediment Hosted Base-Metal Deposits, Sediment Hosted Base Copper Deposits, Isotopes in Exploration, Exploration for Skarn Deposits, Applied Structural Geology for Economic Geologists, Advances in 3D Geological Modelling. In addition seven field trips to the Iberian Pyrite Belt, Parys Mountain/Avoca, Irish Zn/Pb Deposits, Lode Gold Deposits in Dalradian of Northern Ireland, Rehabilitation of Old Mine Sites in Ireland, Fennoscandinavia and to Poland were offered and run.

In addition an extensive social program for delegates and for accompanying persons was organized and attracted an extremely high level of interest.

Of course no conference such as this could be organized without you the delegates, the speakers the poster presenters, the conveners and the session chairmen. The IAEG thanks you for all of your efforts thus far and it behoves me, and behalf of the Organizing Committee, to wish you all a successful and scientifically fulfilling meeting and also to encourage you to enjoy the delights of Dublin and Ireland.

Colin J. Andrew  
Chairman – Technical Sessions  
Navan, Ireland  
June 2007
**Meeting Committee**

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Assessment of bentonite deposits: a challenge for the resource geologist

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ABSTRACT: Assessment of bentonite deposits is a complex task, which is not based only on mineralogical and geological criteria, but must include determination of distribution of the layer charge of smectites. The layer charge affects important physical and chemical properties of bentonites, such as swelling, rheological properties and cation exchange capacity. The layer charge distribution is related to the formation of the bentonite and/or later geological processes, which have affected the deposit. Determination of the distribution of the layer charge is a challenge for the resource geologist, but knowledge of it enables rational exploitation and efficiency during processing.

KEYWORDS: bentonite, smectite, layer charge, bentonite assessment

1 INTRODUCTION

Bentonites are clays consisting essentially of smectites irrespective of their mode of origin. Due to their unique physical and chemical properties they are utilized in a variety of industrial applications, including foundries, oil drillings, civil engineering and environmental applications, animal litter etc (Elzea & Murray 1994). Recent advances include utilization of smectites in the formulation of nanocomposites with improved properties. Prospecting for bentonite deposits begins with recognition of the raw material in the field. A simple guide for recognition of a bentonite is the “pop-corn” texture due to consecutive swelling and contraction (Christidis & Scott 1993). In many occurrences bentonites form beds, stratigraphic markers, often used for geological correlation. Hydrothermal deposits often form irregular bodies controlled by tectonics. A high quality bentonite should be compact, soft and soapy to the feel. Bentonite colour varies considerably according to the nature of the parent rock, the geological history and the distance of the deposit from the surface (buried or exposed).

Although bentonites are relatively common raw materials their evaluation is a rather difficult task, due to the considerable heterogeneity of smectites within a single deposit and the geological history of the deposit, which is often complex. This is especially the case in active geothermal terrains, associated with volcanic activity. The objective of this contribution is to show some recent advances in the evaluation of bentonite deposits, which allow the understanding of some important physical properties and shed light on the mechanism of genesis of deposits. This in turn allows more rational methods of exploration and exploitation of similar deposits.

2 CURRENT METHODS FOR EVALUATION OF BENTONITES

In a previous contribution Christidis & Scott (1993) proposed an evaluation scheme for bentonites, which consists of two main steps. The first step involves confirmation of any field recognition using mineralogical techniques the most important of which is X-ray diffraction (XRD). XRD will enable pure smectite to be distinguished from mixed layer illite-smectite (IS). Possible existence of illitic layers in the clay fraction deteriorates the physical and chemical properties of bentonites. Typical commercial bentonites containing random mixed layer illite-smectite (K-bentonites), exist in the USA (Ota type-smectite California) and Greece (Milos) (Berry 1999, Christidis & Scott 1996). XRD investigation may be complemented by other techniques such as thermal
The importance of qualitative mineralogical investigation of a bentonite must not be overemphasized because the behaviour of the clay in its industrial applications depends on the structure of the smectite and the other minerals present. Therefore in the second step the quality and grade of the deposits is determined. In bentonite deposits the terms quality and grade are used separately in contrast with other raw materials (Ingleshorpe et al. 1993, Christidis & Scott 1993, 1996). Hence quality refers to the performance of the material in its different applications whereas grade refers to the smectite content of the bentonite. The quality of a bentonite can be assessed in the laboratory by sodium carbonate exchange and determination of the swelling efficiency (swelling index) and/or of the liquid limit. Although with these tests the optimum carbonate addition is determined, in industry the optimum sodium carbonate addition usually varies in different applications. The grade of a bentonite can be assessed by measurement of the cation exchange capacity (CEC) and/or its total specific surface area usually with ethylene glycol monoethyl ether (EGME). Both quality and grade can be affected by later geological processes after formation of the bentonite. Important factors are hydrothermal alteration and/or diageneis. For instance grade is affected by illitization or kaolinization of smectite, by formation of smectite with different layer charge and/or by formation of nonsmectitic minerals (Christidis & Scott 1996). Quality is also affected by lowering of the pH of bentonite, by formation of smectite with different layer charge and/or different lattice dimensions. Although in general a high grade bentonite also has high quality, the postdepositional geological history of a bentonite may result in significant exceptions.

Most bentonite deposits contain Ca-smectite (Ca-bentonites), whereas Na-bentonites are rather rare. However most industrial applications use Na-bentonites due to their superior colloidal and binding properties. Hence the industrial practice involves conversion of Ca-bentonite to their Na-rich counterparts using Na-carbonate (a process known as Na-activation). The influence of Na-activation on the colloidal properties of bentonites is unpredictable (Odom 1984). Hence, quality may vary considerably within a bentonite deposit, but the reasons for this have not been well understood. Recent work in our laboratory has shown that layer charge of smectites is a significant parameter, which may vary considerably in a deposit.

The possible extent of variation of smectite layer charge in a bentonite deposit has not been studied in the past mainly due to limitations in the determination of the layer charge. So far there are two main methods used for determination of layer charge, the structural formula method and the alkylammonium method (Laird 1994, Lagaly 1994). The main limitations of the two techniques is that they are time consuming, especially the alkylammonium method. They require the employment of skillful personnel and they have certain limitations related either to the influence of impurities or to analytical constraints, which lead to underestimation or less frequently, to overestimation of layer charge. To the author’s knowledge, there is only one reference on the distribution of layer charge in a bentonite deposit, using only three samples, which nevertheless did not reveal layer charge heterogeneity (Lagaly 1981). Recently a new method for determination of layer charge of smectites has been proposed by Christidis & Eberl (2003). This method has been applied in large bentonite profiles and has revealed systematic trends which are related either to the mode of genesis of bentonites or to later geological processes, which affected the profiles, such as hydrothermal alteration.

3  NEW METHOD FOR MEASUREMENT OF LAYER CHARGE OF SMECTITES

The method of Christidis & Eberl (2003) is based on the comparison of XRD traces of K-saturated, ethylene-glycol solvated smectites with simulated XRD-traces calculated for threecOMPONENT interlayering (fully expandable, low charge 17.1 Å layers, partially expandable, intermediate charge 13.5 Å layers and nonexpandable, high charge, 9.98 Å layers). Measurement of layer charge and charge distribution is possible by means of the LayerCharge computer code (Eberl & Christidis 2002). The program finds the calculated pattern which minimizes the sum of square differences between: a) the experimental and calculated peak positions for the first 6 00l reflections or b) the whole pattern fit of experimental and calculated intensities normalized to the intensity of the most intense peak. Then it assigns the proportion of 17.1Å/13.5Å/9.98Å layers (i.e. charge hetero-
geneity) and calculates the layer charge. Using this method recently Christidis et al. (2006) proposed a classification scheme for smectites according to the layer charge as follows. Smectites with layer charge lower than -0.425 equivalents per half formula unit (phfu) for montmorillonite (-0.365 equivalents phfu for beidellite and nontronite because tetrahedrally charged smectites yield XRD traces like montmorillonites with fewer low charge layers) are classified as low charge smectites. Smectites with layer charge higher than -0.47 equivalents phfu (-0.415 equivalents phfu for beidellite and nontronite) are classified as low charge smectites. Smectites with layer charge between -0.425 and -0.47 equivalents phfu (-0.365 and -0.415 equivalents phfu for beidellite and nontronite) are high charge smectites. Finally smectites with layer charge between -0.425 and -0.47 equivalents phfu (-0.365 equivalent phfu for beidellite and nontronite) are classified as smectites with intermediate layer charge. This classification scheme has been found to be in accordance with the rheological properties of smectites, such as viscosity, yield stress, gel strength and thixotropy (Christidis et al. 2006).

4 DISTRIBUTION OF LAYER CHARGE IN BENTONITE DEPOSITS

The main advantages of the new method of calculation of layer charge, compared to the existing ones, include the simplicity of sample preparation, which does not necessitate specialized personnel and the limited influence of mineral impurities on the determination of layer charge. This method was applied to determine the distribution of layer charge in two vertical bentonite profiles in from Milos, Greece. The bentonite in Profile 1 formed from a pyroclastic flow. In Profile 2 it formed at the expense of a dacitic-andesitic lava. The dimensions of each profile were 130m by 35m and sampling was carried out in a grid with grid-cell dimensions 12m length and 3m height. 70-80 samples were obtained from each profile. The two profiles display different distribution trends of smectite layer charge.

Profile 1 is characterized by an anomaly of layer charge in its lower part dominated by high charge smectites, whereas the rest of the profile contains smectites with intermediate layer charge. Profile 2 is characterized by gradual increase of layer charge from the base to the top of the profile without systematic anomalies. The observed differences are related to different geological processes related to the formation and evolution of the deposits. The layer charge anomaly in the first profile is not associated with bentonitization of the volcanic glass but is related to a hydrothermal event, which postdated the formation of bentonite. The high charge smectite is secondary; it coexists with kaolinite and K-feldspar and is characterized by platy flakes similar to the coexisting kaolinite. In fact the two phases are morphologically inseparable and can be distinguished only from their chemical composition; kaolinite is Al-rich and Mg- and Fe-rich compared to smectite.

The distribution of layer charge in profile 2 is related to bentonite genesis. This is because there is no indication of significant modifications, after the formation of the profile, such as those commonly observed in Milaan bentonites (kaolinization, illitization, silicification or alunitization). The gradual increase of layer charge towards the top of the profile indicates either an increase of octahedral Mg or an increase of tetrahedral Al in the smectite structure. Since there is no indication for systematic variations of Mg or of the Si/Al ratio in the precursor lava, the gradual increase of layer charge indicates a gradual increase of Mg-uptake or/and a gradual release of Si (Al is essentially immobile during alteration) in the same direction. Data from unpublished leaching experiments on acidic volcanic glass, which simulated an open environment, show significant increase of Mg-uptake and release of Si with increasing water:rock ratio and with increasing temperature. Since alteration temperature is expected to be lower at shallower water depths, the increase of Mg-uptake and/or the release of Si is probably related to the increasing water:rock ratio upwards. Therefore the observed systematic variation of layer charge is related to permeability differences during alteration.

5 SIGNIFICANCE OF LAYER CHARGE-ROLE OF THE RESOURCE GEOLOGIST

Assessment of bentonite deposits is a complex task, which takes into account several parameters. The role of resource geologist begins with the discovery and delineation of the deposit in the field, followed by determination of key parameters such as quality and grade. Any possible variations in these parameters must be evaluated, since they are affected by variations in layer charge. For instance an important physical property, which is determined in the case of grade is CEC. This depends not only on the abundance of smectites but also on the layercharge....
charge. Hence for two bentonites with similar smectite content the one with higher layer charge will have a higher CEC. Similarly, in the case of quality, both the swelling efficiency and the liquid limit are affected by layer charge, because they are associated with the so-called crystalline swelling of smectites (cf. Laird 2006). In this sense the layer charge affects the efficiency of Na-activation, because it controls the thickness of smectite quasicrystals enhancing hysteresis in ion exchange. Therefore a new important task for the resource geologist is the determination of possible variations in layer charge within the deposit. This will enable rational exploitation and maximum efficiency during processing.

ACKNOWLEDGEMENTS

This work was funded by the Greek Secretariat of R&D and the Fulbright Institution

REFERENCES

Berry RW (1999) Eocene and Oligocene Otay-type waxy bentonites of San Diego County and Baja California; chemistry, mineralogy, petrology and plate tectonic implications. Clays Clay Miner. 47: 70-83.


Economic Geology of the Ceramic Clays in Castellón, Spain

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ABSTRACT: The tile and clay pavement industry in Spain is mainly located in the province of Castellón. The manufacture of wall tiles, floor tiles and ceramic coating uses red clays as raw materials. The clay raw materials occur in Permo-Triassic sediments, Saxonian and Bunter Sandstone facies, Cretaceous sediments, Weald and Utrillas facies, and Tertiary sediments. The Tertiary clays of the province of Castellón have a variable mineralogical composition with kaolinite, chlorite and some interstratified elements. Montmorillonite is sometimes recognised. The non-clay minerals are quartz, gypsum, calcite and feldspars. Permo-Triassic clays, from a ceramic point of view known as the “arcilla del Moró” have a low carbonate content (<5%) and are mainly used in the press manufacturing of red paste glazed stoneware. The clay minerals typical of the inferior unit and of the “arcilla de Moró” are illite ± kaolinite ± chlorite ± I/S ± K/S. The Cretaceous clays contain quartz, illite, feldspars, hematite, chlorite and calcite. Red clays for ceramic coatings and pavements are mainly extracted in the Valencian Community, in Villar del Arzobispo, La Yesa, Chulilla, Alcora (Más Vell) and San Juan de Moró, although there is a small proportion coming from Teruel province. The total production reaches 9 to 10 Mt/year and the invoicing exceeds 33 M€. The main producer is the national affiliate of the British multinational company WBB, part of the Belgian group SIBELCO, one of the major world-wide producers of industrial minerals. They currently extract 4 Mt/year from their quarries in San Juan de Moró, Higueruelas and Galve and they are the main clay supplier to the industry of Castellón.

KEYWORDS: Ceramic clays, Mineralogy, Economic geology, Ceramic tiles, Castellón province

1 INTRODUCTION

The Spanish tile and clay pavement industry is mainly located in the province of Castellón (Figures 1 and 2). Nowadays, more than 50% of its production is exported. The manufacture of wall tiles, floor tiles and ceramic coating uses red clays as raw materials. White body clays or ball-clays are less than 5% of the total amount. Other raw materials are also consumed, such as kaolin, calcined clays, feldspars, siliceous sand, mineral pigments, etc. It is a major industry, second after Italy in world ranking. The production data (2002-2004) are shown in Table 1. Both red and white or ball clays are consumed. In order to obtain the proper homogeneity, purity and particle size for the final product quality, pre-treatment of the clays is necessary in the manufacturing process. Two treatments are used: i) a dry-via process, or grinding without adding water, and ii) humid-via process or atomization.

The dry-via process is more common among Catalan companies which manufacture ceramic products processed by extrusion (face bricks, tiles), while those located in Castellón mainly use atomization processes. In this process the clay is pulverised whilst suspended in water against a warm air flood. The result is microscopic spheres of clays filled with air. These provide a suitable material for the dry pressing of floor tiles.

During firing the clay minerals and accompanying minerals like quartz, feldspar, calcite, dolomite and haematite, undergo a series of transformations which determine the final properties of the ceramic products (Jordán et al., 1999). The crystalline structures, once they exceed their stability limits, partially decompose and simultaneously new minerals are be-
ing formed. An instant or complete destruction of the pre-existing structure does not occur (Jordán et al., 1999).

Table 1. Spanish production of ceramic tiles (x 1000m²). Source: Ascer

<table>
<thead>
<tr>
<th>Production</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruded</td>
<td>17.511</td>
<td>17.900</td>
<td>18.840</td>
</tr>
<tr>
<td>% total production</td>
<td>2.7%</td>
<td>2.9%</td>
<td>2.9%</td>
</tr>
<tr>
<td>Porcelain tiles</td>
<td>55.475</td>
<td>65.939</td>
<td>76.527</td>
</tr>
<tr>
<td>% total production</td>
<td>8.5%</td>
<td>10.5%</td>
<td>12.0%</td>
</tr>
<tr>
<td>Wall tiles</td>
<td>245.646</td>
<td>246.197</td>
<td>250.051</td>
</tr>
<tr>
<td>% total production</td>
<td>37.7%</td>
<td>39.3%</td>
<td>39.1%</td>
</tr>
<tr>
<td>Glazed floor tiles</td>
<td>332.368</td>
<td>296.963</td>
<td>294.582</td>
</tr>
<tr>
<td>% total production</td>
<td>51.1%</td>
<td>47.4%</td>
<td>46.0%</td>
</tr>
<tr>
<td>Porcelain tiles</td>
<td>55.475</td>
<td>65.939</td>
<td>76.527</td>
</tr>
<tr>
<td>Glazed porcelain tiles</td>
<td>37.168</td>
<td>45.000</td>
<td>57.532</td>
</tr>
<tr>
<td>% total porcelain tiles</td>
<td>67.0%</td>
<td>68.2%</td>
<td>75.2%</td>
</tr>
<tr>
<td>Unglazed porcelain tiles</td>
<td>18.307</td>
<td>20.939</td>
<td>18.994</td>
</tr>
<tr>
<td>% total porcelain tiles</td>
<td>33.0%</td>
<td>31.8%</td>
<td>24.8%</td>
</tr>
<tr>
<td>Glazed tiles</td>
<td>610.840</td>
<td>588.446</td>
<td>602.446</td>
</tr>
<tr>
<td>% total production</td>
<td>93.8%</td>
<td>93.9%</td>
<td>94.1%</td>
</tr>
<tr>
<td>Unglazed tiles</td>
<td>40.160</td>
<td>38.554</td>
<td>37.554</td>
</tr>
<tr>
<td>% total production</td>
<td>6.2%</td>
<td>6.1%</td>
<td>5.9%</td>
</tr>
<tr>
<td>Twice firing</td>
<td>31.140</td>
<td>27.698</td>
<td>25.842</td>
</tr>
<tr>
<td>% total production</td>
<td>4.8%</td>
<td>4.4%</td>
<td>4.0%</td>
</tr>
<tr>
<td>Single firing</td>
<td>619.860</td>
<td>599.302</td>
<td>614.158</td>
</tr>
<tr>
<td>% total production</td>
<td>95.2%</td>
<td>95.6%</td>
<td>96.0%</td>
</tr>
<tr>
<td>Red/buff body</td>
<td>531.207</td>
<td>483.223</td>
<td>480.805</td>
</tr>
<tr>
<td>% total production</td>
<td>81.6%</td>
<td>77.1%</td>
<td>75.1%</td>
</tr>
<tr>
<td>White body</td>
<td>119.793</td>
<td>143.777</td>
<td>159.195</td>
</tr>
<tr>
<td>% total production</td>
<td>18.4%</td>
<td>22.9%</td>
<td>24.9%</td>
</tr>
<tr>
<td>Total ceramic tiles</td>
<td>651.000</td>
<td>627.000</td>
<td>640.000</td>
</tr>
</tbody>
</table>

Table 2. Classification of the raw materials used in the ceramic industry of Castellón.

<table>
<thead>
<tr>
<th>Denomination</th>
<th>% weight</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low carbonate content clays</td>
<td>&lt; 5</td>
<td>Sant Joan de Moró (Cs) Morella (Cs) Villar (V) Higuernelas La Yesa (V) Galve (Te)</td>
</tr>
<tr>
<td>Medium carbonate content clays</td>
<td>5-15</td>
<td>Chulilla (V)</td>
</tr>
</tbody>
</table>
| High carbonate content clays | > 15 | Mas Vell Sitjar Araia (Cs)

The disappearance and the neomineralization by firing in ceramic kilns have extensively been reported in literature. Calcareous clays or marl were the subject of a study by Peters & Jenny (1973) and Pollifrone & Ravaglioli (1973). Capel et al. (1985) studied the formation of gehlenite and calcic plagioclase in calcareous clays. González-Garcia et al. (1990) verified the presence of gehlenite and anorthite phases when firing clays from Guadalquivir valley which were originally composed of illite, kaolinite, quartz and calcite. Jordan et al. (1993, 1999) studied the Cretaceous clays and their behaviour when subjected to rapid firing.

2 RED CLAYS USED IN SPANISH CERAMIC INDUSTRY

The main clay raw materials used in the ceramic industry in Castellón are shown in Table 2. The main feature of these clays and in general of all the sedimentary deposits is the heterogeneity of their mineralogy. This leads to a major variability in the properties of the products. Variation is minimized by using the homogenization systems carried out at the mine site, in the atomizers or separately by the manufacturing companies. In general, such systems consist of building up piles (backlogs) of horizontal layers made up of materials of various qualities coming from different exploitation areas.

The Tertiary clays of the province of Castellón have a diverse mineralogical composition with variations in kaolinite, chlorite and some interstratified elements. Other mineral phases are montmorillonite, quartz, gypsum, calcite and feldspars. The clay fraction is made up of illite and/or kaolinite and/or chlorite and/or interstratified elements. Changes in mineralogy relate to differences in technological properties and the manufacturing process. "Arcilla de Moró" is the commercial name for one of the most widely used clays ever since the 1970s. It was initially used for manufacturing bricks and then for manufacturing ceramic tile bodies. An essential aspect of this raw material is the closeness of its source to the manufacturing centres. This represents an added advantage not
only with respect to the other raw materials of the same characteristics, whether those in Villar del Arzobispo (Valencia) or in Galve (Teruel), but also to new raw materials such as the clay from Morella (Castellón). From a ceramic point of view, the “arcilla del Moró” is classified as a low carbonate content raw material (<5%), mainly used in the press manufacturing of red paste glazed stoneware. These raw materials belong to Upper-Permian (Martín-Martín et al., 2005). The association of minerals of the clay typical of the inferior unit and of the “arcilla de Moró” is made up of illite ± kaolinite ± chlorite ± 1/S ± K/S.

The clay from Morella, determined semiquantitatively by XRD, shows the following mineralogical composition: quartz (33%), illite (14%), sodium feldspar (7%), potassium feldspar (3%), hematite (7%), chlorite (3%) and calcite.

The technological properties of the red clays from Morella make it being very suitable for manufacturing low-porosity product, such as glazed stoneware. The balance of the properties of plasticity-unfloculability-pressibility- is optimum (Sánchez et al., 2005).

3 CLAY CERAMIC INDUSTRY

Red clays for ceramic coatings and pavements are mainly extracted in the Valencian Community (Table 3), in Villar del Arzobispo, La Yesa (1 Mt/year), Chulilla, Alcora (Más Vell, 200,000 t/year) and San Juan de Moró (2 Mt/year), although there is a small proportion - 250,000 t/year- coming from Galve (Teruel).

The total production is around 9-10 Mt/year and the invoicing exceeds 33 M€. A new production centre belonging to the company Vega de Moll, S.A. in Morella (Castellón), is nowadays supplying approximately 500,000-700,000 t/year to the pavement sector. There is a wide diversity in the price paid for the direct from the quarry. For example, the prices of the clays from San Juan de Moró are 3-6 €/t, Galve 3-6 €/t. The sands (200,000 t/year) and kaolin (40,000 t/year) extracted in Villar del Arzobispo-La Yesa are up to 10 and 50 €/t respectively. In this area, kaolin-rich sands are also extracted (300,000 t/year); such sands have an intermediate price. The price of the red clay for bricks is 1.8-2 €/t, in contrast with other prices.

The main producer of clays for ceramic tiles is the national affiliate of the British multinational WBB, part of the Belgian group SI-BELCO. This company is one of the major world producers of industrial minerals. Extraction nowadays extracts 4 Mt/year from their quarries in San Juan de Moró, Higueralas and Galve. This group is the main clay supplier to the industry of Castellón.

Table 3.- Clays for ceramic industry extracted in the Valencian Community (2006).

<table>
<thead>
<tr>
<th>Quarry</th>
<th>Production (t/y)</th>
<th>Price (€/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Villar del Arzobispo</td>
<td>1 Mt/y (red clay)</td>
<td>3-6</td>
</tr>
<tr>
<td></td>
<td>300,000 (kaolin)</td>
<td>10-50</td>
</tr>
<tr>
<td>Alcora (Mas Vell)</td>
<td>200,000</td>
<td>1.8-2</td>
</tr>
<tr>
<td>San Juan de Moró</td>
<td>2 Mt/y</td>
<td>3-6</td>
</tr>
<tr>
<td>Galve</td>
<td>250,000</td>
<td>3-6</td>
</tr>
<tr>
<td>Morella (Vega del Moll)</td>
<td>500,000-700,000</td>
<td>3-6</td>
</tr>
</tbody>
</table>
The remaining production comes from about 20 smaller companies which produce about 250,000 and 400,000 t/year each in their quarries in Villar del Arzobispo, La Yesa, Alpuente and Chulilla.

ACKNOWLEDGEMENTS

Authors would like express their gratitude to: Ricardo García of WBB España SA, and Enrique Domínguez of Cámara de Comercio, Industria y Navegación de Castellón.

REFERENCES


ABSTRACT: Lightweight aggregates (LWA) of natural and artificial origin are currently used in many European countries in various construction engineering applications (precast structural units, road surfacing materials, shallow foundations, loose insulating fill, etc.) as well as in gardening and agriculture (hydroponics and soil conditioning). LWAs are commonly produced by calcination in a rotary kiln of wet clayey material with burnable matter (<5%). The aim of the present study is to characterise the raw materials and the lightweight aggregates (LWA) produced with raw materials derived from Milos Island bentonite deposits overburden, and the Western Macedonia lignite deposits overburden. Fly ash additive was also introduced in some experiments. The sintered products are glassy, containing besides the amorphous phase, a series of neoformed minerals. The internal porosity of the various LWAs produced had differences, leading as a consequence to apparent density and compressive strength dissimilarities. In general, the LWAs formed with the Milos raw materials have better technical properties than that of W. Macedonia. Small amounts of fly ash can be used in mixtures with some of the raw materials. In order to achieve any industrial exploitation of the clayey raw materials tested, besides the sufficient reserves, several technical parameters have to be measured, such as the raw material’s grain size and shape, surface area, permeability and density, presence of deleterious components, and optimum calcining temperature for different mixtures.

KEYWORDS: LWA, bentonite, mining wastes, expanded clays, fly ash, lignite overburden, Greece
3. RAW MATERIALS CHARACTERISATION

The mineralogy by XRD of bulk samples from W. Macedonia and Milos Island are presented in Tables I & II. Field and laboratory examination of a large number of samples collected from the clayey deposit show that they are homogeneous. The W. Macedonian samples are of sedimentary origin, having diverse mineralogy and age. The claystone of Notio Pedio lies above Pliocene lignite seams, composed of carbonates, clay and detrital minerals. The other two clayey rocks overly Upper Miocene lignite layers of xylite-type and could be characterised as clayey diatomite, mainly composed of diatom frustules (opal-A) and expanded clay minerals. They also contain detrital minerals, such as feldspar and quartz. The fly-ash used was from Amynteon power plant, located close to Vegora deposits. It is mainly composed of amorphous material, quartz and minor haematite, anhydrite, gehlenite and portlandite.

The Milos Island samples are of volcanic origin, mainly composed of an amorphous phase (volcanic glass), clay minerals and feldspars. Some samples contain detectable amounts of sulphates, sulphides and silica polymorphs. Their presence is mainly due to hydrothermal alteration of the parent rock by H₂S-rich fluids. Some carbonates are also present.

<table>
<thead>
<tr>
<th>N. Pedion</th>
<th>Vegora</th>
<th>Komnina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Opal-A</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Feldspars</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Smectite</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Illite</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Calcite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Vermiculite</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Chlorite</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>After</th>
<th>Sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>X</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>X</td>
</tr>
<tr>
<td>Feldspars</td>
<td>X</td>
</tr>
<tr>
<td>Diopside</td>
<td>X</td>
</tr>
<tr>
<td>Augite</td>
<td>X</td>
</tr>
<tr>
<td>Clinopyroxene</td>
<td>X</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>X</td>
</tr>
<tr>
<td>Hercynite</td>
<td>X</td>
</tr>
</tbody>
</table>

4. CHARACTERISATION OF THE SINTERED PRODUCTS

4.1. Pelletizing and Calcining procedure

The pulverised materials were mixed in wet conditions with 5% burnable matter, crude oil for Milos Island samples and sawdust for W. Macedonia samples, according to their availability in each place. Water was added to the mixture in a ratio ~1/1, in order to produce spherical shapes without shrinkages. The formed pellets sizing of 0.5-2cm were calcined in a laboratory kiln for 12-15 min in the Department of Geology & Geoenvironment, NKUA. The optimum firing temperature was 1100ºC for the Macedonian samples and 1170ºC for Milos Island samples. The sintered pellets had a diameter slightly higher than the original one, due to escaping gases at the melting stage. They have a brownish colour and mostly retain their original spherical to cauliflower shape.

4.2 Mineralogical analysis of sintered products

The laboratory produced LWAs were examined by XRD to identify the synthetic mineral phases formed during sintering. The results are presented in Tables I & II. The mineralogy of the LWAs is characterised by the predominance of a synthetic glassy phase, and silicates,
mainly mullite, wollastonite, merwinite, sillimanite and hercynite.

4.3 SEM determinations on the LWAs structure

To determine the texture of the clayey material and to identify sulphides, sulphates and other minerals contained in the studied rocks in trace amounts, SEM analysis was performed in the laboratories of the Geology & Geoenvironment Department, NKUA (JEOL-JSM 5600, EDX, OXFORD LINK ISIS300).

The porosity of the various laboratory produced LWAs, both internal and external had differences, the outer being lower than that of the inner, leading as a consequence to apparent density dissimilarities as well as to an influence on the properties of the final products. In order to measure and compare the porosity, the pore size and the internal and external shape of the various LWAs, broken chips of various pellets were examined. Under the SEM, the texture of most of the LWAs is amorphous with spherical to almost irregular pores from <5µm up to 700µm. Commonly, they present a series of pores of different size forming “channels” and “flows” inside the glassy material.

Under the SEM, the diversity and the multiple phases of development of pores, the channels of micro-pores and the unbroken bubbles in some pore channels is clearly visible. No macro-crystalline phases are present inwards or outwards in the LWAs, although neoformed minerals are found by XRD.

4.4 Physical parameters of the laboratory produced LWA

4.4.1. Apparent Density

After producing of about 2kg of LWAs of each category, their apparent density was measured using a volumetric cylinder of 1000ml. The results are diverse. Mean values are presented in Table III.

4.4.2. Fracture load

An adequate series of LWA pellets, each of which had a different size and origin underwent a mechanical shatter by using a special apparatus in TITAN Cement Company laboratories, (Kamari Viotia Plant), in order to measure their fracture load and indirectly their compressive strength. The results are variable and are also presented in Table III.

The experimental determinations showed that the optimum combination of good compressive strength and low apparent density, is found in samples of Ag. Irini and Aspro Chorio at Milos Island, as well as from Vegora in Macedonia. Furthermore, it has been shown that a small amount of fly ash (~5%) can be introduced into the clayey raw materials of Vegora without changing the final properties. Higher amounts of fly ash cause undesirable and poor technical properties (Table III).

Table III: Technical characteristics of the laboratory synthesized LWAs

<table>
<thead>
<tr>
<th>Location/material</th>
<th>Apparent density gr/cm³</th>
<th>Fracture load N/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milos Island Bentonite overburden</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag Irini</td>
<td>0.45</td>
<td>1.82</td>
</tr>
<tr>
<td>Aspro Chorio</td>
<td>0.40</td>
<td>2.48</td>
</tr>
<tr>
<td>Koufi</td>
<td>0.26</td>
<td>0.40</td>
</tr>
<tr>
<td>W. Macedonia Clayey lignite overburden</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notio Pedio</td>
<td>1.75</td>
<td>1.1</td>
</tr>
<tr>
<td>Not.Pedio+5%FlyAsh</td>
<td>1.85</td>
<td>0.95</td>
</tr>
<tr>
<td>Not.Pedio+15%FlyAsh</td>
<td>1.96</td>
<td>0.80</td>
</tr>
<tr>
<td>Komnina</td>
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<td>1.20</td>
</tr>
<tr>
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<td>1.32</td>
<td>1.10</td>
</tr>
<tr>
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<td>1.62</td>
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<td>Vegora</td>
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<tr>
<td>Vegora+5%Fly Ash</td>
<td>1.01</td>
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<tr>
<td>Vegora+15%Fly Ash</td>
<td>1.25</td>
<td>0.90</td>
</tr>
</tbody>
</table>

5. CONCLUSIONS

Both the Tertiary clayey sediments and the Quaternary tuffites/tuffs raw materials led to the laboratory-produced LWAs that have apparent density and compressive strength similar to those of commercial LWAs originating from Denmark and Germany.

The laboratory and commercial LWAs are mostly composed of a glassy phase entrapping honey-comb shaped voids ranging from 5 to 700µm. Some of the pellets derived after calcining are massive with a glaze texture and few pores in their core resulting to apparent density >1gr/cm³. The tested samples, which have a good combination of compressive strength and apparent density exhibit differences, not related to their bulk mineralogy, as most of them have
similar composition. In general, the Milos Island samples, have poor strength and density. In contrast, some of the samples containing smectite clays in percentage ~ 30-40% produce good LWAs, exhibiting good physical and mechanical properties. The viscosity of the melt during calcining, and hence the ability of vapours to be entrapped in it, is also influenced by trace mineral components in the samples such as carbonates. The optimum percentage of the combustible material added in the mixture is ranging between 3 to 5% (Fragoulis et al. 2003). The combustible material used could be crude oil, pet-coke, lignite powder or sawdust, the last one exhibiting the best performance (Alfieris et al. 2005). Comparing the calcining temperatures of the samples, the Milos ones need higher temperature (1170°C), probably due to the presence of volcanic glass, instead of opal-A, which is the main phase in the other samples (1100°C), (Fragoulis et al. 2003). The presence in the pellets from Vegora and Kornina areas, of hercynite and clino-enstatite is related to the presence, initially at the parent rock, of clay minerals and feldspars, while that of cristobalite to the initial presence of opal-A. In the same way the presence in the pellets from Notio Pedio, of wollastonite, is due to the initial presence of dolomite and calcite, as a result of the reaction of quartz with calcite, which gives wollastonite and carbon dioxide, while the corresponding reaction with dolomite creates wollastonite, diopside and clino-enstatite. All the laboratory trials show that the samples with a major content of fly-ash have low compression strength, and thus those pellets from Vegora are more resistant than the Kornina and Notio Pedio ones, principally as a result of the initial clayey content. A possible drawback in the procedure is the higher calcining temperature of Milos Island clay-rich tuffs than the common raw materials of sedimentary origin. In the case that the pelletized samples are very rich in expanded clay minerals (e.g., smectite content ~50%, Milos) they do not exhibit the desirable physical and mechanical properties (Alfieris et al., 2005). The optimum results with respect to the apparent density and compressive strength, appear to be when the smectite content is in the range of 20 to 30%.

On an industrial scale it is possible, depending on the demand, to combine differently the various available raw materials, and thus produce end products with different physical and mechanical properties.

Finally, those of the tested samples with high fracture load with a relatively low apparent density could be used as insulating materials and as aggregates in the production of lightweight concrete.

REFERENCES


The origin of sparry magnesite in the Eastern Alps (Austria): evidence from inclusion fluid and Sr - Nd isotope chemistry

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ABSTRACT: The overall high salinity, the special chemical composition (e.g. high Br-contents) and the Sr and Nd isotope chemistry of the fluids responsible for the formation of the magnesites of the “Veitsch Type” indicate an epigenetic origin in Upper Permian/Lower Triassic. Evapoconcentration of seawater produced residual “bittern” brines which percolated into shallow crustal levels and lead to hydrothermal formation of magnesite stocks in Carboniferous limestones with prominent alteration zones of hydrothermal dolomite.

KEYWORDS: magnesite, hydrothermal fluid, fluid chemistry, Sr isotopes, Nd isotopes

1 INTRODUCTION

In 1850 the world's first deposits of magnesite was discovered in the province of Styria/Austria within Paleozoic series of the Eastern Alps. Soon after the discovery the first industrial application of magnesite was developed mainly for basic refractory lining of blast furnaces of the local steel plants. The rapid application of this new raw material in a quickly growing steel industry triggered the scientific investigation and led to a first general classification of magnesite deposits. In the following decades different genetic models, including a synsedimentary origin or an Eoalpine metamorphic vein-type or metasomatic mineralization were proposed for this type of magnesite mineralization. However, up to now there is no consensus about a genetic model and the principal mechanisms of mineralization for “carbonate hosted sparry magnesite” mineralizations. In this study we present new inclusion fluid and Rb-Sr and Sm-Nd isotope data for the Oberdorf sparry magnesite deposit which provide strong evidence for formation of the magnesite deposits by metasomatic replacement due to infiltrating salinar residual brines which originated in the Upper Permian/Lower Triassic. The results obtained in this study are considered to be of fundamental importance not only for the investigated mineralization but also for the genetic aspects of carbonate hosted sparry magnesite in general.

2 GEOLOGIC SETTING

The Eastern Alps (Fig. 1) are a fold and thrust belt formed in a collisional setting during the Alpine orogeny in late Mesozoic and Tertiary. The Austroalpine nappe system overthrust the Penninic units which are a part of the Adriatic/African system. All units consist of a ± metamorphosed pre-Alpine basement and a Permomesozoic cover. The Greywacke Zone which hosts the most important magnesite mineralizations of the Eastern Alps, forms a Cretaceous stacked imbrication nappe structure at the base of the Upper Austroalpine system. The rock series of the Greywacke Zone range from Ordovician to Carboniferous in age and comprise carbonates, metapelites and metamorphosed acid volcanics.

In the Eastern Greywacke Zone carbonate-hosted sparry magnesite mineralizations occur mainly in Lower Carboniferous strata of the Veitsch nappe. A set of lens-shaped magnesite bodies of various size can be found in a sequence of sericite schists, greywackes, conglomerates and metatuffs. Carbonate series hosting the magnesite bodies are of Upper Tournéan/Viséan age and exhibit shallow water, marine environment. Neither Variscan internal deformation nor metamorphism was identified for the Veitsch nappe. The tectono-thermal overprint is exclusively Alpine (Cretaceous). The grade of the Eoalpine tectono-metamorphic events is generally of lower...
greenschist facies. Minor quartz veins in the magnesite bodies and the ubiquitous occurrence of talc are a consequence of the Alpine metamorphic overprint.

Other magnesite deposits in the Eastern Alps are the Breitenau mine, which is located in the “Graz Paleozoic” and deposits in the Western Greywacke Zone which are in similar geotectonic position as the magnesite mineralizations of the Veitsch nappe.

3 METHODS

3.1 Inclusion fluid chemistry

The carefully handpicked carbonate samples were crushed to a grain size between 0.25 and 1 mm and thoroughly cleaned. 1 g of sample and 5 ml of the leaching solution (DDW) were crushed in an agate mortar. Because of its significance for the origin of the fluids, special attention was drawn on the analyses of anions. The samples were analyzed by ion chromatography. A Dionex system (DX-500) with a micro membrane suppressor was used. Na, K, Li, Ca and Mg were analyzed by ion chromatography using aliquots of the same solution.

3.2 Rb-Sr and Sm-Nd isotope chemistry

Rb-Sr and Sm-Nd element fractions were obtained from powdered samples of carbonate dissolved in hot diluted acetic acid. Special care was provided not to dissolve carbon-rich materials since these are known to contain in part very high amounts of REE. After spiking of the leachates with enriched Rb, Sr, Sm, and Nd tracers, Rb, Sr, and total RE element fractions were obtained by conventional cation exchange chromatography. Sm and Nd were separated from the total RE fractions using columns with HDEHP-coated Teflon powder (Cerrai & Testa 1963). Isotopes were measured using a double Re filament assembly on a ThermoFinnigan Triton TIMS (Sr, Nd, and Sm) and a MAT261 TIMS (Rb) in static mode. Procedural blanks are less than 0.1 % of the relevant sample concentration and are therefore negligible. Precision of the isotope determinations were checked by routine measurement of well-known isotope standards as well as by replicate analyses of carbonate samples.

4 RESULTS

4.1 Investigated profile

Different types of transition from the carbonate hostrocks to the magnesite bodies can be observed. Usually a dolomite zone of highly variable size exists between the country rocks and the magnesite. Alteration phenomena of the dolomite are not very distinct from the hostrock limestone, microscopically a weak recrystallization can be observed.

In this study results are presented for a profile sampled from the Carboniferous limestone (hostrock; MgO/CaO by weight-% < 0.02) into the Oberdorf sparry magnesite deposit. In different underground exposures, the ore body is mineralogically and geochemically character-
ized by an approximately 3.5 m wide contact zone (MgO/CaO of 0.77) mainly consisting of dolomite. Further inward, carbonate of the main ore body (MgO/CaO 1.3 – 98) is built up by sparry magnesite associated with variable but usually small amounts of dolomite.

4.2 Inclusion fluid chemistry

The perfect positive correlation between Cl, Br and Na in the alteration dolomites as well as in the magnesites is of pivotal importance for the question of the mechanism of Br-enrichment. The coherent behavior of Cl and Br and Na and Br proves that halite fractionation is the driving factor for the fluid composition and indicates that Br is not controlled by hostrock reactions or supplied from external sources.

The Na-Cl-Br numbers of the mineralized samples (hydrothermal dolomites as well as magnesites) are significantly lower than the seawater ratio and plot on the extreme end of the seawater evaporation trajectory. The values are between 46 and 90 for the Na/Br ratios and between 89 and 150 for Cl/Br. The dramatic change in the Na/Br ratios at the boundary between the hostrock limestones and the alteration dolomites is shown in Fig. 2.

Li and I also show an extreme increase in the mineralized samples. Whether these high contents are signatures of the original fluid or due to fluid-rock interaction is a matter of further investigations. Results obtained by the chemical analysis of the inclusion fluids were also applied on geothermometers based on semi-empirical cationic exchange reactions using Na/K, Na/Li or Na/K/Ca ratios. Different authors used these thermometers successfully (cum. cit. Kharaka & Mariner, 1989). In this study the best and most reliable results were obtained by the Na/K- and the Na/Li-thermo-meter. According to the geothermometric calculations the fluids in equilibrium with the hydrothermal dolomites and magnesites yielded temperatures of approximately 220°C for the Na/K-thermometer and 190°C for the Na-Li-thermometer.

4.3 Rb-Sr and Sm-Nd isotope chemistry

Sr and Nd isotope ratios are recalculated for an assumed age of 300 Ma. Three samples from the hostrock limestone further away from the contact show almost constant and low $^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd ratios of approximately 0.70826 and 0.51189, respectively (Fig. 3).

The Sr isotope composition fits to distinct maxima in the Carboniferous Sr seawater curve at about 300 to 315 Ma and 355 to 365 Ma. Starting at the contact, both isotope ratios are significantly elevated compared to the hostrock. Interestingly, a hostrock limestone directly from the contact also yields an elevated Sr isotope ratio. The Sr isotope ratio shows a systematic increase with increasing distance from the contact to about 5 m into the ore body. Further inward, the Sr isotope ratio is relatively constant at a maximum value of approximately 0.7101. The reason for the larger scatter in the Nd isotope ratio in the contact zone and the inner part of the magnesite deposit is so far unknown. The offset in Nd isotope ratio between limestones of the hostrock and carbonates within the ore body differs depending on the assumed age. However, assuming geological realistic ages of less than 360 Ma, carbonates from the ore body always show higher Nd isotope ratios than those of the hostrock. Due to their very low Rb/Sr ratios, there is no significant age-dependant variation in the Sr isotope ratio of the carbonates.

5 CONCLUSIONS

Dolomites from the alteration zone and magnesites of the investigated profile of the Oberdorf magnesite deposit exhibit low Na/Br and CI/Br ratios plotting on the seawater evaporation trend, indicating that the fluids acquired their salinity by evaporation processes of seawater. Structural features and the totally different chemical signatures of the hostrock carbonates prove an epigenetic origin of the mineralization (Prochaska, 2000). Temperature calculations based on cation exchange thermometers indicate temperatures of the hydrothermal system of about 200°C.
In an earlier study, Frimmel (1988) argued that Sr isotope data support a sedimentary (s.l.) origin of sparry magnesite deposits in the Eastern Alps. Our Sr and Nd isotope results, however, require a different interpretation. The new data clearly document significant differences in isotope composition between the Carboniferous limestone and the magnesite deposit. Furthermore, the gradual increase in Sr isotope ratio in the contact zone is evidence for mixing processes whereby the original less radiogenic Sr of the limestone is gradually replaced by Sr of more evolved isotope composition in the course of a metasomatic replacement triggered by infiltrating fluids. The relatively high-radiogenic Sr isotopic composition in the main ore body is evidence of a non-marine origin of Sr, as this element (and by inference also Nd) is scavenged by the percolating fluids on their way through crustal rocks. Based on the new inclusion fluid and Sr and Nd isotope geochemistry data, two possible genetic models are proposed:

Deposition of thick series of evaporites is widespread in the Permoscythian strata of the Upper Austroalpine unit. Residual “bittern” brines had been produced in Permian (to Lower Triassic) times in large quantity with high concentrations in Br, Mg, K, and SO4 in the fluids. High heat flow in a rift-environment (Schuster et al., 1999) induced hydrothermal convection systems where residual evaporitic brines percolated into the crust. Where these fluids came into contact with underlying Palaeozoic carbonates, metasomatic stocks of sparry magnesite were formed in a very shallow hydrothermal environment due to the very high Mg/Fe ratio of these fluids. Metasomatism and mimetic crystallization of the marine hostrock carbonates often preserved primary sedimentary textures very well, which lead earlier researchers to postulate syngenetic models.

Another possibility is epigenetic magnesite formation by fluids mobilized during diagenetic processes. In that case buried evaporitic brines (upper Permian to lower Triassic) have been set in motion due to increasing burial in the course of deposition of the Triassic platform carbonates.

Radiometric dating will elucidate the aspect of timing of magnesite formation in the Eastern Alps which is in any case younger than the stacking of the Austroalpine nappes.

The proposed hydrothermal-metasomatic models of Permoscythian evolved evaporitic brines as ore-forming fluids can explain all observed features of the magnesite mineralizations of the Greywacke zone regardless their stratigraphic and tectonic positions. This model is consistent with features as the overall high salinity of the fluids, the uniform and special fluid chemistry and the Sr and Nd isotope chemistry etc. that can neither be explained by sedimentary scenarios nor by Alpine remobilization models.

ACKNOWLEDGEMENTS

Thanks are due to Siegrid Gerlach and Peter Macaj for laboratory assistance during Sr and Nd isotope analyses.

REFERENCES


Magnesium - Raw Materials, Metal Extraction and Economics - Global Picture

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ABSTRACT: Magnesium raw materials are available worldwide. In the free market, the prevailing price of primary magnesium metal determines which combinations of raw material/extraction method are economically viable. Over the last 20 years, China’s exports benefited from favourable currency exchange rates and positive relations with the USA and European countries. Lax environmental regulations, in conjunction with low labour costs, availability of inexpensive energy and a favourable tax regime resulted in China’s domination of the magnesium market. The Pidgeon process (dolomite - main ore, ferrosilicon - reducing agent and coal - energy source) is the main production method in China. It involves lower capital costs but it is less environment-friendly relative to the electrolytic processes favoured in the west. As the magnesium production costs in China are rising and environmental restrictions are being enforced the potential of development of magnesium resources outside of China, especially in North America is increasing.

KEYWORDS: magnesium metal, resources, extraction methods, economics

1 RAW MATERIALS

Magnesium (Mg) is a widely distributed element in nature. There are over 80 minerals that have more than 20% Mg within their crystal structure. However, only magnesite, dolomite, brucite, bishovite, carnallite and olivine (Figure 1) have been used or are considered as raw materials for Mg metal production along with brines, bitterns, fly ash, and serpentine -rich ultramafic rocks (including asbestos tailings). Magnesite and brucite are also commonly used in the production of caustic, dead-burned, and fused magnesia. Although huntite and hydromagnesite have high Mg content, their greatest potential currently appears in flame-retardant applications (Simandl et al. 2001). Dolomite [CaMg(CO₃)₂] and magnesite [Mg(CO₃)₂] are the most commonly used Mg metal ores. Dolomite is a widespread carbonate, available on every continent and is the main Mg ore used in China. Magnesite has higher Mg content than dolomite (Figure 1); however, large mag
nesite deposits are geographically restricted. World magnesite resources are estimated at over 12 billion tonnes with the majority located in China, Russia, North Korea, Australia, Slovakia, Brazil, Turkey, India and Canada. Over 90% of magnesite resources are sedimentary-hosted, either sparry type (also called Mount Brussilof type) as defined in Simandl and Hancock (1998) or Kunvarrara type as defined in Simandl and Schultes (2005). The balance of the resource (<10%) occurs as veins (Paradis & Simandl 1996) or talc-magnesite bodies within ultramafic-rocks (Simandl & Ogden 1999).

Magnesite production is estimated at 19 million tonnes per year and over 85% of it is the sparry variety (Wilson & Ebner 2006). The production of Mg metal from magnesium silicates is technically feasible as demonstrated by the Magnola plant, which operated from 2002 to 2003. However, associated production costs are too high in relation to current Mg-metal prices. Brucite has a higher Mg content than the above listed minerals with the exception of periclase. Unfortunately, large-tonnage, high-grade brucite deposits are uncommon (Simandl et al. 2006). Periclase is unstable in nature and it retrogrades into brucite.

2 EXTRACTION PROCESSES

Known Mg extraction methods belong to either thermal reduction or electrolytic categories (Table 1). Thermal reduction methods (silico-thermic, aluminothermic and carbothermic) operate at high temperatures. The Silico-thermal process relies on the use of ferrosilicon to reduce magnesium oxide to a molten slag at temperatures between 1200°C-1600°C. A reduced gas pressure above the slag produces magnesium vapour. This vapour is condensed at a location removed from the main furnace or in the low temperature zone of the converter. The crowns of condensed magnesium are then re-melted, refined and casted. The Pidgeon, Magnetherm and Bolzano processes were all successfully used in the past (Aghion & Golub 2006). The Pidgeon process is the simplest, oldest, least energy efficient, and most labour intensive production process. However, it requires the lowest capital investment (Table 1). This process is widely used in China, which dominates world magnesium production and effectively controls the price of magnesium metal. Not surprisingly, the environmental impact of Chinese Mg-metal production on global warming is substantial (Ramakrihnan & Koltun 2004). The main advantage of the thermal reduction methods is that, under the right conditions, high purity metal (99.95% Mg) is produced. Dolomite and to a lesser extent magnesite, are the key ore minerals in the production of Mg metal by thermal reduction methods (Table 1).

<table>
<thead>
<tr>
<th>Method</th>
<th>Electrolysis</th>
<th>Thermal Reduction</th>
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<tbody>
<tr>
<td>Raw Materials</td>
<td>magnesite, dolomite, bischofite, carnallite, serpentine, olivine, sea water, brines</td>
<td>dolomite, magnesite</td>
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<tr>
<td>Energy type</td>
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<td>Energy requirements (MWh / tonnes of Mg)</td>
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<tr>
<td>Process</td>
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<td>batch</td>
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<tr>
<td>Capital investment (US $/tonne of Mg capacity)</td>
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<td>≤ 2000</td>
</tr>
<tr>
<td>Manpower requirements</td>
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<td>5X</td>
</tr>
</tbody>
</table>

Table 1. Comparison of Mg metal production methods.

Plants using Mg electrowinning methods are less labour and energy-intensive than thermal reduction processes, but they require higher capital investments (Table 1). There is a large number of technically proven, electrolysis-based processes; however, commercial magnesium electrolysis is conducted most commonly in a chloride melt of mixed alkali metals at temperatures below 700°C (Duhaime, Mercille & Pineau 2002). The feed to the electrolysis process is either anhydrous magnesium chloride, KMgCl₃ produced from the dehydration of carnallite or partially dehydrated magnesium chloride. The latter feed can be derived from a variety of raw materials including dolomite, magnesite, bischofite, serpentine group minerals, sea water or brines (Figure 1). Although pure anhydrous magnesium chloride is probably the preferred feed material, the production of magnesium chloride with low levels of magnesium oxide is difficult due to its hygroscopic nature. Plants based on the electrolytic approach have difficulty achieving metal purity over 99.8%.
although they benefit from continuous operation (Table 1). Considerable research is underway to optimize established and newly proposed methods (Schounkens et al. 2006; Brooks et al. 2006) and a single technological breakthrough may completely alter the current situation. Recent research suggests that the carbothermic route of Mg metal production may have the potential to become the most cost effective production method (CSIRO 2006a, b).

3 ECONOMIC AND ENVIRONMENTAL CONSTRAINTS

In theory, considering all the key parameters such as energy efficiency, labour requirements, environmental impacts and economy of scale, electrolysis should be preferred over the high temperature processes (Table 1) when targeted production exceeds 10,000 tonnes per year. In practice, this is not the case as labour costs, access to inexpensive Mg raw materials and abundant, low-cost energy are controlled in part by geography and political factors. Furthermore, environmental standards vary between countries, and the costs required to adhere to strict western standards are high. It is difficult for a western Mg-producer to successfully compete with the current low cost Mg exports from China and to provide an acceptable return on investment for its shareholders. However, this may change in the foreseeable future. Several small Mg-producing plants in China recently closed because they were unable to satisfy minimum environmental requirements when enforced by the government. This trend may continue if environmental restrictions similar to those used in North America and Europe become the norm in China. Many countries maintain antidumping duties on Chinese Mg imports. Furthermore, the production of Mg is extremely energy-intensive. As China’s economy progresses at a rapid pace, the country is becoming susceptible to the same energy limitations as most developed countries and the availability of inexpensive energy resources that could be allocated to the industry is shrinking. Chinese export taxes may reflect this. In September 2006, China cancelled the export tax rebate on unwrought Mg, Mg alloys, granules and scrap. In November 2006, China introduced a 10% tax on selected silicon metal products. At the time of writing, there were several indications suggesting that China may start to implement a new export tax (5 and 15%) on magnesium in early 2007. The apparent objective of this new tax is to reduce internal industrial energy requirements and to moderate exports of energy-intensive products.

4 INTERPRETATION

China is the world’s largest Mg producer. Its dominance could be affected by changes in trade relations, currency exchange rates, internal environmental standards and increases in energy and labour costs. Under such circumstances, western secondary Mg industry, automakers and the aeronautic industry will be adversely affected by high Mg prices. However, Mg resources outside of China may become amenable to development. British Columbia, in particular, has exceptional potential in terms of sparry magnesite deposits (Simandl & Schultes 2005; Simandl 2002) and good exploration potential for the discovery of brucite deposits (Simandl et al. 2006). It has serpentine tailings from the closed Cassiar mine operation (Voormeij & Simandl 2005) which are chemically similar to those used by Noranda’s Magnola project. It is also home to several Mg-olivine/serpentine deposits. Leader Mining International Inc. is considering developing one of these olivine deposits through its wholly owned subsidiary, North Pacific Alloys Limited. Magnesite deposits outside of China, located near existing infrastructure, in geographic areas with inexpensive energy, may become key sources of raw materials for Mg production.

ACKNOWLEDGEMENTS

Laura Simandl from St. Margarets School in Victoria, BC, Canada provided invaluable assistance in the field during the study of Australian magnesite deposits. Brian Grant, David Lefebure and Melanie Irvine of the British Columbia Ministry of Energy and Mines helped to improve early versions of this manuscript. Melanie Irvine also drafted the figures used in this document.

REFERENCES


CSIRO (2006a) http://www.csiro.au/csiro/content/standard/ps18r.html

CSIRO (2006b) http://www.csiro.au/csiro/content/standard/ps1ce.html


"Digging Deeper" C.J. Andrew et al (editors)
Fluid Chemistry and Stable Isotope Evidence of Shearzone related Talc and Chlorite Mineralizations in Central Sardinia-Italy

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**ABSTRACT:** Palaeozoic metasediments, Hercynian granitoids and Tertiary volcanic rocks occur in the Ottana-Orani district in Central Sardinia. The metasediments are micaschists, marbles and gneisses and are intruded by syn-tectonic leucogranites and by late- or post-tectonic two mica granites. Talc-chlorite and Na-feldspar deposits are hosted within the metasediments and accompanied by intense hydrothermal activity, which postdated the intrusion of the granites. Results of the chemical analysis of the inclusion fluids reveal high concentrations of Br in the mineralizing system. A possible explanation for the high Br contents is fractionation of halite in an endogene system after oversaturation of the mineralizing fluids by continuous formation of hydrosilicates. An extreme evapoconcentration of seawater beyond epsomite precipitation does not seem to be realistic because of the lack of corresponding evaporitic sediments.

**KEYWORDS:** Sardinia, talc, chlorite, fluid chemistry

1 INTRODUCTION

This paper deals with talc-chlorite mineralizations occurring in the central-eastern part of Sardinia. Talc has been produced here since 1930 and presently one mine is operating. The aim of this study is to determine the origin of the dissolved salt content of the fluids that precipitated the mineralizations, and further constrain the timing and origin of the hydrothermal event.

The chemical composition of palaeofluids can be used as geochemical tracer to investigate the original signature and origin of different kinds of inclusion fluids. Analytical work on the chemistry of the inclusion fluids (F, Cl, Br, I, Na, K, Ca, Mg) can provide valuable information on the solution of fundamental problems of the origin of mineralizing fluids and the role of the mineralizing event in the regional geodynamic setting. These investigations may also provide information concerning flow directions and chemical evolution of fluids along the flow path.

The major question of the formation of the talc-chlorite mineralizations in Central Sardinia is the origin and primary nature of the mineralizing fluid. The source of Mg and especially of Na for the very prominent regional albitionization processes is of pivotal importance for the genesis and the geodynamic significance of these mineralizing events.

2 GEOLOGIC SETTING OF THE INVESTIGATED MINERALIZATIONS

Intrusions of Hercynian granitoids into Palaeozoic metasedimentary rocks are widespread in major parts of Central Sardinia. Occasionally, these rocks are covered by volcanic rocks of Neogene age. The granitoid rocks show variable compositions and were emplaced at different crustal depths. The entire suite of rocks includes syntectonic tonalites, granodiorites, quartz diorites and peraluminous leucogranites as well as late-tectonic granodiorites, monzogranites and post-tectonic leucogranites (Cherchi & Musumeci, 1992). The metasedimentary rocks are represented by micaschists, metalimestones and gneisses. The most common granitic rocks in this area are leucogranites and monzogranites which commonly exhibit
different degrees of chloritization and albitization. While partly altered granites still retain their original textures, the completely metasomatized rocks become albitites.

Presently talc is being mined in Sa Matta mine and to a minor extent in Su Venosu mine. Talc formation in this area is clearly related to tectonic structures in a N45E direction, and to a lesser extent in a NS direction (Arthaud F. & Matte PH 1975).

The talc that has been deposited as open-space filling is considered to be a direct precipitate of hydrothermal fluids. It has a pale green color, normally exhibits massive structures and is accompanied by spathic calcite and milky quartz. Hydrothermal circulation also produced major alteration of the Paleozoic rocks with the formation of metasomatic talc and chlorite in the two-mica granitoids and to a lesser extent and only locally in the mica schist. Continuous alteration from the hostrock mineralogy (granite, gneiss) into talc-chlorite rocks is ubiquitous (Fig. 2).

3 ANALYTICAL METHOD

The method used to analyze the inclusion fluids are described by Bottrell et al. (1988). Inclusions in vein quartz, coarsegrained carbonates, feldspar samples but also finegrained hostrock limestones are suitable for the extraction of soluble salts. Regional quartz samples were analyzed to obtain a regional signature of the fluid composition far off the mineralizations. The samples were crushed to a grain size between 0.25 and 1 mm and carefully cleaned. 1 g of the cleaned sample and 5 ml of the leaching solution (DDW) were transferred to a thoroughly cleaned mortar and crushed. Because of its significance for the origin of the fluids, special attention was drawn on the analyses of anions. The samples were analyzed by ion chromatography. A Dionex system (DX-500) with a micro membrane suppressor was used. Na, K, Li, Ca and Mg were analyzed by ion chromatography using aliquots of the same solution.

4 CHEMISTRY OF INCLUSION FLUIDS

The chemical characterization of inclusion fluids is a useful tool to obtain information on the source of solutes in the ore-forming brines and to explore genetic linkages among deposits. By analyzing the chemical composition of the
inclusion fluids, it is possible to pinpoint the origin of Mg for the formation of the talc-chlorite mineralizations and to discuss their geodynamic position.

There are different possibilities for the generation of highly saline fluids and for a possible source of Mg:

- Evaporation processes, which produce highly saline brines enriched in Mg and also in Br once halite begins to precipitate, are often considered responsible for the formation of such brines. Several highly saline brines from the European Variscides are attributed to this process.
- Redissolution of halite by fluids migrating through the crust can produce highly saline fluids. They can easily be recognized by high Cl/Br and Na/Br ratios.
- Finally, concentration of crustal fluids of different origins by hydration reactions generally is considered to be a very efficient mechanism to produce highly saline brines.

The Cl-Br-Na ratios of the fluids yield important information on their origin. Changes in the molar ratios of Na/Br and Cl/Br are very sensitive for fluids being affected by evaporation processes. Fluids that have principally acquired their salinity through evaporitic concentration of seawater show Na/Br vs. Cl/Br values that are lower than seawater. In this case, the molar compositions of the fluids plot along the “evaporation trend”. Fluids that have acquired their salinity from the dissolution of halite have Na/Br vs. Cl/Br values higher than seawater and will plot on the “halite dissolution trend”. Usually surface fluids (e.g. average river water or meteoric water) are also characterized by low Br numbers with respect to Na and Cl.

The most striking features of the chemical composition of the inclusion fluids of the talc-chlorite mineralization of Central Sardinia are the extremely high contents of Br. Evidently the Br-content of the fluid is not easily buffered by hostrock reactions and is a relatively conservative tracer that retains its original signature even at very intense interaction between the fluid and the hostrocks. Calculating the dilution factor of the leached inclusion fluids on the basis of an average salinity of 20 % (~ 121.000 ppm of Cl) the calculated Br-contents of the mineralizing fluids are in the range between 1400 and 5300 ppm. Fluids containing Br-contents in that order of magnitude can only be achieved by effective fractionation processes of a suitable protofluid.

In a Cl/Br versus Na/Br plot (Fig. 3) the investigated fluids plot on the extreme end of the seawater evaporation trajectory. The values are significantly lower than the seawater ratio and correspond to an evapococoncentration of seawater with an evaporation factor of ~ 30 to 40 at Su Venosu and ~ 70 to 80 at Sa Matta. This extremely high evaporation is far beyond epsomite saturation and does not seem to be realistic because of the lack of larger amounts of evaporitic sediments with such high degree of evaporation. Furthermore the ratios between Br and other significant elements (e.g. iodide) do not support an evaporation model for the fluids.

Similar to Br, I is not incorporated in the halite lattice in larger amounts. Therefore a similar behavior to that of Br is expected if halite fractionation is the controlling mechanism of the halogens. However, the Br/I molar ratios of the analyzed samples show an appreciable scattering. The fluids from the recrystallized carbonates from Sa Matta (saddle dolomites) are within the range of the seawater ratios (~

Figure 2. Transition of granitic protolithe in the core and continuous transition into talc-chlorite rocks at the rims

Figure 3: Metasomatic replacement of the hostrock granite by the talc-chlorite mineralization
The fluids from the quartz- and calcite-crystals from Sa Matta and the Su Venosu fluids show very low Br/I molar ratios thus indicating a further enrichment of iodide.

5 DISCUSSION OF THE GENESIS OF THE INVESTIGATED MINERALIZATIONS

The question whether Mg-carbonates are the source of Mg during the hydrothermal event is of major importance for the mineralizing process. Another possibility is that the dolomites occurring with the talc-chlorite mineralization are also a product of an hydrothermal event. In this context the talc mineralizations of Central Sardinia are similar to the Rabenwald talc deposit in Austria, which is the biggest talc deposit in the Eastern Alps. Here also talc-chlorite mineralization occurs in a prominent shearzone together with Mg-carbonates (Prochaska, 1989).

Intense albitization related to a late Hercynian ENE-WSW striking system is an important part of the hydrothermal-metasomatic process. Alpine remobilization processes are being discussed, but the primary formation of the talc-chlorite-albite mineralizations are considered to be pre-Alpine. The totally recrystallized albilites consist of chessboard albite, quartz and clinohlore and subordinately sphene, epidote, rutile and apatite. Because of the close spatial relation of the feldspar and the talc deposits, the consanguineous origin of the feldspar and the talc-chlorite mineralizations frequently is discussed and is one of the major tasks of the current investigations.

The most striking features of the chemical composition of the inclusion fluids of the talc-chlorite mineralization of Central Sardinia are the extremely high contents of Br. By the generally low Na/Br and Cl/Br ratios of the mineralized samples it can be excluded that the highly saline fluids were the product halite dissolution.

Very little is known about the geochemical behavior of iodine and data from fluid inclusions are very rare. It occurs in seawater in very low concentration. Iodine displays a multi-oxidation-state variability and the stable form in seawater is mainly I\textsuperscript{3-} (Fuge, 1990). Absorption of iodide by organic matter is due to the biophile behavior of this element. In this study only I\textsuperscript{3-} was analyzed.

In the Sa Matta deposit the fluid composition generally plot very well on the evaporation trend in the Na/Br-Cl/Br diagram (Fig.3). The Br/I ratios of the Sa Matta fluids are within the range of seawater. This indicates that the alterations (dolomitization) is governed by a big fluid system circulating through the Sa Matta shearzone which is not affected by fluid rock interaction. This system is possibly more dominated by the original fluid signature than the Su Venosu mineralization which is characterized by more scattering Na-Cl-Br ratios (Fig. 3) and by much higher I values indicating an additional I-source and low fluid rock ratios. The highly scattering Br-I ratios in the Su Venosu system are interpreted to be a consequence of a low fluid –rock ratio in this small and divergent vein system.

No selective depletion in Na can be seen in the talc forming fluids in the Na/Br-Cl/Br diagram (Fig.3), which would result in a shift of the plots toward lower Na numbers parallel to the Na/Br axis. This means that the ubiquitous albitization in spatial connection to the talc formation is not related to the talc-chlorite mineralization or in the case of a consanguineous origin albitization occurred after the formation of the talc chloride mineralizations.

ACKNOWLEDGEMENTS

These investigations are done within a project of the Austrian Academy of Sciences. The logistic and financial support of Luzenac Val Chisone SpA and especially the efforts of A. Kristen and F. Fiorelli are highly appreciated. This study was supported by the Dipartimento di Geoingegneria e Tecnologie Ambientali, Cagliari University, Italy.

REFERENCES


Diagenetic and epigenetic celestite deposition in Neogene calcareous series from Cyprus and the Arabian Gulf: a model for evaporite-associated ore and industrial mineral deposits

Dill, H.G., Henjes-Kunst, F.
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ABSTRACT: During the Neogene in the Arabian Gulf area, celestite-gypsum-dolomite deposits evolved syndiagenetically in a sabkha, dominated by algal mats (biostromal celestite deposits—Gulf-type). Celestite deposits in the calcareous roof rocks of the Troodos Ophiolite in Cyprus are located in reefs (biohermal celestite deposits). Both types have elevated Cu, Zn and Pb contents. Syndiagenetic Gulf-type mineralization is a model source of base metal deposits of stratigraphically-controlled fixed or mobile reductants elsewhere. The epigenetic celestite-bearing mineralization of Cyprus-type reflects an advanced stage of brine migration but this brine mobilization failed to create a base metal deposit of its own due to the absence of fixed or mobile reductants, which were present further westward in Tunisia and in Mesozoic through Cenozoic platform sediments in central Europe, where numerous suprasalt metal deposits came into existence.

KEYWORDS: celestite, Neogene, syndiagenetic, epigenetic, model, base metal deposits, SHSCD, Arabian Gulf, Cyprus

1. INTRODUCTION

Strontium averages 0.04 wt. % in the Earth’s crust making it the fifteenth element in the order of abundance (MacMillan et al. 1994). Only celestite and strontianite contain Sr in sufficient quantities to make this element recoverable from mineral deposits, e.g. Mexico (Moore 2002), Argentina, (Brodtkorb et al. 1975), Northern Tunisia (Bouhel 1985) and Spain (Coope 1997). The celestite-bearing beds in Spain form part of a Neogene belt of celestite-bearing calcareous-evaporitic series extending from the Iberian Peninsula through the Mediterranean area into the Arabian Gulf (Dill et al. 2005). At the south-eastern edge of the Troodos Ophiolite Complex celestite deposits were explored in the environs of Maroni, Cyprus, and further eastward, in stratigraphically equivalent Neogene sequences, strontium deposits were found along the Trucial Coast of the Arabian Gulf in Qatar (Dill et al. 2005) and, to a lesser extent, in the United Arab Emirates (Peebles 1999). In the current study, mineralogical, chemical and geological data are presented and a model concerning the origin of the deposits in the Tethyan Ocean is presented. This genetic model on celestite mineralization in the eastern Mediterranean Neogene is also discussed as a potential progenitor of stratiform copper or sediment-hosted base metal deposits (SHSCD) sensu Brown (2003).

2. METHODOLOGY

Samples collected at outcrop were split and one part used for chemical analyses involving major and trace element chemistry by means of X-ray fluorescence spectrometry (XRF) and isotope analyses (S, Sr, Ca). Strontium isotope analyses are of common use in the study of celestite deposits. As a novelty for celestite deposits, $^{44}$Ca/$^{40}$Ca and $^{44}$Ca/$^{42}$Ca isotope ratios have been determined of their country rocks (Dill & Henjes-Kunst 2007). For overview of the geological application of the Ca isotope methods see Fantle & DePaolo (2005). Apart from routine optical methods all samples were
subjected to X-ray diffraction analysis supplemented with the scanning electron microscope (SEM), using an energy-dispersive system (EDS).

3. PALAEOGEOGRAPHY AND PALAEOECOLOGY OF THE CELESTITE-BEARING ENVIRONMENTS

Celestite in the Gulf region was concentrated mainly in an intertidal to supratidal environment passing towards younger series in a more wave-dominated beach environment (Dill et al. 2005). The idea of a sabkha is also mineralogically backed by the presence of the phyllosilicates smectite and palygorskite as well as dolomite and the full spectrum of Ca sulfates (anhydrite to gypsum).

Algal mats are crucial as to the development of sulfate mineralization in this sabkha along the Arabian Gulf and the source rock environment of celestite thus denominated as a “biostromal”. Those species tending to form build-ups like reefs (“bioherm”) are more widespread in Cyprus than in the Arabian Gulf. Celestite in patch or knoll reef limestones in the Miocene units of Cyprus are called a “biohermal” host rock environment.

Detrital minerals such as zoisite, clinopyroxene and volcaniclasts identified in both series leave no doubt that in Cyprus and the Arabian Gulf area basic volcanic rocks sourced the depositional environment (Zagros Mountain Range vs. late Cretaceous Troodos Ophiolite Complex).

4. GEOLOGY AND MINERALOGY OF CELESTITE MINERALIZATION

The well-bedded celestite mineralization in the Arabian Gulf area with the primary sedimentary textures and structures well preserved is interpreted as an early Sr deposition. Celestite is a by-product of anhydrite hydration. Dean (1978) recorded that much more strontium is soluble in the anhydrite lattice than in gypsum, so when anhydrite turns to gypsum all the Sr that cannot enter the gypsum lattice hence precipitates as celestite. Dolomite is not directly evolved in this sulphate transformation process and only acts a facies marker for strong evaporation in an sabkha environment crucial for this sulfate transformation (Warren 1999). In the Neogene beds of Cyprus, no syndiagenetic Ca-Sr sulphate mineralization like that reported from the Arabian Gulf can be found in the calcitic limestones. Textural evidence of grain-to-grain contacts between calcite and celestite are displacive or replacive attesting to Sr- and S-bearing fluids percolating through a calcitic host rock whose reeval and reef-slope lithofacies provided favorable conditions as to permeability and porosity. The entire Sr mineralization is of true epigenetic origin. Syndiagenetic celestite mineralization of Gulf-type has abnormally increased contents of Cu which are transferred by heredity also into epigenetic celestite mineralization of Cyprus-type. In Cyprus-type celestite mineralization also Pb and Zn are abnormally increased but neither deposit under consideration can be worked for anything but celestite.

5. EVOLUTION OF CELESTITE DEPOSITS: A MODEL FOR EVAPORITE-ASSOCIATED ORE AND INDUSTRIAL MINERAL DEPOSITS.

Syndiagenetic celestite-gypsum-dolomite mineralization of Gulf-type took place around 19 to 20 Ma. Based on Sr isotopes a similar age of formation of ca. 20 Ma may also be claimed for the incipient calcite-gypsum mineralization in Cyprus. The epigenetic celestite mineralization was, however, emplaced around 10 Ma based on isotope data.

Abnormally high metal contents like those observed in context with evaporation during the Neogene may shed some light on the development of some world-class sediment-hosted mineral deposits (SHSCD) such as the Kupferschiefer which is an evaporite-associated ore deposit (Kucha & Pawlikowski 1986, Vaughan et al. 1989, Dill & Botz 1989, Speczik 1995, Blundell et al. 2003). The Neogene sabkha along the Trucial Coast of the Arabian Gulf got a significant input from basic volcanioclastics and/or volcanic rocks. Along with the detrital input, Cu leached by meteoric waters was also supplied from the basic source rocks to the Neogene depocentre and concentrated together with celestite during strong evapotranspiration. Stratigraphically-controlled fixed reductants such as the Kupferschiefer or mobile reductants, such as H2S-bearing waters and hydrocarbons, as it is the case in the Dzhezkazgan region, are missing in celestite deposits from Cyprus and the Arabian Gulf. As a conse-
quence, no sediment-hosted stratiform copper deposits evolved in the study area.

In Cyprus, saline oxic brines extracted Cu, Pb and Zn from subsalt sources and migrated through permeable Neogene reef limestones where they created an epigenetic celestite deposit. Its base metal contents still stands at a sub-economic level as neither a stable redox interface exists where these brines can mix with anoxic waters within a pore-fluid environment nor any fluid rich in organics and H2S are present to create a intrasalt (within the Neogene reef limestone) or suprasalt base-metal deposit.

In the Mediterranean region stratabound celestite deposits and Pb-Zn deposits occur side by side in the Algerian-Tunisian border region (Orgeval et al. 1989). This setting from northern Africa may be taken as an example of what could have been resulted from this brine migration if the syndiagenetic and epigenetic celestite deposition in Cyprus and along the Trucial Coast had successfully been brought to an end by the presence of either stratigraphically-controlled or mobile reductants in the late Cenozoic series.

In central Europe (late Permian, Middle Triassic, latest Jurassic) the epicontinental basin was temporarily cut off from the open sea and as a result of extensive evaporotranspiration strontianite and celestite were precipitated (Walther & Dill 1995). Behr et al. (1987) gave a first overview of the fluid inclusion characteristics of mineralizing fluids in central Europe, demonstrating that highly saline brines are typical of the post-Variscan epigenetic fluids. These saline brines have further on directed thoughts to the evaporitic sabkha-type series as the major source for salt-solution supplied brines emplacing the epigenetic base metal and F-Ba deposits in the platform sediments and along the unconformity with the uplifted Variscan basement highs (Dill 1988).

6. CONCLUSIONS

Syndiagenetic celestite-bearing evaporites (Gulf-type) are a model source of base metal deposits of stratigraphically-controlled fixed or mobile reductants elsewhere. The epigenetic celestite-bearing mineralization of Cyprus-type reflects an advanced stage of brine migration relative to the Trucial coast but brine mobilization failed to create a base metal deposit of its own mainly due to the absence of fixed or mobile reductants, which were present further westward in Tunisia and Algeria and in Mesozoic through Cenozoic platform sediments in central Europe, where numerous suprasaltmetal deposits came into existence (Walther & Dill 1995).

ACKNOWLEDGEMENTS

We would like to express our thanks to Dr. S. Nicolides (Geological Survey of Cyprus) and to N. Adamides (Eastern Mediterranean Resources) for their discussion.

REFERENCES


Dill HG, Henjes-Kunst F (2007) Strontium ($^{87}$Sr/$^{86}$Sr) - and calcium ($^{44}$Ca/$^{40}$Ca - $^{44}$Ca/$^{42}$Ca) isotope ratios of the Miocene Dam Formation in Qatar: Tools for stratigraphic correlation and environment analysis. GeoArabia (in press).


ABSTRACT: The Elk Point Basin in Saskatchewan, Canada contains some of the largest deposits of potash in the world. The high ore grade in many mines is affected by zones of disturbance that decrease the ore grade. This mineralogical-geochemical study investigates the geochemistry and mineralogy of such a disturbed zone at the Allan potash mine in Saskatchewan, Canada, and evaluates if they can be predicted using such methods. The data show that the mineralogical system comprises mainly halite and sylvite, with lesser amounts of dolomite, anhydrite, quartz and clay minerals (kaolinite, illite). The dominant geochemical and mineralogical process is the highly negative relationship between halite and sylvite. Many of the elements analysed are below detection limits or do not show any spatial distribution patterns that indicate their applicability as a pathfinder/vector elements for the prediction of anomalous zones. Some elements, however, (Br, As, Li) do show distribution patterns that indicate their applicability as possible pathfinder/vector elements for the prediction of anomalous zones.

KEYWORDS: Potash, Saskatchewan, geochemistry, XRD

1 INTRODUCTION

Saskatchewan is the world's largest producer of Potash and accounts for about 25% of world potash production. The largest single producer is the Potash Corporation of Saskatchewan (PCS), which operates six mines in Saskatchewan, Canada.

In order to maintain their world-class production, PCS is concerned with managing several key risks in their mining activities. One such risk is the pre-mining prediction of anomalous zones of structural disturbance which result in a decrease of ore grade and create potential catastrophic water inflow problems. In order to further understand these problems, PCS and the Mineral Exploration Group at the Saskatchewan Research Council (SRC) have undertaken a detailed geochemical-mineralogical study of an ~800m long panel in the E350N drive that passes through a disturbed mining zone at its Allan mine in Saskatchewan, Canada.

Previous studies have focussed on either a select number of elements, isotopic systematics of fluid inclusions (Chipley & Kyser 1989), the mineralogy of clay seams (Boys et al, 1986; Mossman et al. 1982), or the isotopic profiles of formation waters (Baadsgaard 1987; Jensen et al. 2006). This study represents the first multi-element, multi-technique employed and is a novel approach to understanding potash geochemistry (A Prugger pers comm. 2006).

2 SAMPLING STRATEGY

A total of 34 samples were collected for the project. The sample set comprised 3 samples from outside the anomalous area, referred to as ‘control samples’ and 31 samples across the ~800m panel in E350N, which included both normal and disturbed ground. The dataset included normal ore, leached ore, anomalous halite, washout material, and clay seam material (414 seam).

3 ANALYTICAL TECHNIQUES

Each sample was analysed at SRC by the following techniques: (1) Inductively Coupled Plasma Emission Spectrometry (ICP-ES) Partial Digestion - Ag, As, Bi, Co, Cu, Ge, Hg, Mo, Ni, Pb, Sb, Se, Te, U, V, and Zn; (2) ICP Total Digestion - Al₂O₃, CaO, Fe₂O₃, K₂O, 

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MgO, MnO, P₂O₅, TiO₂, Ag, Ba, Be, Bi, Cd, Ce, Co, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, La, Li, Mo, Nb, Nd, Ni, Pb, Pr, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, U, V, W, Y, Yb, Zn, Zr; (3) ICP whole rock fusion - Al₂O₃, CaO, Fe₂O₃, MgO, MnO, K₂O, Na₂O, P₂O₅, SiO₂, TiO₂, Ba, Cr, Sc, Sr, Y, Zr, loss on ignition. (4) Inductively Coupled Plasma Mass Spectrometry - Br, I; (5) Titration – CO₃ (only 10 representative samples); (6) Gravelometry - insoluble fraction; and (7) Quantitative X-Ray Diffraction.

4 MINERALOGICAL RESULTS

Quantitative XRD results indicate chloride phases (halite and sylvite) to be the predominant phases in all samples, with the insoluble phases (anhydrite, dolomite, quartz, clay) being generally present in minor to trace quantities (Table 1). The insoluble phases generally account for between 0.01 and 5 wt.% of each sample. However, three samples (51521, 51523, 51524) contain anomalously higher amounts of insoluble material; mostly in the form of clay and sulphate minerals.

5 GENERAL GEOCHEMICAL RESULTS AND DISCUSSION

Despite the large number of elements analysed, many of the trace elements are present in quantities below detection limits, e.g. Ce, Co, I, Pb - 1 ppm; U - 0.5 ppm; Eu - 0.2 ppm.

The results provide evidence that the main geochemical-mineralogical control is the highly negative association between the removal of sylvite and its replacement by halite (Fig. 1a). While some of the major elements can be attributed to certain minerals, for example Na → Halite, other elements can be attributed to several minerals, for example Ca → Anhydrite (CaSO₄) and Dolomite (CaMg(CO₃)₂). In contrast, many trace elements are harder to attribute to a single mineral phase.

A number of compatible elements (e.g. Ca and Sr, and Ba and Sr) show a positive correlation, although it is interesting to note that Ca also shows a positive correlation with Si (Fig. 1b), while the XRD results do not indicate the presence of any calcium silicate phases. This suggests that a number of the trace elemental distribution patterns are controlled by the amount non-soluble material within the sample, i.e. the higher the amount of insoluble material, the higher the trace element content of the sample. Such interpretation is further supported by the strongly positive Al-Ti relationship (Fig. 1c). Both of these immobile elements tend not to be affected by post-depositional processes and are not readily incorporated into chloride phases.

<table>
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<tr>
<th>Sample</th>
<th>51502</th>
<th>51509</th>
<th>51512</th>
<th>51519</th>
<th>51521</th>
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<td>96.2%</td>
<td>66%</td>
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</tr>
<tr>
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<tr>
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<td>2.6</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Dolomite</td>
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<td>4.9</td>
<td>0</td>
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</tr>
<tr>
<td>Quartz</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>3.1</td>
</tr>
</tbody>
</table>

6 ELEMENTAL VARIATION

While many of the elements, do not show any pattern with respect to the location of the anomalous zones, e.g. Cu, Cr, Ti, P; some elements do show interesting trends, e.g. K, Br, As, Li. These elements are discussed in detail below.

6.1 Potassium

Potassium contents within the control samples are variable, ranging from ca. 10 to 28 wt%. At the immediate margin of the disturbance, potassium contents are enriched, locally up to 40 wt%. Potassium is generally only present in very low concentrations (<1 wt%) within the area of disturbance, including the washouts. Within the disturbed area, however, a pocket of high potassium (up to 35 wt%) material is present (Fig. 2a). This is, however, limited in spatial extent (ca 100m).

6.2 Bromine

Bromine contents within the control samples range from 2 to 3 ppm. There is an overall decrease on bromine contents with proximity to the disturbance; this however, is more pronounced on the eastern flank of the anomaly than on the western flank (Fig. 2b). Bromine is generally only present in very low concentrations (below detection limits) within the area of disturbance and within the washouts. The pocket of sylvite-rich ore present within this disturbance also contains increased bromine contents (up to 3 ppm). These spatial variations
in bromine suggest that this element may be useful as a pathfinder/vector element for the prediction of zone of disturbance.

It is worth commenting upon that the bromine contents of the entire dataset are very low (2 to 3 orders of magnitude) compared to those from other potash deposits (Anderle et al. 1979; B Roulson personal communications 2006). This suggests that either the original evaporitic sea-water basin had an anomalous chemistry that was out of chemical equilibrium, or, that during diagenesis bromine was removed from the rocks on a large scale. In contrast, Jensen et al (2006) reports formation waters at the PCS Allan containing Br concentrations of up to 5000 mg/l.

6.3 Lithium

Lithium distribution and behaviour across the anomaly is complex. Its content within the potash ore outside the disturbance is highly variable, ranging from ca. 0.5 to 9 ppm. Within the disturbance, several interpretations of the data are possible. One such interpretation is that samples that generally contain ≤2 ppm Li have lower halite contents. The 2 ppm line is not a sharp boundary; rather it represents a grey zone of transition. There are outliers of low and high halite samples that lie on the wrong side of the line; these include the coarse crystalline halite samples, which are a replacement feature, and thus would not be a chemical equilibrium state as the original evaporite sequence.

A second interpretation is that the data show a sinusoidal-shaped best fit line across the disturbance, which is interrupted and overprinted by the anomalous washout material. This sinusoidal shape may be related to variations in the stratigraphic column.

6.4 Arsenic

Arsenic contents range from 0.1 to ca. 4.75 ppm within the samples. The high positive and negative correlation between As-K and As-Na, respectively, suggests that during the replacement of sylvite by halite, arsenic is released into the system. The arsenic variation across anomaly is complex (Figure 2c), and while it does not show a direct correlation with halite, it does broadly agree with the above interpretation. Samples that generally contain ≤1.25 ppm As have higher halite contents. However, the 1.25 ppm line is not a sharp boundary; rather it represents a transition zone of alteration. The data suggest that during the sylvite-halite replacement, a sample may loose up to 4 ppm As. Mass balance calculations using a block of ore material (500m x 500m x 5m) with an initial mineralogy of 75% sylvite (4ppm As) and 25% halite (0.5 ppm As), show that alteration to halite (100%; 1 ppm) would result in a loss of 2.6m³ of As.

7 CONCLUSIONS

This detailed geochemical-mineralogical
study across a disturbed mining zone at PCS Allan in Saskatchewan is a novel approach to studying these disturbances. The data show that the mineralogical system comprises mainly halite and sylvite, with lesser amounts of dolomite, anhydrite, quartz, and clay minerals (kaolinite, illite). Many of the elements analysed are below detection limits or do not show any spatial distribution patterns that indicate their applicability as a pathfinder / vector elements for the prediction of anomalous zones. Some elements (Br, As, Li) do show distribution patterns that may indicate their applicability as pathfinder / vector elements for the prediction of anomalous zones. Many of the trace element distribution patterns are controlled by the non-salt components.

ACKNOWLEDGEMENTS

We would like to thank the PCS for financial support during this project, We thank the PCS and the SRC for permission to publish the study. We are indebted to the Potash Corporation of Saskatchewan technical staff, especially Dr. Arnfinn Prugger, for all their help and stimulating conversations during the project, and the staff at PCS Allan for help with sampling.

REFERENCES


Exploration Controls in the Alabaster Deposits from Quinto Locality, Ebro Valley, Spain.

Fanlo, I.; Subías, I.; Mateo, E. & Biel, C.
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ABSTRACT: Nine cycles of gypsum interbedded with lutites beds have been recognized between 185.7 and 214m height in the sulphate sequence, which belongs to the Miocene Yesos de Zaragoza Formation. The gypsum is secondary and was developed close to the surface owing to the transformation of preexisting anhydrite, in contact with meteoric waters. The main gypsum lithofacies are nodular and intraclastic microbreccias. The quarried horizons display equidimensional fabric with euhedral crystals, coarse grained, uniform optical extinction, oriented fabrics aligned about parallel to bedding, and microselenite crystals. All these features clearly differ from those showed for the rest of gypsum horizons.

KEYWORDS: evaporite, gypsum, alabaster, Ebro Valley, Spain

1 INTRODUCTION

Over 7.2% of Spain’s surface is covered by gypsiferous rock formations. Within the Ebro valley, the south portion of province of Zaragoza and the northwest part of the province of Teruel, contains the largest area of gypsiferous soils in Spain, with 575,000 ha of these formations. These outcrops are mainly Tertiary massive gypsum along with intercalations of carbonates, clays and salts (halite with minor glauberite).

The history of quarrying activity in Zaragoza province seems to begin at least around the VII th century B.C. since alabaster remnants have been found in the ruins of a Celtiberian town near Azaila (59km southeast Zaragoza). Up to now, there are seven companies exploiting alabaster deposits in an area (2620 km²) with dozens of quarries that produce a variety of kinds of alabaster including the most precious of all, the transparent “Scaglione”. About 95% of the world’s supply of alabaster is produced in this district, whose estimated reserves exceed 50Mt. However, a few studies dealing with the characterization of the productive levels of alabaster have been made (Díaz 1994).

The present study was conducted to characterize the main alabaster horizon and evaluate a new one recently discovered in one of the quarries belongs to LISAR, S.L. Company, located in Quinto, a small village 40km southeast of Zaragoza. Mineralogical, textural and stratigraphic features of the aforementioned horizons

Figure 1: Geological map of the Ebro Basin and the study area (simplified from ITGE, 1995)
lead us to define both stratigraphic control and the best productive levels in order to correlate with other outcrops exploited in the area.

2 GEOLOGICAL SETTING

The Ebro Basin is one of the three main Tertiary sedimentary basins in the Iberian Peninsula. The basin lies in a triangular topographic depression, and is a composite foreland basin with foredeeps on both its northern and southern margins. The basin is flanked by the collisional Pyrenean orogen to the north (Muñoz & Casas 1997) and basement-involved deformational belts of the Iberian Ranges and Catalan Coastal Ranges to the southwest and southeast, respectively (Fig. 1). Syntectonic strata flanking the orogenic belts include a thick section of coarse clastic deposits along the southeastern and southwestern margins of the Ebro Basin, where they range in age from late Palaeocene to early or middle Miocene (Villena et al., 1996). Base-level rise consequent upon complete tectonic closure of the Ebro Basin in Miocene times caused major sediment aggradations and partial burial of the adjacent orogens (Coney et al. 1996). The continental evaporite formations of the Ebro Basin were formed in two main types of evaporitic lacustrine system: high and low concentration systems (Ortí, 1990). The studied alabaster horizons correspond to the high concentration lacustrine systems type (chloride-sulphate lakes).

At the beginning of the Miocene an extensive playa-lake was developed in the central sector, and the Yesos de Zaragoza Formation was deposited (Ortí, 1990). This Formation outcropping over a large area (11000 km²) in the central sector of the Ebro Basin is a thick sequence comprising up to 3000m of horizontal beds of gypsum with anhydrite in depth and includes halite and glauberite deposits up to 120m thick (Torrescusa & Klimekowitz 1990).

3 METHODS AND MINERALOGY

Detailed stratigraphic observation and sampling was carried out in the LISAR gypsum quarry (N41°27’39.7’’ and W00°32’59.8’’). Thirty samples were studied by microscopic
and X-Ray Diffraction means. Diffractograms were run between 2 and 60º 2θ on a Philips PW1729 X-ray diffractometer using Cu Kα radiation at scan speed 3º 2θ/min.

Gypsum is abundant in the studied section. Nine cycles of gypsum interbedded with beds of lutites have been recognized between 185.78 and 214 m. above sea level, corresponding to the lowest of the three productive units exploited in the quarries. Anhydrite and celestite are scarce in the gypsum beds, while the lutites are composed of quartz, illite, with minor chlorite and kaolinite; carbonates are always present, either calcite and/or dolomite.

4 GYPSUM LITHOFACIES

Textural study indicates that all the gypsum is secondary, with the exception of small cracks filled with fibrous gypsum. This secondary gypsum developed close to the surface owing to the transformation of preexisting anhydrite in contact with meteoric waters. The identification of secondary gypsum after (precursor) anhydrite is based on the presence of microscopic relics of anhydrite and some characteristic textures, such as the alabastrine (Figure 2A), porphyroblastic and the megacrystaline textures (Ortí 1977).

The gypsum beds are 20-90cm thick. The productive alabaster horizon (185.7m height), 60cm thick, is at the bottom of the sequence. There is another nodular horizon (212m height) next to the top of the sequence, which shows similar features than those of the productive bed, although its thickness (25cm) prevents exploitation. In addition, a red gypsum horizon of 60cm thick crops out at 210m height in the same locality, but it is absent in another quarries. Finally, there is an alabastrine gypsum horizon at 202.5m height of 50cm thick, which has been mined sporadically.

The following original gypsum lithofacies are recognized:

a) Nodular. It is the main lithofacies and it consists of white, fine-grained, alabastrine secondary gypsum nodules of 20-60cm diameter. These nodules are elliptical or spheroidal in shape, occasionally enterolithic, and show a chicken-wire pattern.

b) Intracratic microbreccias. This lithofacies corresponds to in situ deformation and only partial brecciation of layers of nodular gypsum. It forms layers from 10cm to 20cm interbedded with clay beds, up to 20cm, showing horizontal stratification. The fabric is densely packed, with subordinate fine-grained matrix surrounding the clasts. The size of the clasts is up to 1 cm in diameter. Inside the gypsum clasts, the lithofacies is nodular. Fibrous gypsum infill fractures, forming discontinuous horizontal and vertical veins that disrupt bedding. This type of gypsum is due to the volume increasing as a consequence of the hydration of anhydrite to form gypsum at relatively shallow depths without great overburden (Jowett et al. 1993).

5 MICROSCOPIC CHARACTERIZATION OF THE ALABASTER

The minerals accompanying gypsum are anhydrite, celestite, carbonates and clays.

The observed gypsum type depends on its position in the sequence. The highest horizon (212m height) is made up of anhedral microcrystalline alabastrine gypsum (Figure 2A), with some medium size gypsum subhedral crystals, which commonly have undulose extinction and form an interlocking mosaic in which individuals are difficult to distinguish. Microscopic relics of anhydrite are very scarce and occur exclusively in larger gypsum crystals. Clay minerals and micritic calcite and dolomite are present in small cracks and fractures, along with coarse-grained gypsum. In this horizon celestite is abundant, in general as euhedral and piramidal crystals up to 100µm.

Downward, the horizons are made by coarse-grained gypsum with abundant fibrous crystals infill fractures. This gypsum displays a poorer quality, the crystals show a non-uniform optical extinction and the presence of anhydrite prisms relics clearly have increased. In some thin sections it is possible to find heterometric aggregates composed by alternation of alabastrine gypsum with laminate of medium gypsum crystals with allotriomorphic shape and non-uniform optical extinction. Celestite is very scarce.

Between 196.6 and 194.5m height an intracratic microbreccias horizon occurs. It consists of microclasts of alabastrine gypsum ranging from µm to mm in diameter (Figure 2B). Some clasts are composed by megacrystalline gypsum with nonuniform optical extinction. There is porphyroblastic gypsum formed by medium and coarse crystals, allotriomorphs in shape with irregular boundaries indicative of dissolution. Coarse crystals of fibrous gypsum fill fractures (Figure 2C) and a mixture of clay and
micrite disrupts all the rock (Figure 2B). Anhydrite is very common in all the types of gypsum, except for fibrous type. Celestine is absent.

By contrast, the quarried horizons (202.5 and 185.7 m height) display textural features that clearly differ of those showed by the aforementioned gypsum horizons. Generally, they show an equidimensional fabric with euhedral crystals, coarse grained, uniform optical extinction and oriented fabrics aligned about parallel to bedding. There are microselenite crystals with marked exfoliation (Figure 3D). Laths of anhydrite are common, while carbonates, clays and celestite are absent.

6 CONCLUSIONS

The quarried horizons (185.7 and 202.5 m height) show specific features to be used as control criteria and as a guide for alabaster exploration because of both their position and properties.

Upsection, a new horizon (210 m height) has been discovered. In spite of its thickness (60 cm), the textural characteristics do not show such a good quality as the quarried ones. However a stratigraphic correlation on the basis of the quarried horizons allows one to recognize this horizon all over the district to check if a better quality can be found.

Moreover, the highest horizon (212 m height, 25 cm thickness) should be explored to define possible further economic zones.

ACKNOWLEDGEMENTS

The authors wish to thank to Mr. Juan de Dios Guerrero and Lisar S.L. Company for providing assistance in the fieldwork and access to quarries. We gratefully acknowledge the support provided by Convenio Ibercaja-Universidad de Zaragoza (Project IBE2004-CIE-05).

REFERENCES


Instituto Tecnológico y Geominero de España (1995) Mapa geológico de la Península Ibérica, Baleares y Canarias, 1:1.000.000. Madrid


Evaporate minerals in the Khur and Biabanak Playa, Central Iran

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ABSTRACT: Continental playas are one of the major sources of evaporate minerals. Several playas and salt pans are presently known in Iran, one of which is Khur and Biabanak playa, locating 140 km east of the city of Anarak, in the state of Esfahan, central Iran. Field-work and borehole investigations indicate that the average depth of brine is 20 to 25cm below the surface and the thickness of the salt crust is about 6m. The average composition of the brine using different analytical methods indicate that the main minerals in the Khur and Biabanak brine are halite, sylvite, carnallite, and calcium-chloride. The total estimated reserve of the brine is about 150million m$^3$ with an average density of 1.22g/cm$^3$.

KEYWORDS: Evaporate minerals, Playa, Khur and Biabanak playa, Iran

1 INTRODUCTION

One of the industrial minerals that is very important in producing fertilizers and other industrial products is potassium hydroxide (KOH), produced from potassium chloride (KCl) that occurs in different amounts in the brines of salt lakes and playas.

Continental playas are constructed of stratiform salt units, commonly with the greater volume of salts forming in halite-dominated evaporitic mudflats and salt pans (Warren, 1999). Several salt lakes, playas and salt pans in Iran have been examined for extracting potassium chloride from their brines or salt plugs. Among the lakes, Orumieh Lake in the state of western Azarbayjan, Gavkhuni Lake in the state of Esfahan, Namaque lake in the state of Qom and Maharlu Lake in the state of Fars are important.

Playas and salt pans at Torud in the state of Semnan, Tabas in the state of south Khorasan, Sirjan in the state of Yazd and Khur and Biabanak in the state of Esfahan have been studied. Khur and Biabanak playa located at 33 28’ to 34 28’North latitude and 54 16’ to 54 30’East longitude has the most promising potash potential in Iran. This playa is located 140km east of Anarak in the state of Esfahan, about 800 metres above sea level.

2 METHODS OF INVESTIGATION

More than 2000 boreholes have been drilled in the Khur and Biabanak area. The average depth to the brines is 20cm below the surface and the thickness of the salt crust is about 6 m. This playa has a typical stratiform beds, of platform evaporates with a thickness ranging from 5 to 10 m with lesser volumes of the bittern salts of Warren's (1999) classification of ancient evaporates. Extraction of the evaporate minerals follows the following stages:

a) The brine will be pumped to special constructed ponds.

b) The Solar heat will evaporate the water until the density of the brine increases from 1.214 to 1.36 gr/cm$^3$. At this stage most of the halite mineral precipitates.

c) The dense brines will then be pumped to the next ponds for evaporation until the density of the brines increase from 1.36 to 1.45 g/cm$^3$.

At this stage most of the potassium chloride, magnesium chloride, and the rest of the halite mineral will precipitate. The evaporates formed at the bottom of the ponds will then be carried to the factory in order to increase the purity of the salts and also increase the grade of their mineral contents (Ahmadzadeh Heravi, 1999).
The Torud and Khur playas cover about 7000 km² and are located in central Iran (Stocklin, 1968), and the area can be divided into three sub zones. The northern sub zone is called the Torud playa and the other two that are in the intermediate and southern sub zone are called the Khur and Biabanak playa respectively. The area of Khur and Biabanak playa is approximately 2000 km². The geology of this playa is very simple. It includes:

1) Salt crust that is composed of white crystalline and black halite. This unit is very porous and is crowded with abundant bubbles and fine clay particles. In the salt cracks of the various parts of the playa, abundant streams of brine occur, sometimes indicating locally with upward movement of the brines. The age of this unit is Eocene. In some parts of the salt crust clayey substances and salt solidify and form a rounded wall shape with a height of approximately 50cm. These features are locally called "bowl of kavir". Polygonal cracks are also present on the surface of the salt crust, filled with halite resulting from ascending salt from lower units via capillary movements of the brines.

2) A moist zone is present with liquid derived from the surrounding alluvial cones. On the surface of this zone a thin halite crust occurs over a silt-clay sedimentary layer that contain light salty brine.

3) Silt and clayey flats indicate that the water table in this unit is deeper relative to the other two units. Field work in this unit during rainy seasons is almost impossible and all of the exploration activities are stopped in these seasons due to poor ground conditions.

4 MINERALOGY AND GEOCHEMISTRY

Various analytical methods, including atomic absorption spectrometry, flame-photometry, and wet chemical analyses were used to determine the chemical composition of the evaporate minerals and the average composition of the brines (Table 1). The results of the brine are:

\[
\begin{align*}
NaCl &= 230 \text{ g/l,} \\
MgCl_2 &= 80 \text{ g/l,} \\
CaCl_2 &= 50 \text{ g/l,} \\
NO_3 &= 6.3 \text{ g/l,} \\
KCl &= 6g/l, \\
Li &= 30 \text{ ppm.}
\end{align*}
\]

The main minerals recognized in the brines are halite, sylvite, carnallite, and calcium chloride. The grade of the salt at the bottom of the sedimentation ponds reaches about 99 percent. After drying, the grade of the salts decreases to about 96 percent due to the impurities that are caused by desert winds. In the precipitates of the ponds the percentage of different chemical salts reaches to the following amounts:

- $MgCl_2 = 27$ to $33$ wt percent
- $KCl = 18$ to $22$ wt percent and
- $NaCl = 12$ wt percent.

5 EXPLORATION

In order to determine the amounts and the grade of the potential evaporate minerals in Khur and Biabanak playa, geologists from the Geological Survey of Iran have dug many shallow pits 30 to 70 cm deep in various places on the playa in different seasons. The water levels are deeper during the dry seasons. About 2000 shallow pits throughout the playa were dug to determine the thickness of the brine-bearing salt crust and several exploration wells were drilled with an average depth of 15m. The thickness of the brine-bearing salt crust was estimated to be about 6m. A layer of fine grain sand and silty clay underlies the salt crust in the playa. The porosity of the salt crust is estimated to be about one percent. The total volume of the brines in the Khur and Biabanak playa is estimated to be more than 600 million m³ With an approximation of 75 percent recovery the total recoverable brines would be about 450 million m³. Since the extraction of the brines is planned to be about 15 million tonnes of brine per year, the estimated amount of available products would be about 50,000 tonnes of potassium chloride, 30,000 tonnes of magnesium chloride and 300,000 tonnes of sodium chloride per year, over an estimated duration of this stage of operation of 30 years.

6 METHODS OF EXTRACTION

Extraction of the brines in the Khur and Biabanak playa will start with digging several channels 3 to 4m width and about 4m depth. The brines from the channels are transported to the evaporating ponds. During the process of evaporation in the evaporating ponds the sodium chloride starts precipitating and the density of the remnant brines increase. The average amounts
of potassium chloride, magnesium chloride and calcium chloride in the remaining brines gradually increase.

This process continues until the density of the brines reaches about 1.362 g/cm³ (Table 1). At this stage, the brines would be transported to the carnallite extraction ponds. The evaporation process in the carnallite ponds continues until the density of the brine reaches 1.450 g/cm³.

During this stage of evaporation most of the potassium chloride and magnesium chloride precipitates. The remnant brine should immediately be removed from the carnallite extraction ponds because at the densities higher than 1.450 g/cm³ calcium chloride starts crystallizing and covers the entire carnallite layer.

Detail sampling and analyses in different seasons indicate that there is a higher input of rainwater to the brines during the winter, thus, the average amounts of KCl, CaCl₂, MgCl₂, NO₃, and Li decrease whereas the amount of NaCl increases. This relationship reverses in the summer or dry season, during which the amounts of KCl, CaCl₂, MgCl₂, NO₃ and Li increase while the amount of NaCl decreases. Processing the minerals from the brine and extracting large amounts of KCl, grading up to 90 percent, is planned from the facilities being prepared in the Khur and Biabanak playa.

### 7 CONCLUSIONS

Studies on about 60 salt pans, playas and salt lakes in Iran indicate that only three could be considered for the potential production of evaporate minerals. Of these three the Khur and Biabanak playa in the state of Esfahan is most promising due to the relatively high potassium and magnesium enrichment and the low enrichment of calcium sulphate. In order to extract evaporate minerals the brines should be pumped to different ponds in which various salts can be extracted. The more important factors that affect the extraction processes are sunshine, wind, and the amount of yearly rainfalls. These factors all affect the density of the brines in the playa, and during the process of mineral extraction.

The reserve in the brine of the Khur and Biabanak playa is estimated to be about 150 million m³. The average thickness of the salt layer, located 20 to 50cm below the surface, is about 6m and the average density of the brine is 1.22.

### REFERENCES


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**Table 1. Chemical composition of the Khur and Biabanak evaporate samples of various densities**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Density g/cm³</th>
<th>NaCl g/l</th>
<th>KCl g/l</th>
<th>MgCl₂ g/l</th>
<th>CaCl₂ g/l</th>
<th>pH</th>
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<td>Channel brine</td>
<td>1.215</td>
<td>228.02</td>
<td>6.18</td>
<td>43.74</td>
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<tr>
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<td>11.02</td>
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<td>6.37</td>
<td>5.72</td>
<td>226.87</td>
<td>426.71</td>
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MAGMATISM AND ORE GENESIS
IN THE TETHYAN ARC

EDITED BY:
KALIN KOUZMANOV
IRENA PEYTCHEVA
ALBECHT VON QUADT
INTRODUCTION

The Mesozoic and Cenozoic Tethyan collage stretching from Europe across southern Eurasia is an extremely complex geologic terrain caught between colliding continents. Ore deposits across the region are known and have been mined for thousands of years. Many world-class and large deposits, such as Bor, Chelopech, Sar Cheshmeh, Angoran, and Kisdaladag and Copler to name a few, are also known. Although quite complicated, the geodynamic setting of the Tethyan collage is reasonably well known as a result of decades of geologic investigation. However, a similar understanding of the metallogenic evolution of Turkish part of this collage is not available or only sparsely known. Turkey is currently receiving exploration interest for epithermal and porphyry Cu-Au deposits in the Pontides and Anatolides-Taurides that stretch from the west across the central to the eastern parts of the country where they continue into Iran.

Crucial to understanding the metallogenic evolution of Turkish metallogenic belts is a reliable time-based geological framework of events. This framework provides important constraints on the following questions: What is the nature and timing of the magmatic arc? When did the various types of ore deposits form, and under what conditions? This paper seeks to establish a petrochemical and geochronological framework in reconstructing the geological evolution of the late Cretaceous to Middle Eocene magmatism, and in identifying the temporal relationship between magmatism and mineralization in eastern-southeastern orogenic belt (SEAOB) of Turkey (Figure 1). The resulting framework can be linked to the Tethyan belt in Eastern Europe, and provides a basis for
remotely examining the Tethyan belt in Iran to the east. The U-Pb age dating was carried out on the zircon separates by Laser ablation ICP-MS techniques. Ar-Ar dating was carried out on the hornblende, biotite, K-feldspar, phlogopite and sericite separates, and these were radiated at the McMaster Nuclear Reactor in Hamilton, Ontario. Then, the samples were analyzed at the Noble Gas Laboratory, Pacific Centre for Isotopic and Geochemical Research, University of British Columbia, Vancouver, BC, Canada. The analytical and sample preparation methods are given in http://www.eos.ubc.ca/research/pctigr/.

2 MAGMATISM IN EASTERN-SOUTHEASTERN TURKEY

The tectonic environments in SE Turkey are related to the northward subduction of African-Arabian plate beneath the Eurasian plate (Anatolides sensu stricto) (Aktas & Robertson 1984; Yilmaz 1993; Yilmaz et al. 1993; Beyarslan & Bingol, 2000; Sengor et al. 2003) initiated during late Cretaceous (about 90 Ma) and culminated at middle Miocene times (Parlak 2005; Robertson & et al. 2005). The recent geologic data reveals that generation and evolution of magmatism in SEAOB reflects subduction through Bitlis-Zagros system. The regional geologic data and the recent findings confirm that this subduction is a two-fold subduction (Robertson et al. 2005); an earlier phase is by northward subduction of oceanic crust of southern Neo-Tethyan ocean beneath eastern Taurides (Malatya-Keban platform) forming suprasubduction zone environment (SSZ; Parlak et al. 2004; Robertson et al. 2005) (90 Ma) and related ophiolitic rocks, ensimatic arc-type rocks. The next phase is the subduction of SSZ type oceanic crust (Andean type subduction) beneath eastern Taurides that gave rise to arc magmatic rocks (82.3 to 77.5 Ma) intruding the SSZ ophiolites and metamorphosed platform carbonates. At the advanced stages of subduction, it is highly likely that a hinge retreat or a roll-back mechanism took place during latest Cretaceous (74.3 to 71.3 Ma), and calc-alkaline to alkaline magmatic rocks were formed.

In general, the geochemical signatures of all late Cretaceous-Tertiary igneous rocks are suggestive of magmatic-arc and post-collisional to late orogenic magmas. Field relations, petrographical and geochemical data are consistent with a combination of magma-mixing, fractional crystallization, and contamination by crustal melts observed across the whole belt. Contamination of mantle magmas by crustal melts predominates in the southwest diminishing towards the rocks emplaced earlier in the southern and northern part of the belt. Hinge retreat coupled with advanced orogen-parallel extension, is consistent with the generation of crustal-contaminated mantle melts (71-70 Ma) in the northern part of the belt. An incipient rupture in the case of slab roll-back process is likely to occur in between arc (south) and post-collisional (north) magmatic settings. The result is increased extension and invasion of hot asthenospheric mantle through open windows, and consequent partial melting of broken slab producing calc-alkaline magmas at early-middle Eocene (54.3 to 44.4 Ma) having subduction and/or arc signatures inherited from the earlier subducting slab during late Cretaceous (82.3 to 77.5 Ma).

<table>
<thead>
<tr>
<th>Type of mineralizations</th>
<th>Name of deposits</th>
<th>Age of alteration</th>
<th>Composition of igneous rock</th>
<th>Age of igneous rocks</th>
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<td>Porphyry Cu-Au</td>
<td>Nazarasi</td>
<td>77.6±2.0 (Ar-Ar)</td>
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<td>82.9-77.5 (Ar-Ar)</td>
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<td>IOCG</td>
<td>Hasancelebi</td>
<td>69.9-68.6 (Ar-Ar)</td>
<td>Sy-tr</td>
<td>74.4-71.3 (Ar-Ar,U-Pb)</td>
<td>Post-COLG, Roll-back (alkaline)</td>
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<td>Mz-mzd</td>
<td>73.5-73.4 (Ar-Ar)</td>
<td>Post-COLG, Roll-back (calc-alkaline)</td>
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<td>Porphyry Cu-Mo-F</td>
<td>Keban</td>
<td>74.0 (Ar-Ar)</td>
<td>Sy-tr</td>
<td>71.0-69.9 (U-Pb)</td>
<td>Post-COLG, Roll-back (alkaline)</td>
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<td>Copler</td>
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<td>54.3-47.1</td>
<td>Gr-mzd</td>
<td>50.4 (Ar-Ar)</td>
<td>Incipient rupture, Arc (?)</td>
</tr>
</tbody>
</table>

Table 1. General characteristics of the mineralization in SE Turkey; sy-syenite; di-diorite; tr-trachyte; mz-monzonite.
Figure 1. Simplified geological map of southeastern Turkey (modified from 1/500,000 geological map of Turkey.)
3 TEMPORAL LINK BETWEEN MINERALIZATION, MAGMATISM, AND SUBDUCTION EVOLUTION IN SE TURKEY

The U–Pb zircon and Ar-Ar age data for magmatic rocks and associated alteration zones from the Cu-Au porphyry deposit at Baskil, the Cu-Mo-F porphyry deposits at Keban, IOCG deposits at Hasancelebi and Divirgi, Fe-skarn deposits at Karamadazi and Horoz, Cu-Au porphyry deposits at Copler and Kabatas confirmed that there are three distinct metallogenic phases during an evolving orogen along Bitlis-Zagros subduction system (Table 1). The earlier magmatic activity in SE Turkey started at the southern border of the SEAOB with the intrusion of large monzodiorite, granodiorite-granite body at 82.9±0.43 to 77.5±2.7 Ma into metamorphosed basement rocks of Tauride platform by an Andean-type subduction, which is coeval with the ore forming process at Nazarusağı (Baskil) deposit. This is defined as the first metallogenic epoch (phase-I) during which the Cu-Au porphyry systems at Baskil formed. The change in the subduction geometry by a hinge retreat (slab rollback) coupled with incipient orogen-parallel extension on the over-riding plate caused the generation of postcollisional calc-alkaline melts at 74.4±0.5 to 73.4±0.4 Ma which is coeval with the formation of IOCG deposits at Hasancelebi and Divirgi. Further increase in the roll-back or regional extensions created partial melts that were emplaced into the metamorphic terrains along transtensional, deep crustal structures. High precision U-Pb and Ar-Ar ages confirmed that this event took place at 74.1 to 69.9±0.5 Ma which is contemporaneous with the IOCG systems in Divirgi and Hasancelebi, and porphyry to skarn type Cu-Mo-F mineralization at Keban. Combined with the age data from the IOCG and Cu-Mo-F porphyry related magmatic rocks and alteration zones, the time interval between 74.1±0.5 to 69.9±0.5 Ma is defined as the second metallogenic epoch (phase-II) in an evolving extensional setting in central-eastern transect. This time is regarded as the main metallogenic epoch that produced the majority of mineralization in southeastern Turkey. The slab break or incipient rupture was coupled with crustal scale structures and co-magmatic shallow intrusions at 54.3±1.7 to 44.4±0.6 Ma, which is coeval with the Cu-Au porphyry and Fe-skarn mineralizing process at Copler-Kabatas and Karamadazi-Horoz deposits, respectively (phase-III). This is an important era during which the economic porphyry and Fe-skarn mineralizations were formed in SE Turkey.

ACKNOWLEDGEMENTS

The work presented here is part of an ongoing research project carried out by the authors at the Mineral Deposits Research Unit at UBC, Canada. The work is generously sponsored by Teck Cominco Ltd and Barrick Gold Corp.

REFERENCES


Magmatic influence on the zonation of the Palaeogene epithermal mineralization in the Central-Eastern Rhodopes, Bulgaria and Greece

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ABSTRACT: Tertiary epithermal deposits in the Rhodope Massif exhibit an increase of Cu and Au and decrease of Pb-Zn and Ag, from the Central Rhodopean vein and carbonate replacement deposits (Madan, Laki), through intermediate-sulphidation deposits (Chala, Madjarovo, Zvezdel) in the E Rhodopes, to high-sulphidation deposits (Perama Hill, Sappes) in the SE Rhodopes. These geographic variations coincide with: (1) the changing composition of their host magmatic rocks, from predominantly silicic types in the Central Rhodopes through strongly fractionated shoshonitic to high-K calc-alkaline (NE Rhodopes) to calc-alkaline and high-Cr/Ni shoshonitic (SE Rhodopes) rocks, and (2) decreasing degree of crustal contamination, reflected in their radiogenic isotope signatures. The observed variations may reflect asymmetric asthenospheric uplifting, extension and thinning of the crust under the Eastern and Central Rhodopes.

KEYWORDS: Rhodope Massif, magmatism, extension, metallogeny

1 INTRODUCTION

In a recent paper, Marchev et al. (2005) demonstrated that epithermal deposits and their host rocks in the Rhodope Massif exhibit well-expressed geographic variations. The large vein and carbonate replacement Pb-Zn deposits (Madan and Laki), hosted predominantly by high-grade metamorphic rocks in the eastern part of the Central Rhodopes, are associated with felsic dykes and ignimbrites; intermediate-sulfidation (IS) Pb-Zn-Cu±Ag-Au epithermal deposits (Chala, Madjarovo, Zvezdel) in the NE Rhodopes are hosted by shoshonitic (SHO) to high-K calc-alkaline (HKCA) volcanic rocks, and high-sulphidation (HS) deposits in the SE Rhodopes, Greece (Perama Hill, Sappes), are hosted in calc-alkaline (CA) to HKCA and high-Cr/Ni shoshonites.

This study presents geochemical data of the Cretaceous-Oligocene (39-26 Ma) magmatic rocks that are spatially and temporally associated with ore deposits and discuss the implication of the changing ore-metal composition found in the Rhodope epithermal systems.

2 GEOLOGICAL SETTING

The Rhodope Massif in southern Bulgaria and northern Greece is a part of the Alpine-Himalayan belt in the northern part of the Aegean region. During the late Cretaceous-Eocene times it has experienced subduction-collision events, accompanied by two periods of magmatism: the first during the latest Cretaceous-Lower Eocene (69-42 Ma) time, and the second during late Eocene-early Oligocene (39-26 Ma) this reference is not correct (Marchev et al., 2004). These magmatic periods coincide with two episodes of crustal extension in the region that differ both in mode and style: an early Tertiary ductile extension/exhumation of several metamorphic core complexes below low-angle detachments; and (2) a subsequent late Eocene-Miocene brittle extension through high-angle faulting. Within this changing tectonic environment, the composition of the magmatic products also changes with time. late Cretaceous-Palaeocene magmatism is represented exclusively by plutons composed of amphibole-biotite granodiorite and biotite- and two-mica granites. In contrast, late Eocene-Oligocene magmatism is represented by volcano-plutonic
suites and intrusives with gradually changing compositions from predominantly felsic in the Western and Central part of the Massif to largely variable in K and Si in the Eastern Rhodopes. Magmatic rocks associated with epithermal deposits

The locations of discrete magmatic centers that are spatially and temporally associated with the epithermal ore deposits are shown in Fig. 1. The magmatism is part of a large magmatic belt, which spread over the entire Rhodope Massif and extends to the NW into the Serbo-Macedonian Massif and Vardar zone and to the SE into Turkey.

The Pb-Zn hydrothermal deposits in the Madan ore field, although hosted in metamorphic basement rocks, show a close spatial relationship to the local igneous rocks; no porphyry mineralization is known from the area. Igneous rocks are represented by felsic dyke swarms and the large ignimbrite flows of the Kotili-Vitinia and Perelic volcanic areas, followed by younger dykes and subvolcanic bodies of latite and HKCA andesites. The rocks are character-
ized by highly enriched values of Sr and Nd isotopic ratios (Fig. 1).

The most important IS epithermal deposits (Chala, Madjarovo, and Zvezdel-Pcheloyad) are hosted in the SHO and HKCA magmatic rocks of the Borovitsa, Madjarovo and Zvezdel paleovolcanoes. Occasional occurrences of Cu-Mo porphyry mineralization have been identified in close spatial proximity. Intermediate rocks predominate in all three volcanic areas, with felsic varieties being voluminous in Borovitsa and subordinate in Madjarovo and Zvezdel. Shoshonitic rocks in the Borovitsa volcanic area are also accompanied by rare UK rocks and high Ba-Sr trachybasalts. Small intrusive bodies of gabbro, monzonite and syenite intrude the lavas in all three volcanic complexes.

The least evolved rocks have similar primitive mantle-normalized element patterns, typical of the subduction-related magmatism, with peaks at Rb, Ba, Th, K and Pb and troughs at Nb and Ti. Borovitsa rocks show the most enriched Sr and Nd isotopic signatures, followed by Madjarovo and Zvezdel (Fig. 1).

The major deposits of HS epithermal style (Sappes and Perama) are located in the volcanic areas of Kirki-Essimi and Petrota graben. Spatially associated with them are numerous un-economic porphyry mineralizations (Voudouris et al. 2003). Volcanic activity of the Kirki-Essimi is dominated by intermediate and acid lavas, domes and subvolcanic bodies and subordinate mafic lavas. Petrota graben consists of early rhyolitic ignimbrites, SHO andesites and dacites, followed by late HKCA andesites (Ar- kias & Voudouris, 1998; Christofides et al., 2003; Marchev et al. unpubl. data). Compared to the SHO and HKCA rocks from Bulgaria, CA rocks from Kirki-Essimi and Petrota have the lowest K and trace-element contents. The Petrota SHO differ from those in Bulgaria by exhibiting higher contents of Ni and Cr. These rocks are similar to the high-Mg basaltic andesites and andesites, recently divided by Agostini et al. (2005) but differ from them by higher K content and lower Mg contents.

Compared to the SHO and HKCA rocks from the north, the rocks from Petrota graben (Fig. 1) exhibit considerably more mantle Sr isotope signature. Two samples from the neighboring Loutros-Feres-Dadia yield even more mantle Sr and Nd isotopic values.

3 RELATIONSHIP BETWEEN EPITHERMAL DEPOSITS AND MAGMATISM

The genetic link between epithermal mineralization and Palaeogene magmatism has been recently demonstrated by Marchev et al. (2005). The following major points support their genetic relationship:

1) The precise $^{40}$Ar/$^{39}$Ar and U/Pb ages show either direct relationship to specific magmatic events or coincidence of age of mineralization with the late stage of the volcanism.

2) Pb and Sr isotope analyses of sulfides and gangue minerals and the local igneous and metamorphic rocks show predominantly magmatic source with small or negligible contribution from the basement rocks in the volcanic-hosted deposits and a larger contribution in the metamorphic-hosted deposits.

3) The coincidence of the change in the metal association in the deposits with the geochemical signature (composition and isotopic variations) of the magmatic rocks from W to SE.

4 MAGMATIC INFLUENCE ON THE METAL COMPOSITION OF THE ORE DEPOSITS

Previous studies (Marchev et al. 2004) demonstrated that the late Eocene-early Oligocene magmatism in the Rhodope Massif shows clear geographic compositional variations which is expressed as a progressive decrease of the felsic/basic-intermediate rock proportions and radiogenic isotope compositions, coinciding with decreasing crustal thickness from W to SE. This zonation was interpreted to reflect different degree of fractionation and assimilation during the passage of magma through the crust. Overall, the situation seems to reflect an asymmetric style of extension; much stronger in the Eastern Rhodopes and weaker in the Central and Western Rhodopes. In addition, isotopic features of the studied rocks from the E Rhodopes show the effects of less crustal contribution to the magma budget, with the order of emplacement from high Ba-Sr basalt and SHO (34-32 Ma), through HKCA (32-31 Ma) in Bulgaria, and Kirki-Essimi and Petrota andesites and SHO (32-27 Ma). A final alkaline volcanism (28-26 Ma) represents OIB-like asthenospheric-derived mantle melts, with no evidence of crustal contamination. This sequence has been interpreted by Marchev et al.
(2004) to reflect progressively decreasing amount of crustal contamination as a result of advanced crustal thinning associated with asthenospheric uplift and tectonic extension. Similar temporal change from SHO and CA magmas, through high-Mg and finally by Na-alkaline basalt is also typical for the Miocene-Pliocene magmatism in the Aegean region and Western Anatolia (Agostini et al. 2007). Recent tomographic images of the region (Spackman et al., 1993; Bijwaard & Spackman, 2000) show a high-velocity zone in the upper mantle beneath the region, which appears to provide heat and asthenospheric magmas for the OIB basalts. Underplating of such magmas at the crust/mantle boundary was proven by findings of mafic and ultramafic xenoliths in the Eastern Rhodope’s alkaline basalts (Marchev et al. 2006). Emplacement of these magmas caused thermal reset, extension and thinning of the crust. Therefore, different degrees of melting accompanied by fractional crystallization and contamination at the base of the crust and during the passage to the surface could produce the whole range of magmas observed in the Rhodopes. The elevated contents of Au and Cu in the Eastern Rhodope deposits probably reflects originally higher contents of these elements in the mantle magmas, whereas crustal contamination dilutes their concentrations and introduces Pb from the Rhodope basement rocks.

5 CONCLUSIONS

The change in the ore-metal composition in the Rhodope epithermal systems from prevailing Pb-Zn in the Central Rhodopes towards Cu-Au in the Eastern Rhodopes reflects the variation of the crust/mantle element budget in the spatially associated magmatic rocks.

The magmatism and epithermal mineralization is most likely formed in an extensional “back-arc” environment. Differences in the composition of the magmas are the results of differing styles of extension in the Central and Eastern Rhodopes.

Convective removal of the subcontinental lithosphere and underplating of asthenospheric-derived magmas at the crust/mantle boundary caused continuous thinning of the crust, decreasing crustal input and increasing amount of more pristine mantle component in the source magmas.

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
Upper Cretaceous magmatic evolution and related Cu-Au mineralization in Bulgaria and Serbia

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ABSTRACT: The Apuseni–Banat–Timok–Srednogorie (ABTS) belt of extensive calc-alkaline magmatism and Cu–Au mineralization is related to the subduction of the Tethys ocean beneath the European continental margin during the late Cretaceous time. Major economic porphyry-style and high-sulphidation ore deposits are restricted to certain segments along the belt and are aligned on the Panagyurishte corridor (Central Srednogorie) in Bulgaria and the Timok region in Serbia. Present study reviews and compares the geology, geochemistry and geochronology of igneous events in these two regions and some features of the related Cu-Au mineralization. In the Central Srednogorie the U–Pb dating of zircons from subvolcanic intrusions and major plutons, supplemented by published Ar-Ar and Re-Os age data for the hydrothermal ore deposits reveal a general younging of magmatism from ca. 92 Ma in the north (Elatsite deposit) to ca. 78 Ma in the south (the barren Capitan Dimitrijevo pluton). In Timok region the magmatism seems to start at 90-86.6 Ma (first phase) and to end with the intrusion of plutons about 82-78 Ma. Economic Cu–Au mineralizations in both sections are related to subvolcanic or volcanic suits and are dated in the range of 92 to 86 Ma in Bulgaria and mainly about 86-84 Ma in the Timok zone. Magmatism and ore formation in individual magmatic–hydrothermal complexes along the profiles are much shorter lived. The lack of mineralization in the time span 86-78 Ma might be explained with the more deeply eroded mid-crustal plutons, while the hydrothermal deposits are linked with shallow intrusions. The age progression correlates in both profiles with an isotope-geochemical trend (Sr-Nd WR and Hf-zircon data) of decreasing crustal input into mantle-derived magmas. The age and geochemical trends are explained as a consequence of slab retreat during oblique subduction. Later on, trenchward the characteristics of the Cretaceous magmatism changed to more crustal influenced, which could be related to continent accretion from the south and the start of continent collision. In the Ridanjkrepoljin Zone in Serbia subvolcanic dacites are dated at ~70 Ma and in the Rhodopes granitoid plutons in Rila-West Rhodopes and in the Eastern Rhodopes (Chuchuliga and Rosino) revealed U-Pb zircon ages in the range 67-70 Ma. Contemporary the mineralization type changed from Cu-Au to Pb-Zn-Cu with lower ore grades than that of the Turonian-Coniacian deposits.

KEYWORDS: copper-gold, ABTS-belt, magmatism, zircon dating, isotope tracing, tectonic

1 INTRODUCTION

The ABTS belt (Popov et al. 2000) is part of the Tethyan Eurasian Metallogenic belt (Jankovic 1997) and includes some of the best examples of porphyry copper and Cu–Au epithermal ore deposit in Europe, in a broadly similar subduction setting to the Circum-Pacific region (e.g. Sillitoe 1991; Tosdal & Richards 2001). Active mines include Majdanpek, Bor and Veliki Krivelj in Serbia and Elatsite, Chelopec and Assarel in Bulgaria. Several attempts have been made to relate large-scale tectonic processes and the resulting magmatism in the ABTS belt with associated Cu–Au mineralization (Jankovic 1997; Berza et al. 1998; Ciobanu et al. 2002; Popov & Popov 2000). A new package of high precision U-Pb zircon data, including geochemistry and isotope tracing have been produced and partly pub-
lished during the GEODE program of the European Science Foundation and the SCOPES joint research projects of SNF. In the present study we focus on the geological, geochronological and isotope geochemical characteristics of Cretaceous magmatic rocks in the Central Srednogorie Zone of Bulgaria (Fig. 1) and its extension in the adjacent Rhodope region as well as in the Timok and Ridan-Krepoljin belts in Serbia. We then consider the changes in the tectonic environment and magmatic style across the belt as crucial for understanding why economic deposits were formed in some locations and at specific times.

Figure 1. Tectonic sketch map of the Balkan Peninsula with the distribution of the Cretaceous magmatism (modified after Dabovski 2006, pers. comm.) with the new and published age data. Data for the Eastern Srednogorie are from Georgiev et al. 2006 and unpublished.
2 TIMING AND SOURCES OF THE CRETACEOUS MAGMATISM IN CENTRAL SREDNOGORIE AND IN THE RHODOPE MASSIF

The geology of the Panagyurishtse district consists of pre-Mesozoic metamorphic and igneous rocks, fallout and overburden by abundant late Cretaceous magmatic and sedimentary rocks, and partly covered by Tertiary sedimentary rocks. Andesitic magmas predominate in the northern and central Panagyurishte district, whereas granodioritic to gabbro intrusions are more abundant in its southern part. Rhyodacites and rhyolites only occur in the central and southern Panagyurishtse district.

The magmatic rocks associate with (a) the Cu–Au porphyry deposits at Elatsite, Medet, Assarel and Vlaykov Vrush, and (b) with the epithermal deposits at Chelopech and Elshitsa. The intrusions at Velichkovo, Vetren, Capitan Dimitriev and Gutsal (Fig. 1) are barren. High-precision U-Zr dating (von Quadt et. al., 2005) revealed that the Cretaceous magmatism started at the northern end of the Panagyurishtse district with the emplacement of shallow intermediate dykes and small bodies into the basement rocks of the Balkan zone (Fig.1) at 92.10 ± 0.3 Ma, which is coeval with the beginning of ore formation process at the Elatsite Cu–Au porphyry deposit. The magmatic evolution of the Cretaceous belt then shifted to progressively younger ages towards the southern border of the Srednogorie zone against the Rhodopian zone, where the Capitan Dimitriev intrusion has an age of 78.5 ± 0.15 Ma. In contrast to the published K–Ar data (scatter of 40 Ma) U-Pb zircon dating shows a time span of magmatic activity of only ca. 14 million years (Fig. 1) within the N-S transect trough Central Srednogorie. The time span of the economic Cu-Au deposits is about 6 Ma (92.1 – 86.1 Ma).

Recent studies give evidence for late Cretaceous magmatism also in the southerly adjacent Rhodope massif. The First Unit of Hbl-Bi granodiorites of the Rila-West Rhodopes batholith reveals U-Pb zircon ages of 69.26 ± 0.26 Ma (Belmekin body in Rila Mountain) and 66.79 ± 0.29 Ma (Grantcharitsa body in the W Rhodopes) (Fig. 1). In the Eastern Rhodopes the Chuchuliga and Rosino granites yield very similar ages of 68.94 ± 0.40 Ma and ~70 Ma respectively (Marchev et al., 2006). However, the Elatia granitoid in the Central Rhodopes (Greece) is Palaeogene in age (55.48 ± 0.22 Ma) according to the recent U-Pb TIMS zircon dating. The Upper Cretaceous magmatic rocks in the Rhodopes preserve the mixed crust-mantle source characteristics, but with more remarkable crustal input. The granodiorites of the Rila-West Rhodopes show ε-Nd (70) values in the range of -3.3 to +0.6 and initial strontium ratio of 0.7064-0.7066, and one apatite sample of Chuchuliga granite yields 87Sr/86Sr isotope ratio of 0.70616. Sr-Nd data are in agreement with the mixed crust-mantle composition of the magmatic zircons in the Cretaceous magmatic rocks, as they reveal slightly positive ε-Hf values from +0.5 to +2.7 in Chuchuliga granite and from +1.6 to +5.3 in Rila granodiorite. It must be noted that inherited zircons, contaminating the magma are crustal dominated with negative ε-Hf (69) values between -5 to -7.

3 THE CRETACEOUS MAGMATISM IN SERBIA: TIMING AND SOURCE

Late Cretaceous magmatism of East Serbia is developed along two belts: the Timok Magmatic Complex (TMC) in the East, and Ridanj-Krepoljin Zone (RKZ) in the West (Fig.1). Subparallel distribution of the TMC and RKZ, analogous petrographic and petrochemical characteristics and considerable overlap in time of magmatic activities all indicate that these two belts are broadly related to a single geotectonic regime. In the TMC the volcanism may be roughly divided into two stages: (a) Turonian (?)–Santonian, developed mainly in the Eastern part, dominated by subaerial andesitic volcanism; and (b) Santonian–Campanian in the western parts, mostly subaqueous, represented by basaltic andesites. They were followed by granitoid intrusions (third phase). The trace element distribution as well as the REE pattern of rocks from different magmatic suites in TMC and RKZ show very similar pattern. Several geochemical characteristics, e.g. the depletion of Ta-Nb, point to a subduction related process for these magmatites. Sr, Nd and Pb tracing of several magmatic rocks in TMC and RKZ give 87Sr/86Sr ratios between 0.70388 and 0.706050, ε-Nd of about +2 (corrected for T–85 Ma). They are in good agreement with the new HF-zircon data ranging from +9.5 to +13.0 in TMC and between +4.0 and +5.0 in RKZ. Isotope-geochemical data reflect the mantle-dominated composition of the Upper Cretaceous volcanic rocks in East Serbia, contaminated slightly (TMC) or abundant (RKZ) with crustal compo-
nants. Contemporary with the shifting of the volcano from TMC to RKZ, the type of the mineralization changes from Cu-Au in TMC to Pb-Zn-Cu in RKZ (Karamata et al. 1997).

U-Pb zircon analyses date the start of the first magmatic phase in TMC at 86.29 ± 0.32 Ma in Veliki Kravelj, ending at 84.66 ± 0.5 Ma (timozites), but published Ar-Ar data give evidence for older 89.0 ± 0.6 Ma magmatism (Clark & Ulrich 2004). Ore bearing magmatism in the deposit Veliki Kravelj extended about maximum 0.6 Ma. U-Pb zircon analyses for the second volcanic cycle show ages between 82.27 Ma and 81.79 Ma, whereas the plutonic rocks of the third phase intruded in the interval 82.73 ± 0.03 Ma and 78.62 ± 0.44 Ma (Majdanpek, Valja Strž). A dacite from Krepoljin (RKZ) is dated at about 70 Ma (Fig. 1).

4 CONCLUSIONS

The Cretaceous Apuseni-Banat-Timok-Srednogorie belt developed as an Andean-style, calc-alkaline magmatic arc during northward subduction as a result of the convergence of Africa and Europe. Magmatism was dominantly andesitic-dacitic and, concurrently with ore formation, migrated progressively from north to south (Fig. 1) along cross-arc corridors and is attributed to rollback or hinge retreat of the subducting slab. Economic ore formation occurred during short time intervals and was asynchronous along the belt, as documented by the two major ore districts: between 92 and 86 Ma within the Bulgarian Panagyurishte district, and around 86-84 Ma in the Serbian Bor-Majdanpek district. Ore styles include porphyry-Cu and high-sulphidation Cu-Au epithermal deposits, which are roughly coeval in a given locality. Ore formation was located along belt-parallel pull-apart basins, and likely occurred during changes in principal stress axe orientations. Post-ore basin sedimentation and tectonics, and different erosion levels explain variable preservation states of the ore deposits. With progressive plate convergence and collision, the geodynamic activity gradually moved southward into the Rhodope massif, which represents a large accretionary wedge along the Srednogorie belt. An early syn-collisional stage was accompanied by late Cretaceous granodioritic-granitic magmatism and extension in the Rhodope massif at 67-70 Ma. The continuation of the Cretaceous magmatic evolution in Serbia and Bulgaria show similarities in geochemistry, ages and ore deposits, consequently the Ridadj-Krepolin zone may continue to S and SW into the Rhodopes. The continuation of the Serbian Ridadj-Krepolin belt into Romania to north should be remapped based on the new U-Pb zircon ages: the 76-79 Ma old intrusions of Ocna de Fier (Ciobanu et al. 2002) and Surduc (Wiesinger et al., this volume) rather belong the third phase of TMC (Fig. 1).

REFERENCES


Ciobanu CL, Cook NJ, Stein H (2002) Regional setting and Re-Os age of ores at Ocna de Fier Dognecea (Romania) in the context of the banatitic magmatic and metallogenic belt. Min Deposita 37, 541–567.


Miocene magmatism and ore formation in the South Apuseni Mountains, Romania: New genetic and timing constraints

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ABSTRACT: The South Apuseni Mountains mineral district (“Golden Quadrilateral”), Romania, hosts some of the largest porphyry Cu-Au and epithermal Au-Ag vein deposits in Europe. This study provides the first high-precision U-Pb dating of Miocene magmatic and hydrothermal events in the central (Barza magmatic complex) and northern (Rosia Poieni-Rosia Montana-Bucium) sectors of the district. In the Barza complex which is one of the most intensively mineralized magmatic structures in the district, mineralized intrusions are spatially associated with coeval barren subvolcanic bodies. We propose geochemical and time constraints on the porphyry ore formation (Valea Morii porphyry Cu-Au deposit) within the magmatic complex. The neighbouring Rosia Poieni porphyry Cu-Au and Rosia Montana epithermal Au-Ag deposits, located in the northern part of the “Golden Quadrilateral” are the largest operating mines in the South Apuseni Mountains. Rosia Montana is a breccia-hosted low- to intermediate-sulphidation epithermal system, related to strong phreatomagmatic activity due to shallow emplacement of a dacitic dome structure. The Rosia Poieni deposit, situated about 4km NE of Rosia Montana, is a porphyry copper system with a high-sulphidation epithermal overprint. Together with the existing 40Ar-39Ar data, the new results show clearly that the two deposits belong to two separate magmatic-hydrothermal systems, the porphyry copper system of Rosia Poieni being about 3 Ma younger than the nearby Rosia Montana epithermal deposit.

KEYWORDS: porphyry, epithermal, U-Pb dating, zircon, LA-ICP-MS, Apuseni, Romania

1 INTRODUCTION

Calc-alkaline Miocene magmatism in the South Apuseni Mountains was related to transtensional and rotational tectonics. The magmatic activity was focused within NW-SE oriented extensional basins and developed mainly between 14.7 and 7.4 Ma (Rosu et al. 2004). These structures host some of the Europe’s largest porphyry Cu-Au and epithermal Au-Ag deposits, both associated with shallow subvolcanic intrusions. One of the particularities of the South Apuseni district (also called “Golden Quadrilateral”) consists of the common spatial association between porphyry Cu-Au and epithermal deposits. Some recent studies (Alderton & Fallick 2000; Wallier et al. 2006) demonstrated that the mineralizing fluids in both systems have a dominantly magmatic origin, however a direct genetic link between the large porphyry and associated epithermal deposits in the area is still controversial.

This study is focused on two magmatic structures in the South Apuseni Mountains – the Barza magmatic complex and the Rosia Montana-Bucium volcano-intrusive structure (Fig. 1), hosting different styles of hydrothermal systems. We studied mineralized and barren intrusions from the Barza magmatic complex (one of the most intensively mineralized magmatic centres in the district), where based on field relationships, whole rock major and trace element geochemistry, U-Pb dating on magmatic zircons, and zircon trace element, REE and hafnium geochemistry, we propose geochemical and time constraints on the porphyry ore formation.

The second task of this study was to highlight the temporal and genetic succession of magmatic and hydrothermal events within the Rosia Montana-Bucium volcano-intrusive structure, hosting the largest operating mines in
the South Apuseni Mountains – Rosia Poieni porphyry Cu-Au deposit and Rosia Montana breccia-hosted epithermal Au-Ag deposit (Fig. 1). Bucium-Tarnita is a porphyritic stock cut by epithermal veins, located in the southernmost part of the structure (Fig. 1).

Figure 1. Simplified geological map of the South Apuseni Mountains mineral district. Location of Valea Morii, Rosia Poieni and Rosia Montana deposits is indicated as well (after Bostinescu 1984, modified).

2 GEOLOGICAL SETTING

Porphyry and epithermal deposits in the “Golden Quadrilateral” are spatially and genetically associated with Miocene calc-alkaline and alkaline magmatic rocks, cropping out either in intra-mountain basins, or in clusters of magmatic bodies that are oriented roughly NW-SE (Bostinescu 1984; Rosu et al. 2004; Fig. 1).

The Barza magmatic complex (~8km in diameter; Fig. 1) is situated in the central part of the district, as part of the Zarand-Brad Basin. The basement in the area consists of Mesozoic island arc volcanics (basalts, basaltic andesites, andesites and rhyolites) and diorite-granodiorite subvolcanic intrusions, and Upper Cretaceous-Palaeocene sediments. These rocks are covered by Miocene sedimentary and volcano-sedimentary (Badenian) formations. The magmatic complex itself is build up by Sarmatian-Pannonian volcanic and subvolcanic rocks. Volcanic rocks consist of pyroclastics and flows. Subvolcanic intrusions have mainly andesitic composition with different proportions of the rock-forming minerals: amphibole-pyroxene-, amphibole-biotite-quartz andesites etc. In the central part of the complex the porphyry Cu-Au deposit of Valea Morii is hosted by a relatively small dioritic stock. The porphyry mineralization is overprinted by epithermal Au vein formation, which is extensively developed to W and NW, crosscutting the subvolcanic intrusion of Barza.

The Rosia Montana-Bucium volcano-intrusive structure occupies the northern sector of the district (Fig. 1). The Rosia Montana deposit is intimately related to a diatreme breccia complex associated with two dome-like dacitic bodies. The Rosia Poieni deposit is hosted by the Poieni diorite porphyritic stock, about 4 km NE of Rosia Montana. Rotunda type volcanic andesites and their pyroclastic derivates, cropping out in the area between the two deposits and also east and south of Rosia Poieni, have a sub-horizontal basis and they cover the volcanoclastic breccia and dacites from the Rosia Montana structure, as well as earlier folded Cretaceous sedimentary rocks.

Twenty-six unaltered rock samples from the Barza magmatic complex and 28 samples from the Rosia Montana-Rosia Poieni sector have been studied for major and trace elements. Five carefully selected samples from each structure have been used for U-Pb dating on zircon, including samples from barren and mineralized magmatic host rocks, as well as intraminalization dykes.

3 RESULTS

Major and trace element analyses show normal calc-alkaline character of magmas from the Barza complex. Studied magmatic rocks have mostly andesitic composition. Just two samples plot into the dacite field. All rock samples are medium-K in composition. Incompatible element abundances normalised to the
primitive mantle show well expressed depletion in Nb and Ta and enrichment in LILE and Pb, characteristic features of subduction-related magmas. Sr content is usually low and no adakitic tendency has been observed. REE patterns are also very similar for mineralized and barren intrusions. They do not show a Eu anomaly.

Magmatic rocks from the Rosia Montana-Rosia Poieni area also show normal calc-alkaline signature. They are more evolved at Rosia Montana, where they have dacitic composition, compared to Rosia Poieni, where the compositions plot within the andesitic field. Samples from Rosia Poieni intrusion and related volcanics display “adakitic-like” signatures (Rosu et al. 2004). Samples from Rosia Montana show a small Eu anomaly, not detectable in the Rosia Poieni samples.

Figure 2 is a summary diagram for the timing of magmatism and ore formation in the Rosia Montana-Bucium volcano-intrusive structure and the Barza magmatic complex, summarising the existing Ar-Ar and K-Ar data and the U-Pb dating from the present study.

Bracketing the timing of porphyry ore formation at Rosia Poieni and Valea Morii was possible by dating the main host intrusions and intraminerallization dykes. The timing of magmatism and related porphyry mineralization at Rosia Poieni ranges within the narrow interval of 9.42-9.16 Ma. \(^{40}\)Ar-\(^{39}\)Ar dating of the high-sulfidation epithermal veining overprinting this porphyry system is in progress.

The magmatic activity in the Rosia Montana area took place in the time interval 13.6-13.2 Ma and was immediately followed by the economic hydrothermal mineralization (13.24-12.71 Ma; Fig. 2a).

Porphyry ore-formation at Valea Morii occurred between 11.41 and 11.30 Ma, about 1 Ma after the main volcanic activity (Fig. 2b). Magmatic activity continued during and after the porphyry ore-formation. The Ciresata intrusion which is clearly post-dating the porphyry formation at Valea Morii by about 0.5 Ma is cut by epithermal Au-bearing veins, thus confirming the possible timing of the white mica alteration accompanying the epithermal mineraliza-
tion at 10-11 Ma (Lips, 2002).

Zircons from all studied samples show extremely consistent chondrite-normalised REE patterns. A small Eu anomaly is present in samples from Barza and Rosia Montana. Slight increase of the Eu/Eu*, Nb/Ta and Th/U ratios has been recorded as a function of the crystallisation age of zircons. These data suggest a slightly increasing mantle component of the magmas with time. A positive Ce anomaly is considerably higher for the mineralized Valea Morii intrusion and the intraminerallization dyke, compared to the samples from barren intrusions in the Barza complex, suggesting a higher oxidation state of the parental magma during the stage of porphyry ore-formation.

Epsilon hafnium signatures of zircons also show a progressive increase with time (Fig. 3).

Figure 3. Epsilon Hf values of zircons from mineralized and barren intrusions from the Barza magmatic complex and magmatic rocks from the Rosia Poieni and Rosia Montana deposits versus U-Pb zircon ages.

Different ε-Hf values for zircons from the central and northern part of the district could be due to differences in the basement and different degree of basement assimilation. Rosia Poieni-Rosia Montana samples display increased mantle component signatures compared to the Barza samples.

4 CONCLUSIONS

This study provides the first high-precision U-Pb dating of Miocene magmatic and hydrothermal events in the South Apuseni Mountains. The results show clearly that despite their proximal location, and the magmatic character of the mineralizing fluids in both, the Rosia Montana and Rosia Poieni deposits belong to two separate magmatic-hydrothermal systems.

The porphyry copper system at Rosia Poieni is about 3 Ma younger than the neighbouring Rosia Montana epithermal deposit, which is much longer than the thermal lifetime even of a very large upper-crustal magma chamber.

Despite the similarities observed for major and trace element distribution between mineralized and barren intrusions from the Barza magmatic complex, some small but crucial differences in zircon geochemistry (trace elements, REE and hafnium isotopes) could help for better understanding the magmatic and geochemical factors controlling the porphyry ore formation in this magmatic structure. The mineralized Valea Morii intrusion crystallised clearly in more oxidised conditions compared to the surrounding barren intrusions.

REFERENCES


Multiple intrusions and brecciation events and their role in precious metal mineralization at Rośia Montană, Apuseni Mountains, Romania

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ABSTRACT: Rośia Montană is an epithermal gold deposit with a current reserve of 214.9 million tonnes at an average grade of 1.46 grams per tonne (g/t) gold and 6.9 g/t silver for a total reserve of 10.1 million ounces of gold and 47.6 million ounces of silver (using a 0.6g/t Au cut-off). Rośia Montană is a low- to intermediate-sulphidation ore deposit hosted in a maar-diatreme system emplaced within Cretaceous flysch-type sedimentary rocks and intruded by dacite dome structures. Various types of ore bodies occur at Rośia Montană: veins, stockworks, breccias, impregnations and placers. This study is focused on breccia structures that provide important evidence concerning the genesis and the control of precious metal mineralization at Rośia Montană. Breccia-related mineralization has been identified to have occurred and be hosted in pre-, syn-, late and post-mineralization breccias.

KEYWORDS: Rośia Montană, breccia structures, Au-Ag mineralization

1 INTRODUCTION

The Rośia Montană Au-Ag deposit is located in western Romania within an historical mining district known as “Golden Quadrilateral”, situated in the southern Apuseni Mountains.

The Apuseni Mountains host several Tertiary calc-alkaline volcanic centres representing three main episodes of activity between 14.8 and 1.6 Ma (Roșu et al. 2004). The country rock consists of Cretaceous shallow-marine to flysch type sedimentary rocks emplaced over metamorphosed Palaeozoic and Precambrian basement. The Rośia Montană deposit is situated within a NNW-trending structural corridor associated with strike-slip faulting, along with Frasin-Rodu epithermal deposits and the Roșia Poieni and Bucium – Tarnița copper-gold porphyry deposits.

2 EVOLUTION OF VOLCANISM AT ROȘIA MONTANĂ

Volcanic activity commenced in Roșia Montană at about 13.5 Ma (Roșu et al. 2004; Kouzmanov et al. 2005) with dacite emplacement. In the same perimeter volcanic activity continued with 9.3 Ma Rotunda type andesites (Roșu et al. 2004) and finished with 7.4 Ma Detunata type basaltic andesites. All these volcanic rocks are well developed and cropping out at the surface. The time span of phreatomagmatic activity indirectly documented so far (Roșu et al. 2004; Manske et al. 2006) is at least of 2.5 Ma (13.5 to 11 Ma). Phreatomagmatic breccia structures, blind or outcropping are well developed at Roșia Montană, having also an important role in the control of mineralization.

3 BRECCIA TYPES, EMPLACEMENT AND IMPORTANCE FOR MINERALIZATION

The Roșia Montană deposit shows a widespread occurrence of breccias, several of them being relatively high grade Au-Ag ore bodies. Different genetic breccia types have been already described (Tamaș 2002; Feier et al. 2004; Minuț et al. 2004; Wallier et al. 2006) but ongoing exploration has enabled the identification of new bodies and to understand their role in mineralization. Mineralization identified has occurred pre-, syn-, late and post-mineral breccia events.
3.1 Pre–Mineralization Breccias

The major lithological unit that occurs within the Roşia Montană deposit is represented by breccias emplaced in the maar-diatreme complex, locally named Vent Breccia (Fig. 1). This structure is the expression of the first phreatomagmatic pulse in the Roşia Montană area.

During the quiescent time spans of this early hydrovolcanism, several sedimentary sequences formed within the Roşia Montana maar (reworked vent breccia). The Roşia Montană maar-diatreme continued to act as favourable loci for subsequent volcanic pulses as well as superimposed brecciation events.

Closely postdating the Cetate dacite emplacement within the Roşia Montană diatrem was the polymictic Cetate breccia pipe (XPO) (Tǎmaş 2002). It is now located between the Black Breccia, Vent Breccia and Cetate dacite and can be found in the central and eastern parts of the Cetate open pit.

The Cârnic polymictic breccia body (XPO1) is the next known phase which intruded up along a NE trending structures cutting across the Cârnic dacite dome. The violent intrusion of this body has created “crackle breccia” zones within the dacite along its NW margin. The crackle breccias form the monomictic breccias (XMO), which occur as a crackle to mosaic breccia with a rock flour matrix. This breccia is interpreted to occur at the intersection of NW and NS trending structures.

The Cetate and Cârnic polymictic breccias are matrix-supported. The most frequent clasts are dacite, Cretaceous sedimentary rocks and basement rocks. The matrix has a grey colour and is composed of small fragments and rock flour of the same lithologies as the clasts. The large scale exploitation of Cetate and Cârnic polymictic breccias is due to the superposition of later multiple mineralization events within these breccia bodies, including subsequent impregnations, stockwork veining, superimposed vein sets (milky quartz, amethyst quartz, Mn-...
mentary rocks beneath and adjacent to the vent rocks, as well as along structural alignments. The Sandy breccia (XCF) is a narrow (25-50m diameter) pipe that cuts the Cârnic dacite to the NW, at the structural intersection between NW and NE trending faults. The breccia is dark-grey to black, strongly silicified and consists of medium to coarse sand-grain size (0.1 – 1cm) clasts. The breccia contains good gold and high silver grades.

A polymictic breccia (XPO2) body occurs in the foot-wall of the Sandy breccia body. The Sandy breccia is probably the fluidized channel of this breccia body along which the clasts were intensively milled. XPO2 is similar in composition to the XPO1 body.

NW of the Cetate dacite occurs the Carpeni XPO breccia together with monomictic crackle breccia rimming this to the south. The mineralization appears to be mostly associated with a hydrothermal breccia cement, consisting of carbonates (rhodochrosite, calcite) and quartz. The majority of the hydrothermal breccia is hosted by the monomictic breccia (XMO) but also by the surrounding re-worked vent breccia as well as the XPO unit. The Carpeni XPO breccia is interpreted to be situated along a NNW major “structural” trend between Cetate and Orlea and Țărina to the north.

A number of sub-vertical XPO polymictic breccia bodies (150 x 60m) also occur within the “vent-breccia” to the north of the “maar-diatreme” within the Igre and Țărina areas (150 x 60m), associated with small dacite (up to 1 m) dykes. These are seen to be emplaced alongWNW trending structures and emplaced from outside the central throat of the maar-diatreme. All are well mineralized.

3.2 Syn-Mineralization Breccias

Syn-mineralization phreatomagmatic breccia structures may contain mineralized fragments (mainly dacite), with evidence of pre-brecciation mineralization (e.g. veining not continuing into the matrix). Additionally the phreatomagmatic breccias have been locally reworked by subsequent hydrothermal induced brecciation events (phreatic breccias). The phreatic breccias occur mainly at the contact between phreatomagmatic breccias (vent breccia, polymictic breccia bodies) and the host rocks, as well as along structural alignments.

Phreatic breccias located within the sedimentary rocks beneath and adjacent to the vent breccia and sediment contact occur at Igre, Găuri, Coș, and east Cârnic areas. These breccias are made up of locally derived rock fragments cemented by a hydrothermal cement composed of carbonates (calcite, rhodochrosite), quartz and common sulphides (pyrite, subordinate galena, sphalerite and rare chalcopyrite; Minuț et al., 2004).

In the Cârnic and Cetate Massifs, the contact between the dacite and the polymictic breccias are locally reworked by phreatic brecciation (Tamaș 2002; Feier et al. 2004). The phreatic breccias have quartz-adularia cement with some chinga veining. Phreatic re-brecciation affected both the XPO and XMO units and is associated with a strongly developed silicificed halo and an increase of vugs and veining.

Within this type of phreatic breccias a complex mineralogical assemblage consisting of common sulphides (galena, pyrite, sphalerite, and chalcopyrite), Ag minerals (native silver, achatite, stephanite, polybasite-pearceite, Ag-tetrahedrite) and Au-Ag alloys have been described (Tamaș et al. 2004).

Archaeological research work conducted by the Company enabled a study of the mineralized structures exploited since the Roman times (Cauuet et al. 2003). One such structure termed the Roman Structure corresponds to a NNW trending structure hosting intensive brecciation (phreatic) and veining. The Roman Structure is represented by a series of more or less columnar structures separated by breccia dykes and vein structures.

Most vein structures from Roșia Montana have a brecciated texture. Fragments of the host rocks, as well as fragments from earlier deposition events, are cemented by subsequent hydrothermal minerals, notably carbonates and quartz. Furthermore, breccia pockets, ranging in size from centimetres to metres can also occur especially at the intersections of two or more structures.

3.3 Late – Mineralization Breccias

The Black Breccia, locally named Glamm, borders the eastern part of the Cetate polymict breccia. This is a polymict breccia with dacite, sediment and metamorphic clasts held together by clay to sandy soft matrix. This breccia unit is mostly barren except for a late stage sub-vertical N-S trending vein swarm (western dip) which crosscut the breccia. These are comprised of mostly carbonates (calcite, rhodochrosite and rhodonite) and common sulphides.
Unconsolidated “mud” breccia dykes (elongated, structurally controlled) have been mapped at surface (Cârnicel) as well as underground at Cârnic (i.e. XPO3). The breccia is generally barren and has a soft, clay matrix. Silicificied zones occur as narrow zones along the contacts and within cross-cutting structures.

3.4 Post–Mineralization Breccias

Post-mineral brecciation, driven by late intrusive events generated blind unaltered and unmineralized phreatomagmatic breccias. An example is the large breccia body situated in Corna Valley (1 km diameter projected to surface) located in the southern part of the Roșia Montană maar-diântre. The breccia is distinct because it is the only breccia body that still contains primary magnetite. According to Manske et al. (2006) the Corna Valley breccia is approximately 1 Ma younger than the mineralization (12.71 ± 0.13 Ma).

4 CONCLUSIONS

The gold-silver mineralization at Roșia Montană deposit is interpreted to represent an epithermal system related to the ongoing development and emplacement of a series of breccia bodies. These breccia bodies are the result of multiple phreatomagmatic eruptions. The structural control on the formation of the breccia bodies and the location of mineralization are seen to be related. Exploration activities comprised of the detailed sampling and mapping of underground workings as well as at surface allowed the identification of new breccia bodies and their controlling structures and to be able to place their timing in the overall metallogenesis of the deposit.

The ore bodies hosted in phreatic breccias represent very often phreatic re-brecciation of previous phreatomagmatic breccias and are located preferentially along the contacts of phreatomagmatic breccia bodies and host vent breccia and dacite bodies. Vein structures that crosscut the breccias as well as the dacite host rock are also related to the phreatic events and are considered to be late stage events.

REFERENCES


Cinnabar-pyrite mineralization associated with fluorite replacement bodies in the Chiprovtsi silver-lead deposit, northwestern Bulgaria

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ABSTRACT: A cinnabar-pyrite mineralization is found within the fluorite replacement bodies in the eastern part of the Chiprovtsi silver-lead deposit. The mineralization has simple composition comprising pyrite, cinnabar and smaller amounts of metacinnabar, marcasite, galena, chalcopyrite and minerals of the tetrahedrite-tennantite and polybasite-pearceite series. The colloform pyrite is enriched in As (0.66-3.27 wt.%), Sb (0.67-1.04 wt.%), Ni (0.32-0.60 wt.%) and Cu (0.58-0.86 wt.%). The tetrahedrite-tennantite minerals have complicated composition, with Sb/As ratio ranging between 0.43 and 3.13. Polybasite contains As up to 2.47 wt.%, thus is classified as antimonpearceite. The fluid inclusion study of quartz and calcite showed low temperatures of formation – 140-160°C, marking the final stage of fluorite forming processes. The formation of colloform pyrite suggests a near surface, non-equilibrium ore-forming environment.

KEYWORDS: cinnabar, colloform pyrite, fluid inclusion, Chiprovtsi Ag-Pb deposit

1 INTRODUCTION

Chiprovtsi is one of the largest lead-silver deposits in northwestern Bulgaria. The mine has been closed since 1999 after producing 4.79 Mt at 1.84% Pb since 1951 (Milev et al. 1996), but new prospecting activities on the fluorite bodies in the eastern part of the deposit have been underway recently. In addition, one of the largest mercury occurrences in Bulgaria is spatially associated with these fluorite replacement bodies.

2 GEOLOGICAL SETTING

The Chiprovtsi lead-silver deposit is hosted in low-grade metamorphic rocks (marbles and schists) of the Diabase Phyllitoid Complex (Precambrian - early Ordovician age) (Kalvacheva 1986; Carrigan et al. 2003) (Fig. 1). The formation of the main Pb-Ag metasomatic replacement mineralization is considered to be of Carboniferous age (Amov et al. 1981) and it is stratabound within thick siderite and calcite marble layers in the metamorphic series. The genesis of the deposit remains uncertain and it has been classified as being both granite intrusion-related and stratabound teletermal types of mineral deposits (Atanassov & Pavlov 1983; Dragov et al. 1991). According to several previous authors (Dragov et al. 1991; Zidarova & Zidarov 2000) the large metasomatic fluorite bodies, which replace calcite marbles, were formed much later than the main Pb-Ag economic mineralization with a hypothetical age of late Cretaceous or Palaeogene. The origin of the hydrothermal fluids, causing fluorite deposition is still uncertain.

3 SAMPLING AND ANALYTICAL TECHNIQUES

Polished sections were made from representative samples, collected from metasomatic nests and veins crosscutting the fluorite bodies on 495 and 606 levels of the Lukina Padina section of the Chiprovtsi mine. The mineral relationships in about 35 polished sections were studied by reflected light microscopy.

Microprobe analyses were performed by a JEOL Superprobe 733 electron microscope equipped with an ORTEC energy-dispersive system at the Geological Institute, BAS. The accelerating voltage of the probe was 26 keV. The following standards were used: pure metals Ag, Ni, Co, Sb2S3 (for Sb), FeS2 and CuFeS2 (for Fe), Cu3AsS4 (for Cu, As and S), ZnS (for
Zn), CdS (for Cd) and HgS (for Hg). Fluid inclusion microthermometric measurements were made on single quartz crystals (2-5 mm long) and calcite plates (1-2 mm in size) using a Chaixmeca heating-freezing stage.

4 MINERALIZATION DESCRIPTION

The cinnabar-pyrite mineralization is observed as crosscutting veinlets, metasomatic nests and breccia fillings within the earlier formed fluorite bodies. It is considered as being the final stage of the fluorite forming process. This mineralization has a simple composition, consisting predominantly of pyrite, cinnabar, various carbonates and lesser amounts of metacinnabar, marcasite, galena, chalcopyrite, minerals of the tetrahedrite-tennantite and polybasite-pearceite series.

Pyrite is presented in 3 morphological varieties: 1) as large, fractured grains, intergrown with carbonates in veins crossing the fluorite bodies; 2) Colloform and radial aggregates (Fig. 2) replacing the quartz-carbonate matrix, and; 3) Small euhedral crystals in cinnabar or as inclusions in transparent quartz crystals.

The colloform pyrite forms breccia fillings with cinnabar, metacinnabar and quartz, or metasomatically replaces the carbonates. The two varieties (1 - fractured and 2 - colloform) are enriched in As (0.66-3.27 wt.%) and Ni (0.32-0.60 wt.%), as some colloform pyrite specimens also contain Sb (0.67-1.04 wt.%) and Cu (0.58-0.86 wt.%); however, the small pyrite inclusions in quartz do not contain either As, Sb, Ni or Cu.

Previous studies of the colloform pyrite (Atanassov & Pavlov 1983) report cobalt content, which was not confirmed by our microprobe study.

Arsenic enrichment in colloform pyrites from other deposits has been observed by Bonev & Atanassova (2006).

The quartz crystals grow almost at the end of
pyrite crystallization, grabbing tiny pyrite arsenic-free crystals (Fig. 3).

Figure 3. Photomicrographs of the cinnabar-colloform pyrite association, showing cross sections of quartz crystals containing cinnabar and pyrite inclusions.

Cinnabar seems to be a relatively late product of the mineralization, since it embraces quartz crystals, colloform pyrite and the small euhedral pyrite grains, although somewhere cinnabar inclusions in quartz are also recorded. Small metacinnabar grains were observed within cinnabar aggregates together with the pyrite inclusions. No trace elements were detected in the cinnabar.

Marcasite is observed together with the large (type 1) fractured pyrite. The other minerals - galena, chalcopyrite, tetrahedrite-tennantite and polybasite are earlier than cinnabar and colloform pyrite, but are later than the large pyrite. They are probably formed after the reprecipitation of fluorite. Common feature of the tetrahedrite-tennantite minerals is their complicated composition containing Zn (up to 7.29 wt.%), Fe (up to 11.61 wt.%), Ag (up to 5.26 wt.%), Cd (up to 0.34 wt.%), Sb (up to 22.28 wt.%) and As (up to 13.34 wt.%).

The Sb/As ratio is ranging between 0.43 and 3.13, showing a wide variety of members of the tetrahedrite-tennantite series. Polybasite contains As up to 2.47 wt.%, thus is classified as antimonpearceite.

5 FLUID INCLUSION STUDY

A microthermometric fluid inclusion study was performed on small, euhedral, transparent quartz and calcite crystals, collected from cavities in samples from 495 and 606 levels of the Lukina Padina section of the mine.

Figure 4. Homogenization temperatures ($T_h$ °C) of fluid inclusions measured in calcite and quartz crystals from Lukina Padina mine section.

The quartz crystals are 1-2 mm wide to 2-5 mm long. Some of them contain cinnabar inclusions up to 150 µm in size. The fluid inclusions are secondary, rare, up to 10 µm in size, usually distributed in groups along microfractures parallel to faces of m {1010}. The measured homogenization temperatures ($T_h$) are low – ranging from 100 to 160°C (Fig. 4). Calcite is predominantly small to medium-grained, rarely found as transparent to translucent euhedral crystals up to 1-2 mm in size. The fluid inclusions are observed everywhere, relatively large in size – up to 20-50 µm. The measured $T_h$ are also low, between 100 and 140°C. The composition of the studied fluid inclusions belongs to the H2O-CO2 system. The
observed low temperatures confirm the late origin of the colloform pyrite-cinnabar mineralization.

6 DISCUSSION AND CONCLUSIONS

According to the proposed new theory of colloform pyrite formation (Bonev & Atanassova 2006), it could be concluded that the formation of these aggregates took place in highly saturated forming fluids and rapid simultaneous crystallization of multitude <001> needle-like individuals in open space. Cinnabar commonly occurs as a late product of hydrothermal processes related to intrusive or volcanic activities. The F and Hg^{2+} reach highest saturation in acid solutions, thus a low pH of the fluids is also suggested, as a result of which the carbonate host was partly dissolved releasing Ca^{2+} and CO_3^{2-} in the fluids. This fact, together with the near surface position of the formation, significantly increases the oxygen fugacity, resulting in neutralization of the ore-forming fluids and cinnabar and fluorite precipitation.

According to fluid inclusion study of fluorites (Zidarova & Zidarova, 2000) the fluorite-forming process took place within the 230-180°C interval. The colloform pyrite-cinnabar mineralization marks the final stage of the ore-forming process at 170-150°C. The source of the F and Hg is unknown and possibly does not coincide with the source of the widespread Carboniferous Ag-Pb mineralization. Recent Nd-Sr isotope study of fluorites (Zidarova et al., 2005) suggests mixed, but crustal dominated origin of the fluids, although they consider mantle degassing as the possible source of fluorine.

ACKNOWLEDGEMENTS

This study is supported financially by the National Science Foundation grant NZ-MU-1507/05.

REFERENCES


Cathodoluminescence textures and trace element content of igneous and hydrothermal quartz – a case study from the Elatsite porphyry Cu-Au (PGE) deposit, Bulgaria

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ABSTRACT: Systematic study of igneous and hydrothermal quartz from the Elatsite porphyry Cu-Au (PGE) deposit has been performed using a combination of scanning electron microscopy cathodoluminescence (SEM-CL) and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) techniques. SEM-CL textures of quartz reveal a complex history of quartz growth and later fracturing, dissolution and reprecipitation. We use these textures to distinguish among multiple generation of quartz precipitated at different time in an individual vein and to relate this quartz to specific events. Twelve trace elements were measured by LA-ICP-MS in order to determine how the CL zonation of quartz is correlated with trace element abundance variability. LA-ICP-MS data of different quartz generations reveal two groups of trace elements, ones that co-vary with luminosity while the others remain uniform. Bright luminosity correlates with the high total abundance of trace elements in quartz, including Al, K, Na and Ti. Concentrations of P and Ge demonstrate no relationship with the quartz luminescence.

KEYWORDS: quartz, cathodoluminescence, trace elements, LA-ICP-MS, porphyry, Elatsite

1 INTRODUCTION

Scanning electron microscopy cathodoluminescence (SEM-CL) is an efficient method for visualizing microtextures in minerals, which can not be observed using optical microscopy. In environments like porphyry copper deposits with multiple quartz-precipitation events, these cryptic textures bring insight into timing and physical conditions of quartz growth. One of the key factors controlling the cathodoluminescence of quartz is the incorporation of trace elements (Götze et al. 2001). Several studies (i.e. Landtwing & Pettke 2005; Rusk et al. 2006) have explored the relationships between CL response and the trace element content of quartz crystals. There is a general consensus that luminosity variations in quartz relate to compositional zoning in Mn, Al, Li, Na, Ti, Ge and Fe, but the details of this correlation are not fully resolved.

In this study we tried to apply this method on samples from the economically important porphyry copper deposit of Elatsite, Bulgaria. At Elatsite numerous well-preserved textures indicating magmatic-hydrothermal transition processes have been observed. Igneous-hydrothermal structures, called vein dykes (Heithersay & Walshe 1995), consisting of magmatic aplitic material and selvages of prismatic hydrothermally grown quartz were studied. The presence of these composite quartz-aplite veins is assumed as one of the most illustrative evidences of coeval processes of magmatism, hydrothermal activity and mineralization. We analyzed different quartz generations in order to unravel the genesis of the composite quartz-aplite vein-dykes and their relationship with the main ore stages at Elatsite.

In this study we used SEM-CL to distinguish between magmatic and hydrothermal quartz and to study the relation between the two types during transitions from a dominantly magmatic to a dominantly hydrothermal vein-filling regime. Based on the CL textures LA-ICP-MS analyses have been performed to quantify the distribution of trace elements. The aim of the study is to constrain the trace element distribu-
tion in the quartz and its relation to the SEM-CL response.

2 GEOLOGICAL SETTING

The Elatsite porphyry Cu-Au (PGE) deposit is the largest operating open pit mine in Bulgaria. It is located on the Etropole ridge of the Western Balkan Mountains at the northern end of the Panagyurishte ore district of the Central Srednogorie Zone. The Srednogorie Zone is part of the Apuseni-Banat-Timok-Srednogorie Magmatic and Metallogenic Belt of the Alpine-Balkan-Carpathian-Dinaride orogenic system. A number of important ore deposits, mainly Cu-Au-(Mo), are associated with this belt. Elatsite is one of the few porphyry copper deposits worldwide with distinct enrichments in PGE, mainly Pd and Pt.

The mineralization at Elatsite is associated with late Cretaceous sub-volcanic bodies and porphyry dykes intruded into the metamorphic rocks of the Berkovitsa group (Cambrian age) and granodiorites of Vezhen pluton (Carboniferous age). The magmatic system of the deposit is built up by several dyke generations grouped into two stages (von Quadt et al. 2002). The “ore-productive” stage includes quartz-monzodiorite porphyries, granodiorite porphyries and K-feldspar-rich thin aplitic dykes. The later dyke stage comprises mafic dykes (microdiorites, micro-monzodiorites, diorite porphyries and their quartz-bearing varieties). Three types of alteration are distinguished at Elatsite: potassic, propylitic and phyllic alteration. Five successive stages of mineralization are distinguished in the deposit. A particular characteristic of Elatsite is an early magnetite-bornite-chalcopyrite association containing PGE, Co, Ni, Te, Se, Bi, Au and Ag but the main association of economic importance is the quartz-pyrite-chalcopyrite association.

3 METHODS AND SAMPLES

Several samples, some of them with multiple changes between magmatic and hydrothermal fillings have been studied. Systematic study of igneous quartz from granodiorite porphyries, early stockwork veins, composite quartz-aplite veins (consisting of magmatic aplitic material intruded into already existing, hydrothermally formed quartz veins) and quartz-pyrite-chalcopyrite veins have been performed.

SEM-CL and LA-ICP-MS analyses were performed at ETH Zurich. CL signals have been recorded as grayscale images. In order to compare the CL response at the location of 40 µm laser ablation pit, average gray value of these zones of interest were quantified using the Scion Image image-analysis program (http://www.scioncorp.com). The resulting values range between 0 (black) and 255 (white). The brightness and the intensity of the CL-images strongly depend on the analytical conditions used (Rusk et al. 2006). Therefore, the comparison of gray values acquired at different imaging sites requires an internal standardization of the CL response (Landtwing & Pettke 2005). This normalization was done assuming that the average gray value of the uniform quartz from the aplites is identical for all of the CL images (146).

Based on CL textures twelve trace elements were measured by LA-ICP-MS – Li, Na, Mg, Al, Si, P, K, Ti, Fe, Ga, Ge, Sn. Analytical conditions were similar to those used by Landtwing and Pettke (2005).

4 RESULTS AND DISCUSSION

4.1 CL textures and intensity of quartz luminescence

Igneous quartz from the granodiorite porphyries shows weakly contrasted, relic growth zoning and luminescence with high intensity.

SEM-CL reveals the complex multigenerational history of early stockwork vein (vein-I; Fig. 1), consisting mainly of quartz (Q1 and Q2); and of the later quartz-aplite veins (vein II), built up of symmetrical quartz in the selvage (Q3) and quartz (Q4) + feldspar (Q4+Fs) in the central part.

SEM-CL images of vein-I, containing quartz, feldspar, chlorite, calcite, magnetite, bornite and chalcopyrite, reveal two separate generations of quartz (Fig. 2). CL-dark cores (Q1) are overgrown by CL-gray quartz (Q2) associated with K-feldspar and ore minerals. CL-dark quartz has the lowest luminescence intensity. The presence of ore minerals indicates that this later bright overgrowth formed during the mt-bn-cpy stage. The hydrothermally precipitated prismatic quartz (Q3) from the selvage of the vein-II (Fig. 1) has euhedral growth zones ranging in luminosity from CL-bright (intensity 241) to CL-gray (intensity 97), indicating growth in an open space.

Aplitic dykes often have small thickness ranging from few mm to several cm. They
show two different textures: aplitic and micro-
porphyritic. Quartz from the aplites (Q4) has a
CL-gray luminescence and shows weak internal
zoning.

Figure 1. SEM-CL image of different quartz generations
in a composite vein-dyke, cutting previously formed
hydrothermal quartz vein.

Figure 2. SEM-CL image of two quartz generations in
vein-I. Abbreviations: Q – quartz; Fs – K-feldspar; mt –
magnetite; bn – bornite; cpy – chalcopyrite.

Straight to irregular-walled thin quartz-ore
veinlets cut both vein-I and vein-II (Fig. 1). The
disseminated ore minerals in the aplitic veins
are associated with oscillatory zoned quartz.
They both developed in the open space zones of
the vein. Quartz from these quartz-pyrite veins
(Q5) has an oscillatory zoning and a wide range
of intensities (between 62 and 198).

4.2 Trace element content of quartz and
correlation with CL-response

The incorporation of trace elements in
quartz, either substitutionally for silicon or in-
terstitially, is considered as one of the key
factor controlling the cathodoluminescence of
quartz.

The most prominent substitutional ion of
Si$^{4+}$ is Al$^{3+}$ that is charge-balanced dominantly
by $K^{+}(Si_{1}^{4+}Al_{1}^{3+}K_{1}^{+})$ as illustrated by the good
positive correlation between Al and K (Fig. 3),
and to lesser extend by and Na$^{+}(Si_{1}^{4+}Al_{1}^{3+}Na_{1}^{+})$.
Li$^{+}$ does not appear to be important. Charge
balance of Al$^{3+}$ with P$^{5+}(Si_{2}^{4+}Al_{1}^{3+}P_{1}^{5+})$, xeno-
time-type substitution, does not exhibit a sys-
tematic correlation. The sum of the trivalent
elements Al and Ga is charge-balanced by the
sum of Li, Na, P and K.

Concentrations of Al, K, Na, and Ti vary
considerably with CL intensities of the quartz
crystals, revealing a generally positive correla-
tion between trace elements concentrations and
CL intensities (Fig. 4).

Lowest concentrations of trace elements
were detected in the dark-luminescent quartz
(Q1) from the early stockwork veins, where Ti
concentration is close to or below detection
limits. The highest concentrations of these ele-
ments were observed in the bright luminescent
bands of the zonal quartz from the salband of
vein II. There is an overlap in the range of Al,
K, Na and Ti concentrations among quartz from
granodiorite porphyries, idiomorphic zonal
growth quartz, aplitic quartz and the quartz
from the pyrite-quartz veins.

5 CONCLUSIONS

The igneous quartz from the granodiorite
porphyries and aplites has the same CL tex-
tures, does not exhibit significant differences in
CL intensity and trace elements content.

Quartz from the salband of the vein dykes
(Q3) and from the quartz-pyrite veins (Q5)
show euhedral growth zoning ranging in luminescence with higher concentrations of trace elements in the bright luminescent zones.

Quartz from the early stockwork veins (Q1 and Q2) exhibits different CL texture and is significantly less luminescent than quartz from all other generations. This quartz, which has the least CL intensity at Elatsite, has very low Ti content. These different CL features and trace element contents imply a different origin of the early stockwork vein quartz.

Figure 4. Trace elements concentrations (ppm) plotted against the CL intensity.

The CL-response of quartz from Elatsite porphyry copper deposit is variable and relates to the sum of trace elements incorporated into the quartz structure, with bright luminescence for growth zones enriched in trace element content. Concentrations of K, Al, Ti, and Na are variable and these of Li, Ge and P are uniform across the various CL zones observed. Trivalent cations substituting for Si⁴⁺ require charge compensation. In the example of Elatsite, charge balance is often achieved by incorporation of alkali metals. K⁺ dominates by far. Quartz shows a trace element signature that is charge balanced by the sum of measured trace element concentrations.

ACKNOWLEDGEMENTS

We are grateful for the hospitality of the management of the Elatsite Mine, Etropole, especially to mine geologists. Further our thanks go to Albrecht von Quadt and Thomas Pettke from ETH Zurich for discussions and their help with the analytical work.

REFERENCES


Precise U-Pb geochronology, Hf isotopes and trace element distribution in zircons are combined in the present study to define the time and sources of the magmatism in the Medet and Assarel deposits. Together with the structural data for the region they can help to test the widespread idea for the generation of both deposits in a common magmatic and hydrothermal system and to infer possible changes in the ore-forming processes, which did not allowed the generation of big high-grade deposits south of Medet and Assarel in Central Srednogorie, Bulgaria. The U-Pb-zircon dating of the magmatism in Medet and Assarel deposits suggests a short lived, <1 Ma main ore phases. Each deposit appears to have formed during a unique, resolvable, southward progressing pulse from 90.59 ± 0.29 Ma to 90.12 ± 0.36 in Medet, and from 89.90 ± 0.26 Ma to 89.13 ± 0.28 in Assarel. Geochemical data (including isotope data) indicate a possible common upper crustal chamber for both deposits as the magmatic products are similar in their age as well as in the Hf-zircon and whole-rock geochemical features. Zircon inheritance with Lower Paleozoic age and mantle to crust-mantle ε-Hf characteristics emphasize the role of the MASH zone (related to the mantle-crust boundary) in the formation of the Upper Cretaceous magma. The coherence of the magmatic, hydrothermal, and tectonic events from north to south suggests a dominating steady-state tectonic environment, but on a district scale the formation of the ore occurred during distinct metallogenic pulses and suggests short-lived tectonic events. Changes from NNW-SSE to E-W (trans)tension in the time of formation of Medet and Assarel deposits appear to be favorable for the ore deposition, among with the other ore-forming factors.

KEYWORDS: copper-porphyry, Assarel-Medet, Srednogorie, U-Pb dating, zircon, ε-Hf, ore-forming factors

1 INTRODUCTION

World-class Cu-porphyry and Au-epithermal deposits in Eastern Europe are hosted by an elongated belt of intensive calc-alkaline Late Cretaceous magmatic activity, known as the Apuseni-Banat-Timok-Srednogorie belt (Popov et al. 2000; Fig. 1a). The belt is considered to extend further to the east into northern Turkey and Iran, and SE Afghanistan, reaching the Himalayas and building the “Tethyan Eurasian Metallogenic Belt” (Jankovic 1977). Extensive U-Pb dating of zircons from volcanic to plutonic rocks in the central parts of the Srednogorie tectonic zone (Central Srednogorie or Panagyurishte region) in Bulgaria revealed a general younging of the magmatism from ~92 Ma in the north (the region of Elatsite and Chelopech deposits) to ~78 Ma in the south (Von Quadt et al., 2005). It is explained as a consequence of slab retreat during oblique subduction (Von Quadt et al. 2005; Chambeort & Moritz 2006) or of postcollision slab break-off (Neubauer 2002; Handler et al. 2004).

The Medet and Assarel deposits are situated in the central parts of Panagyurishte region (Fig. 1b). Medet deposit was the first producing Cu-porphyry type deposit in Eastern Europe.
(Ushev et al., 1962), which made it important for the progress of the mining industry of the whole region. 163 million tonnes (Mt) of ore have been mined from the Medet deposit in the period 1964-1993 at an average grade of 0.32% Cu and 0.1 g/t Au. The Assarel deposit was found about 10 years later and came in production in 1976 with more than 350 Mt resources at an average grade of 0.44% Cu and Au as by-product (Strashimirov et al. 2002). The deposits are of special interest as at the time of their generation, some ore-forming factors (tectonic stress, magma source, fluid regime?) changed that were crucial for the further formation of high-grade deposits in Central Srednogorie. For the present study we used precise U-Pb geochronology, Hf isotopes and trace element distribution in zircons and whole-rock geochemistry to define the time and sources of the fertile and barren magma. In combination with the structural data for the region of the deposits they will help us to constrain better the geodynamic evolution and to test the widespread idea for the generation of both deposits in a common volcanic-plutonic centre and magmatic-hydrothermal system (Bogdanov 1987; Popov et al. 1996) and finally to infer possible changes during the ore-forming processes.

Figure 1. Tectonic sketch map of the Balkan Peninsula with the position of Apuseni-Banat-Timok-Srednogorie (ABTS) belt; b) Geological map of the northern part of Central Srednogorie (modified after Popov & Popov 2000).

2 TIMING AND MAGMA SOURCES OF THE MAGMATISM IN THE MEDET DEPOSIT

The region of the Medet deposit is build up by high-grade metamorphic rocks (Lower Palaeozoic and older protoliths, metamorphosed at Variscan time) and Carboniferous granites to gabbros. The basement is intruded by the rocks of the Medet pluton a small shallow stock-like body (~3 km$^2$). The pluton is built up by the following main phases (Chipchakova 2002; Strashimirov et al. 2002): (i) quartzmonzodiorites (QMzdr); (ii) granodiorites (Gdr; as well as transitions between Q-diorite and Gdr). Aplitic veins accompany and a high-K Gdr-porphyry dyke cross cut all these rocks. The ore-related hydrothermal alteration of the wall rocks is K-silicate type in the central parts of the deposit and phyllic to propylitic to the periphery (Chipchakova, 2002). Published K-Ar (Lilov & Chipchakova 1999) and 40Ar-39Ar dating (Handler et al. 2004; Lips et al. 2004; Fig. 2) suggest a magmatic and a hydrothermal activity over more than 10 Ma.

For the present study, we dated the main rock varieties in the Medet deposit by the conventional U-Pb single zircon method. The data define a start of the magmatism at 90.59 ± 0.29 Ma (or 90.36 ± 0.48 Ma) with the intrusion of the QMzdr and the almost contemporary Pl-Hbl Gdr porphyry at 90.47 ± 0.30 Ma, whereas zircons from a crosscutting aplitic vein in the granodiorite crystallized at 90.12 ± 0.36 Ma. Re-Os molybdenite ages are slightly older ~91 Ma (Zimmerman et al. 2005) but generally in agreement with these data. Magmatic activity was accomplished at 89.26 ± 0.32 Ma, the time of the intrusion of a post-ore Gdr-porphyry dyke. The time span of fertile magmatism in
Medet deposit was less than 1 Ma., consequently K-Ar and Ar-Ar younger ages of sericite have to be linked to low-temperature fluids heated probably by hot magma in upper/middle crust chambers in Central Srednogorie.

3 TIME AND SOURCE CONSTRAINTS ON THE MAGMATISM IN THE ASSAREL DEPOSIT

The Assarel deposit is situated ~6 km SW of Medet. It is associated with and partly hosted by coeval volcanic rocks, which are thought to represent a volcano-plutonic edifice (Popov et al. 1996). The volcanic rocks are andesite-basaltic and trachyandesitic in composition (Popov et al. 1996). Recently Nedialkov et al. (2006) distinguished the following volcanic succession: (i) Hb andesites and latites, (ii) Hb-Py to Px-Hb basaltic andesites and (iii) Bi-Hb andesites, Q-andesites to dacites. The volcanic rocks are intruded by comagmatic porphyritic shallow bodies and dykes, which are subdivided in three stages (Nedialkov et al. 2006): (i) Q-diorite to QMzdr porphyries; (ii) QMzdr to Gdr porphyries and (iii) granite porphyries (syn- to post-ore?). The hydrothermal alteration, related to the formation of the Assarel copper-porphyry deposit consists of K-silicate and K-silicate-propylitic to propylitic, propylite-argillic, phyllic-argillic and advanced argillic (Strashimirov et al. 2002).

Published K-Ar data about the main magmatic activity and hydrothermal alteration in Assarel deposit are generally in the same time interval as in Medet – from 91 to 81 Ma (Lilov & Chipchakova 1999), but the fresh andesites and trachyandesites were sampled outside of the deposit. Our new U-Pb zircon dating revealed again a narrow time-span of less than 1 Ma: 89.90 ± 0.26 Ma (mean 206Pb/238U age 90.06 ± 0.22 Ma) for the Q-diorite porphyry body in the deposit and mean 206Pb/238U age of 89.13 ± 0.28 Ma for a cross-cutting Hb-diorite porphyry dyke, whereas the Bi-Hb andesites (from the volcanic succession) yield an age of 89.67 ± 0.78 Ma. Zircon inheritance in the last two samples (as in the rocks of Medet deposit) is mainly Lower Palaeozoic with negligible influence of the Variscan host rocks (one grain in the andesites). The ε-Hf values of the concordant Upper Cretaceous zircons (corrected for 90 Ma) range from -2 to +5 (between -0.5 and +2.3 in the Q-diorite porphyry, Fig. 3). The Palaeozoic inheritance in the zircons is only in few cases from continental-crust materials (negative ε-Hf at 90 Ma), and the majority of the 350 to
500 Ma corrected values are positive from +2 to +8. The data argue again for an active interaction of the Cretaceous mantle-derived magma with lower/middle crust materials.

4 CONCLUSIONS

The U-Pb-zircon dating of the rock-succession in the Medet and Assarel deposits suggests a short lived, <1 Ma ore-related magmatism. Each deposit appears to form during unique, resolvable, southward (SW) progressing pulses. However, isotope and geochemical data indicate a possible common upper crustal chamber for both deposits, as the magmatic products are similar in their age as well as in the Hf-zircon and whole-rock geochemical features. Characteristic for the Assarel and Medet magma was the assimilation of Lower Palaeozoic materials, which were themselves of mantle to mantle-crust origin. The similar 90 Ma corrected ε-Hf zircon values of inherited and newly saturated zircons (mainly between -1 to +2) emphasize the role of the MASH zone (related to the mantle-crust boundary) in the formation of the Cretaceous magma. In the Central Srednogorie this is a unique feature of both deposits and the two volcanic phases of the Chelopech magmatic complex (Stoykov et al. 2004).

The coherence of the magmatic, hydrothermal, and tectonic events from north to south suggests a dominating steady-state tectonic environment, but on a district scale the formation of the ore in distinct metallogenic pulses suggests short-lived tectonic events. Handler et al. (2004) and Chambefort & Moritz (2006) discussed already the change of the (trans)stension direction from NNW-SSE in Elatsite and Chelopech to E-W in the southern parts of Central Srednogorie. This change was forced by N-S compression, explained by microcontinent accretion to the subduction complex (Handler et al., 2004). Medet and Assarel appear to have formed during this change, which was favorable for the ore deposition.

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
ABSTRACT: The advanced argillic alteration of Breznik is developed in the upper Cretaceous volcanic rocks of the western part of the Srednogorie Belt. New mineralogical data give evidence of supergene jarosite and micrometric grains of alumino-phospho-sulphates (APS) infilling the fractures crosscutting the tabular grains of hypogene alunite. Raman spectrometry of APS shows the low crystallinity of these grains and their probable supergene formation. The mineral source crosscutting the hydrothermal zone is characterized by a low pH at 3, high sulphate, Fe, Ca, Mg and Sr contents, suggesting a leaching of the fresh and the hydrothermally altered volcanic rocks. Strontium, oxygen and sulphur isotopes on water and sulphates confirm these results. Jarosite data need further investigations.

KEYWORDS: Advanced argillic alteration, weathering, Raman spectrometry, stable isotopes, Srednogorie Belt, Bulgaria

1 INTRODUCTION

The Breznik Au occurrence is located at 40 km west of Sofia in the Western Srednogorie zone, part of the Banat-Srednogorie structural and Cu-Au metallogenic belt (Popov 1996). Breznik is well known for its barren advanced argillic alteration developed in the Upper Cretaceous volcanic rocks (Crummy et al. 2001). The mineralogical and isotopic studies show that alunite was of magmatic-hydrothermal origin (Lerouge et al. 2006). For the first time also, alumino-phospho-sulphates (APS) were observed in alunite of Breznik, whereas they were observed elsewhere in other alunite occurrences of the Srednogorie Belt (Kunov 1999; Georgieva et al. 2003). The presence of a mineral source characterized by a low pH close to the zone of advanced argillic alteration provided evidence of weathering of this alteration. This work presents new mineralogical and isotopic data on alunite and APS, in order to distinguish hypogene and supergene minerals.

2 GEOLOGICAL SETTING

The Breznik Au occurrence is hosted by an Upper Cretaceous volcano-intrusive structure with andesite-basaltic volcanoclastics and a massive porphyritic body of gabbronoritic composition at 300-350m (Crummy et al. 2001). The volcano is developed in a linear magma-conducting zone, resulting from the intersection of deep N120 and N70 trending faults (Panayotov et al. 1982). The central part of the structure consists of coarse-blocked volcanoclastic rocks with andesitic, trachyandesitic and trachybasaltic fragments, crosscut by dykes of basaltic composition. The margins of the structure are made up of thick tuffs, marls and sandstones that host a trachyandesitic body.

Mineralized structures show a E-W orientation, following the regional fault trend. The NE-SW structures are universalized. Two types of mineralization, high-sulphidation- and low-sulphidation- types, were identified in the deposit (Crummy et al. 2001). The first one, located in the northern part, is a Au-Ag-Te-Bi-Mo ± Pb, Zn ore, consisting of pyrite, enargite, tennantite, goldfieldite, bismuth minerals. It is associated with a proximal quartz + kaolinite + alunite advanced argillic alteration evolving at depth in a quartz + sericite alteration and a distal propylitic alteration. The second one, located in the southern part, is a Au-Ag-Mn-(Co-Ni) ± Pb, Zn ore, represented by a quartz-
sericite-carbonates vein network.

In the area a source of mineral water crosscuts the alteration zone.

3 MINERALOGY

Two types of samples from the advanced argillic alteration are distinguished depending on the initial volcanic rock: lava and tuff.

Hydrothermally altered lavas have preserved a volcanic microlitic texture. They are totally transformed into large patches of tabular crystals of alunite in a matrix of quartz.

Hydrothermally altered tuff consists of volcanic elements in a matrix of medium-grained alunite, fine-grained quartz and kaolinite/dickite. Volcanic elements have not preserved any initial magmatic texture. They are essentially replaced by mineralized quartz. Ore consists of pyrite, chalcopyrite, bornite, chalcocite, enargite and loellingite. The presence of kaolinite/dickite and alunite suggests temperatures of 200-250°C (Lerouge et al. 2006).

In both types of samples, jarosite is present as infilling between tabular grains of alunite, indicating processes of weathering.

A study of tabular alunite with scanning electron microscope provides evidence of a K-Na chemical zoning and alumino-phospho- sulphates (APS). Two types of APS are identified. In hydrothermally altered lava, tabular crystals of alunite are slightly fractured and APS occur as micrometer-sized bands in zoned crystals. In hydrothermally altered tuff, the patches of alunite are highly fractured and the cores of the patches are infilled by numerous pseudocubic 10- to 50-μm grains of APS. The crystals of tabular alunite show a persistent K-Na chemical zoning but no APS band is observed.

Chemical analyses of alunite using electron microprobe indicate Na₂O contents up to 1.04-2.75 wt % (Table 1). Those characteristics are valuable for alunite of all the advanced argillic alteration zones in the Srednogorie zone (Kunov 1999; Lerouge et al. 2006).

APs bands in alunite and pseudocubic grains of APS are characterized by different Ca/Sr and S/P. The highest analyzed S/P is 1.4:0.6 in the bands of APS in tabular grains of alunite; their Ca/Sr is close to 4.

Pseudocubic grains have typical composition of woodhouseite-svanbergite solid solution with a Ca/Sr ratio equal to 2 and a S/P ratio close to 0.9:1.1.

4 RAMAN SPECTROMETRY

Raman spectrometry was used to characterize alunite and APS. The spectra were performed using a XY800 DILOR equipped with an Olympus microscope (objx80ULWD), an exciting radiation of 514.5nm of ionised argon laser (50 mW).

The structure of alunite has been well studied. It is composed of SO₄²⁻ tetrahedra and AlO₃(OH)₄ octahedra, both somewhat distorted and each forming a layer in a direction (Stoffregen et al. 2000). Each SO₄ tetrahedron has one O atom bound to Al, producing a C3v instead of Td. Alunite exhibits Raman spectral features due to vibration of sulphate groups, hydroxyl groups, Al-O bonds and lattice vibrations. Sulphate vibrations occur for the sulphate ion due to symmetric (v₁ 980-1020 cm⁻¹) and asymmetric (v₃ 1100 cm⁻¹) stretching and symmetric (v₂ 480-508 cm⁻¹) and asymmetric (v₄ 613 cm⁻¹) bending modes (Frost et al. 2006).

Table 1 – Electron microprobe analyses of alunite (Alu) and APS.

<table>
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<th>lava</th>
<th>APS</th>
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<td>F</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.040</td>
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<tr>
<td>Total</td>
<td>83.955</td>
<td>83.503</td>
<td>83.020</td>
<td>84.820</td>
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</table>

Structural formulae calculated on the basis of 11 Ox.

| K     | 0.655| 0.264| 0.539| 0.049|
| Na    | 0.143| 0.243| 0.376| 0.041|
| Ca    | 0.056| 0.388| 0.043| 0.506|
| Al    | 2.690| 2.879| 2.860| 3.000|
| Ba    | 0.015| 0.063| 0.000| 0.063|
| Ce    | 0.005| 0.013| 0.002| 0.016|
| La    | 0.000| 0.004| 0.000| 0.016|
| Nd    | 0.000| 0.000| 0.004| 0.009|
| Sr    | 0.014| 0.075| 0.000| 0.246|
| P     | 0.113| 0.674| 0.035| 1.135|
| S     | 1.792| 1.389| 2.024| 0.905|
| Cl    | 0.002| 0.000| 0.001| 0.005|
| F     | 0.049| 0.000| 0.000| 0.009|

"Digging Deeper" C.J. Andrew et al (editors)
Figure 1 - Raman spectra of pseudocubic grains of APS and of zoned tabular alunite (K-rich and Na-rich).

The Raman spectra of alunite from Breznik show an intense band around 1025 cm\(^{-1}\) corresponding to the SO\(_4\) symmetric stretching bond (Fig. 1). A small band around 1077 cm\(^{-1}\) is attributed to the \(\nu_3\) asymmetric stretching modes. A band around 654 cm\(^{-1}\) is attributed to the \(\nu_4\) bending mode. Two bands in the 480-508 cm\(^{-1}\) area are ascribed to \(\nu_2\)-bending modes. A band around 234 cm\(^{-1}\) is attributed to OH…O hydrogen bond stretching. The bands are cation dependent: bands of Na alunite show an apparent shift to lower wavenumbers.

The Raman spectrum of the pseudocubic APS shows numerous bands which are common with alunite spectra (163, 234, 344-381, 484, 654, 1025, 1077 cm\(^{-1}\)). The substitution of sulphur by phosphorus combined with the substitution of K/Na by Ca/Sr, is marked by occurrence of new small peaks (at 172, 520, multiplets around 620, 984 cm\(^{-1}\)), large bands (~234, 381, 1077 cm\(^{-1}\)) and a slight shift to higher wavenumbers. The bands at 172, 520, around 620, 984 cm\(^{-1}\) are present in the svanbergite spectrum. The large bands may suggest a low degree of crystallinity.

5 CHEMISTRY OF WATER

Mineral water was sampled in the source crosscutting the zone of advanced argillic alteration. The water is colored in orange, due to its high iron content. The pH in the source is measured at 3. The chemical analysis of water (except iron) shows also important content in Ca, Mg, SO\(_4\), Sr and Rb (Table 2).

The low pH may be due to the weathering of sulphides, but also the equilibration of water with advanced argillic alteration. The water chemistry results of the weathering of fresh and hydrothermally altered volcanic rocks. The high contents of Fe, Ca, Mg, Sr and Rb may result of leaching of propylitic and sericite altered rocks (Hikov, 2004). On the other hand the low concentrations of PO\(_4\), K and Na could be partly explained by the secondary deposition of APS and jarosite.

Table 2 - Chemical composition of water of Breznik.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Cl</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
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<td>430</td>
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</table>

6 STABLE ISOTOPES

Stable isotopes on sulphates of the advanced argillic alteration and on water from Breznik were performed in order to estimate the part of the weathering of the advanced argillic alteration in the mineral water source. Oxygen, sulphur and hydrogen isotopes of alunite were analyzed using analytical methods described in Lerouge et al. (2006). Results are given in Table 3. Analytical uncertainties are ± 0.8 ‰ for hydrogen and ± 0.1 ‰ for oxygen of water, ± 0.3 ‰ for oxygen and sulphur of sulphate.

Table 3 - Isotopic data on water and on sulphates.

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<tr>
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<th>lavas</th>
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<td>(\delta^{18}O_{water}) (V-SMOW)</td>
<td>-10.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\delta^{18}O_{alunite})</td>
<td>13.7</td>
<td></td>
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<td>(\delta^{18}O_{Jarosite})</td>
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6.1 Strontium data

The \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of alunite from Breznik is quite close to the range of \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios which characterize the volcanism of the Timok-Srednogorie belt, taking account the age correction (0.7039-0.7061 after 90 Ma correction; Kouzmanov 2001). This data confirms the magmatic-hydrothermal origin of the alunite of Breznik (Kunov 1999; Lerouge et al. 2006).

The \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of jarosite is quite close to the \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of alunite in contact with, suggesting a common source of strontium for both sulphates.

The \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of the water is slightly
higher than the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of alunite and jarosite, but remains in the range of the volcanism of the Timok-Srednogorie belt.

6.2 Sulphur and oxygen data

The $\delta^{34}\text{S}$ of sulphates in water at +3.6‰ is slightly higher than the sulphides $\delta^{34}\text{S}$ of magmatic origin from the porphyry copper deposit of Vlaykov Vruh, the epithermal deposit of Elshitsa (Kouzmanov 2001) or from the acid-sulphate deposits (Lerouge et al. 2005, 2006) in the Timok-Srednogorie belt. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of alunite in hydrothermally altered tuff and lavas are characteristic of magmatic-hydrothermal alunite (Lerouge et al. 2006). The $\delta^{34}\text{S}$ of jarosite is intermediate between $\delta^{34}\text{S}$ of sulphides and $\delta^{34}\text{S}$ of alunite. If it is confirmed, that could suggest a preferential mobilization of sulphides during the weathering, but also a slight destabilization of alunite. The $\delta^{18}\text{O}$ of jarosite is high relative to classical value of supergene jarosite.

7 DISCUSSION

The chemistry and the isotopic signature of the mineral source from Breznik strongly suggest interaction between water and advanced argillic alteration. On the other part, infilling fractured alunite by jarosite, the presence of micrometric pseudocubic grains of APS instead of bands in the more fractured samples, their large Raman peaks are argue in favor of the partial weathering of the hypogene alunite / APS –kaolinite / dickite ± sulphides assemblage to form secondary APS with a low crystallinity and jarosite. The isotopic signature of jarosite is however unusual and need further investigations.

REFERENCES


Postmagmatic evolution of platinum-group and base-metal mineral assemblages in Palaeozoic ophiolitic chromitites from the Dobromirtsi massif, Rhodope Mountains (SE Bulgaria).

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ABSTRACT: The distribution of platinum-group and base-metal minerals in the metamorphosed ophiolitic chromitites of the Dobromirtsi ultramafic massif (Rhodope Mountains, SE Bulgaria) show that in the altered zones of chromites and in the silicate matrix between chromite grains, there is an increase in the proportion of Ni-rich, S-poor sulphides and As-rich minerals, relative to the unaltered zones of the chromite. This distribution is interpreted in terms of postmagmatic evolution of the chromitites: Ocean-floor metamorphism followed by hydrothermal alteration, associated with greenschist-amphibolite facies regional metamorphism causing S leaching followed by supply of additional S, As and minor Sb and Sn.

KEYWORDS: metamorphosed ophiolite chromitite, platinum-group mineral, base-metal minerals

1 INTRODUCTION

Platinum-group mineral (PGM) and base metal mineral (BMM, including Fe-Ni-Cu sulphides, Ni arsenides and sulpharsenides, and Fe-Ni alloys) assemblages occurring in ophiolitic chromitites are the result of a combination of primary magmatic processes and different late alteration events (e.g. Stockman and Hlava 1984; McElduff & Stumpfl 1990; Gervilla et al. 2005).

Oceanic floor metamorphism serpentinization (e.g. Stockman & Hlava 1984; McElduff & Stumpfl 1990), regional metamorphism-related hydrothermal alteration (e.g. Zaccarini et al. 2005), and weathering, mainly lateritization (e.g. Augé & Legendre 1994), have been invoked to interpret the replacement of the primary parageneses and the formation of the secondary, postmagmatic PGM and BMM assemblages.

The aim of this paper is to explain, through a detailed mineralogical study, how magmatic PGM and BMM assemblages of nine chromite deposits from the Dobromirtsi ultramafic massif were modified during the different postmagmatic events that affected the ultramafic rocks.

2 GEOLOGY

The Dobromirtsi ultramafic massif is located in the Rhodope Mountains (SE Bulgaria). It crops out over 11 km² and has a SW-NE oriented, elongated shape (Figure 1). The western part of the body is trusted over Palaeozoic metamorphic rocks (biotitic gneisses hosting amphibolite bodies), while the eastern part is covered by continental sediments bearing Oligocene volcanic rocks. The ultramafic rocks consist of harzburgites and dunites with tectonite fabric, as well as minor, cross-cutting pyroxenites. Ultramafic rocks were affected by the regional greenschist-amphibolite facies metamorphism. It is possible to identify two different foliations in the ultramafic body: an earlier one, probably related to plastic flow in mantle conditions (black on Figure 1), and a late mylonitic one (white on Figure 1), which overprints the mantle foliation and can be attributed to the crustal emplacement of the body or to the greenschist-amphibolite facies metamorphism, that affected the Central Rhodopes. Chromite bodies, recognized in the Dobromirtsi massif are all concordant to the mylonitic foliation of the host peridotites and locate along a single, dunite-rich horizon.
3 DISTRIBUTION OF PLATINUM GROUP AND BASE METAL MINERALS IN THE CHROMITITES

The study of PGM and BMM in chromitites from nine ore bodies of the Dobromirtsi massif is based on the characterization of a total of 532 mineral grains. PGM are less abundant (29 \%) than BMM (71 \%), but both occur in three different textural locations: (i) included in unaltered (fresh) chromite crystals (23 \%); (ii) included in altered chromite (39 \%); and (iii) dispersed in the altered silicate matrix, between chromite grains (38 \%).

3.1 Platinum group minerals

About 61 \% of the identified PGM occur included in fresh chromite crystals, far from cracks and altered zones. Laurite is the most abundant phase (86 \%), followed by Os alloy (11 \%), Ir alloy (1 \%), irarsite (1 \%), and a mineral with a composition close to IrS (1 \%). These PGM occur as single (isolated) grains (\textit{e.g.} laurite - Figure 2a), in diphase inclusions (\textit{e.g.} laurite accompanied by Os or Ir alloys, irarsite, Ir-sulphide and/or BMS) or in polyphase grains (\textit{e.g.} laurite with Os or Ir alloys, irarsite, Ir-sulphide and/or BMS). All of these minerals usually show idiomorphic habits with polygonal sections, partially rounded in some cases. The grain sizes are less than 20 \mu m.

Some 22 \% of the identified PGM are located in altered chromite. As in fresh chromite, laurite is the most abundant PGM (56 \% of the identified grains) followed by Os alloy (24 \%), Ru alloy or oxide? (2 \%) and one grain of Ru-pentlandite. Most of these minerals occur as isolated grains, although some diphase and polyphase grains have also been recognized. Diphase grains consist of laurite, associated with irarsite or Os or Ru alloy. Polyphase grains comprise laurite or irarsite grains attached to Os alloy and/or BMS. Laurite crystals display euhedral-subhedral morphology and often show altered (partially corroded - Figure 2c) crystal faces with S depletion towards the rims. Irarsite and some of the Os and Ru alloys grains show subhedral-anhedral (rounded) shapes. In some cases they also display corroded and porous textures. As in fresh chromite, the PGM grains are all smaller than 20 \mu m.

PGM in the silicate matrix, represent 17 \% of the ore minerals identified. Their mineral assemblage is dominated by the members of the irarsite-hollingworthite solid solution series (43 \%), followed by laurite - 25 \% (significantly lower then in chromites). Other, less abundant PGM are Ru alloy or oxide? (18 \%), undetermined phases, containing Pd, Sn, Cu (7 \%) and Rh, Os, Sb (4 \%), as well as minor Ir-sulphide. The crystal shape of these PGM is anhedral, with rounded to irregular crystal faces (Figure 2e) and locally showing S depletion towards the grain boundaries. Grain sizes vary from < 1 \mu m (microinclusions of PdSnCu in Fe hydroxides replacing sulphides, and RhOsSb included in Ni sulphides) to 20 \mu m (laurite-irarsite aggregates).

3.2 Base metal minerals

Only 7 \% of the identified BMM, occur in fresh chromite and all of them are Fe-Ni sulphides. The identified phases are pentlandite (17 grains), heazlewoodite (6 grains) and millerite (3 grains). Similar to PGM, BMM occur as isolated grains, or form diphase or polyphase inclusions with PGM, usually show euhedral to subhedral shape and grain size below 20 \mu m.

In altered chromite, BMM represent 47 \% of the identified grains. The analyzed phases, in order of abundance are: pentlandite (83 grains), heazlewoodite (6 grains) and millerite (3 grains). Similar to PGM, BMM occur as isolated grains, or form diphase or polyphase inclusions with PGM, usually show euhedral to subhedral shape and grain size below 20 \mu m.

In altered chromite, BMM represent 47 \% of the identified grains. The analyzed phases, in order of abundance are: pentlandite (83 grains), godlevskite (55 grains), heazlewoodite (25 grains), maucherite (5 grains), orcelite (3 grains), chalcopyrite (3 grains) and gersdorffite (2 grains). Pentlandite, heazlewoodite, and godlevskite occur at altered grain boundaries of chromite and show euhedral to subhedral morphology. Chalcopyrite is found as anhedral, single grains. Maucherite replaces pentlandite.
and heazlewoodite and orcelite is associated with godlevskite (figure 2d) or, exceptionally, as single isolated grains. Gersdorffite is always associated with Ni or Ni-Fe sulphides in the form of small inclusions within or at the rims of these sulphides.

Figure 2. PGM and BMM assemblages in the studied chromitites.

The percentage of BMM identified in the silicate matrix is quite similar to that of altered chromite (46 %). However the relative proportions of the minerals are different: pentlandite is much more abundant (135 grains) than heazlewoodite (30 grains), godlevskite (3 grains), maucherite (3 grains) and gersdorffite (2 grains). Non-quantified Fe hydroxides replacing pentlandite have been identified too. BMM show anhedral shape with variable but relatively large grain sizes (<20 µm to > 150 µm) (Figure 2f).

4 DISCUSSION

Like in other ophiolite chromitites, PGM and BMM included in unaltered chromite crystals can be interpreted as primary minerals and represent faithful records of the physical and chemical conditions, prevailing during their magmatic crystallization, prior or coeval with chromite (e.g. Stockman & Hlava 1984; Augé & Johan 1988; Gervilla et al. 2005). However, the mineral assemblages observed both in altered, frequently porous chromite and in the altered silicate matrix, containing higher proportions of Ni-rich sulphides (heazlewoodite and godlevskite) and As-rich minerals (members of the irarsite-hollingworthite solid solution series as well as maucherite, orcelite and gersdorffite) suggest that these assemblages formed, or at least were modified by some postmagmatic event (Stockman & Hlava 1984; McElduff & Stumpfl 1990, Garuti & Zaccarini 1997; Garuti et al. 2006). The replacement of pentlandite and heazlewoodite by maucherite and the subhedral-anhedral, frequently corroded crystal shape of most grains also support this suggestion.

The abundance of S-poor, Ni-rich sulphides relative to their proportion in fresh chromite as well as the presence of Ru alloy (or oxide?) at the rims of corroded (partially desulphurized) laurite crystals in the silicate matrix, but especially in altered chromite, points to an origin of these assemblages related with serpentinitization/ocean-floor metamorphism. During this process olivine is replaced by serpentine and minor magnetite, producing significant amounts of H₂ (e.g. Bach et al. 2006), which contributes to strongly lower both fO₂ and fS² by its reaction with O₂ to form water and with S² to form H²S. In this environment sulphides tend to equilibrate with the generated H₂-rich fluids giving rise to sulphides, progressively impoverished in S and alloys (Eckstrand, 1975). Minimum fO₂ and fS² conditions are reached when minor olivine still remains in the serpentinite (Frost 1985) and H₂ production stops when olivine is consumed. As a consequence, later hydrothermal fluids circulating in olivine-free serpentinites can contribute to increase fO₂, fS² and, eventually, supply other anions like As. This could explain the concentration of As-rich minerals in altered chromite and matrix. A primary, magmatic origin of arsenides can be ruled out because of their absence in fresh chromite.

As (and minor Sb and Sn) introduction in the system could take place late, during ocean-floor metamorphism or, alternatively, by hydrothermal alteration of the serpentinites during the regional, greenschist-amphibolite facies metamorphism that affected the Central Rhodopes. The second interpretation is more realistic, considering the abundance of arsenides and sulpharsenides in other localities in the Central Rhodopes (e.g. Tarkian et al. 1991) where chromitite is hosted by talc rocks. A possible
source of As and Sb could be the surrounding gneisses which are strongly mineralized in the nearby Madan area. S-rich, As- and Sb-bearing fluids derived from these gneisses could also contribute to increase the amount of Fe-Ni sulphides (especially pentlandite) in the matrix, which is much more abundant than expected in serpentinites derived from fresh peridotites by ocean-floor metamorphism.

After the greenschist-amphibolite facies metamorphic event, sulphides altered to Fe hydroxides. The latter locally contain minute grains of an undetermined PdSnCu phase, suggesting that Pd either remained immobile during the alteration of pentlandite or was supplied by low-temperature oxidizing fluids.

ACKNOWLEDGEMENTS

This research has been funded by the Spanish Project CGL2004-00622-BTE and the Junta de Andalucía Research Group RNM 131.

REFERENCES


High- and intermediate sulphidation Au-Ag-Te mineralization in a shallow submarine setting, Milos island, Greece: Mineralogy and geological environment of formation

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ABSTRACT: Shallow submarine epithermal deposits of western Milos postdate an earlier high-sulphidation alteration event and contain both intermediate and high-sulphidation ores with sulphides, sulphosalts and tellurides. The presence of hessite, petzite, altaite and native gold in sub-seafloor stockwork zones at Profitis Ilias, of high-sulphidation tennantite-enargite bearing sub-seafloor stockwork zones and breccias rich in Mo, W and Bi at Triades-Galana-Agathia, as well as the high activity of sulphur as evidenced by the low-Fe content in sphalerite, suggest that magmatic fluids may have played a role in the evolution of the western Milos hydrothermal systems. A renewed magmatic-hydrothermal pulse during the reactivation of the Milos gulf NW-SE trending lineament, combined with partial emergence of the northern sector area resulted in the silver sulphosalts-hematite bearing veins at Kondaros-Katsimoutis-Vani.

KEYWORDS: shallow submarine epithermal, high- and intermediate-sulphidation, tellurides, Milos island

1 INTRODUCTION

Shallow submarine and transitional to subaerial volcanic rocks of W. Milos (Stewart & McPhie 2003, 2006), contain precious and base metal deposits such as the Mavrovouni, Profitis Ilias, Chondro Vouno, Triades-Galana, Katsimoutis-Kondaros and Vani. These deposits display a number of geological, mineralogical and geochemical characteristics that are in part typical of VMS deposits and in part resemble epithermal gold deposits. The mineralization has been considered either as Kuroko-type, transitional VMS to epithermal, or as shallow submarine to subaerial epithermal (Hauck 1984; Vavelidis 1995; Plimer 2000; Liakopoulos et al. 2001; Kilias et al. 2001; Stewart and Mc Phie 2003, 2006; Alfieris et al. 2004; Naden et al. 2005; Alfieris and Voudouris 2005, 2006; Alfieris 2006).

2 GEOLOGICAL SETTING

The island of Milos is located in the central part of the south Aegean active volcanic arc (Fig. 1). Calc-alkaline volcanic products in W. Milos were emplaced during the late Pliocene to Pleistocene under transitional submarine to locally subaerial conditions, as a result of explosive volcanism of submarine volcanic edifices (Stewart & McPhie 2003, 2006; Alfieris 2006). An initial (3.5-3 Ma) felsic explosive and intrusive activity has been followed by effusive volcanism (3-1.4 Ma) that formed numerous dacitic-rhyodacitic-rhyolitic and andesitic domes/ lava domes, emplaced at shallow depth in the near or on the seafloor creating a series of hyaloclastite products intercalated locally with shallow marine sediments (Fig. 1). Some of the domes gave origin to bedded pumiceous tuffs. During the late Pliocene to late Pleistocene times extensional tectonics resulted in four main fault trends: NW–SE, N-S, NE-SW and E-W. All the deposits are genetically related to the submarine subvolcanic dome complexes, and are mainly hosted in shallow submarine to subaerial acid pyroclastic products (fine ash tuffs and coarse ignimbrites) at Profitis Ilias/Chondro Vouno, or in syn-volcanic intrusions and their autoclastic facies at Profitis Ilias/Chondro Vouno, Triades-Galana, Kondaros-Katsimoutis, Vani; in breccias of different origin (hydrothermal, hyaloclastic) at Triades-Galana, Mavrovouni, and as stratiform horizons at Vani.
3 PRE-ORE SILICIC AND ADVANCED ARGILLIC ALTERATION

Alteration mapping in W. Milos established a sequence of alteration zones, including pre-ore silicic (massive and vuggy silica), advanced argillic and argillic alteration, as well as syn-ore quartz-sericite-pyrite and scattered adularia-sericite centres to intermediate argillic and propylitic alteration zones. The earliest recognized advanced argillic alteration in W. Milos is characterized by intergrowths of alunite ± quartz ± cristobalite, kaolinite ± dickite ± pyrophyllite ± diaspore, halite and pyrite surrounding vuggy and massive silica rocks. This assemblage is considered to be of hypogene magmatic-hydrothermal origin (Rye et al. 1992) and was formed prior to the brecciation and mineralization of the felsic subvolcanic rocks, i.e. before their intrusion within the early acid pyroclastic series. Outcrops of hypogene advanced argillic alteration have been recognized at Kondaros, Agathia, Profitis Ilias and Chrondo Vouno). Colloform and fine-grained pyrite and natroalunite crystals are disseminated through the matrix of the vuggy and massive silica rocks at Agathia and Kondaros (Fig. 2a). Microprobe analyses of alunite (Table 1) suggest that they represent members of the alunite-natroalunite solid solutions series. Elevated contents in Ba, Sr and Ca substituting for Na, K and P₂O₅ substituting for SO₄ are consistent with their hypogene magmatic-hydrothermal origin. Coarse grained alunite filling veins in Kondaros area is considered to be of magmatic steam origin (Rye et al. 1992).

4 MINERALIZATION

Mineralization at Profitis Ilias/Chondro Vouno comprises base-metal sulphides and native gold related to NE-SW to NW-SE trending epithermal veins hosted within illite ± adularia altered rhyodacitic cryptodomes and pumice tuffs (Plimer 2000; Kilias et al. 2001; Stewart and McPhie 2003, 2006; Naden et al. 2005; Alfieris 2006). A telluride-bearing mineralization observed in the deeper levels of Profitis Ilias...
deposit is characterized by hessite, altaite, petzite, native gold, galena, chalcopyrite and low-Fe sphalerite (Fig. 2b; Alfieris & Voudouris 2006). Chalcopyrite is replaced by covellite, bornite, chalcocite and second generation of galena and sphalerite (Fig. 2c). At Triades-Galana the mineralization is hosted within a NE-SW trending breccia zone and a quartz-barite vein system with galena, low-Fe sphalerite, tennantite, chalcopyrite and enargite (Hauck 1984; Liakopoulos et al. 2001; Alfieris et al. 2004; Alfieris & Voudouris 2005). Oxidized breccias contain up to 176 ppm Mo, 677 ppm W and 2575 ppm Bi.

Table 1. Representative microprobe analyses of alunite from western Milos

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<td>84.09</td>
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<td>85.24</td>
<td>85.14</td>
</tr>
</tbody>
</table>

Table 2. Number of atoms on the basis of 11(O)

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
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<th>5</th>
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<tbody>
<tr>
<td>K</td>
<td>0.428</td>
<td>0.648</td>
<td>0.387</td>
<td>0.029</td>
<td>0.092</td>
<td>0.741</td>
</tr>
<tr>
<td>Na</td>
<td>0.444</td>
<td>0.245</td>
<td>0.499</td>
<td>0.895</td>
<td>0.837</td>
<td>0.078</td>
</tr>
<tr>
<td>Ca</td>
<td>0.009</td>
<td>0.008</td>
<td>0.008</td>
<td>0.002</td>
<td>0.002</td>
<td>0.017</td>
</tr>
<tr>
<td>Ba</td>
<td>0.016</td>
<td>0.016</td>
<td>0.009</td>
<td>0.001</td>
<td>0.001</td>
<td>0.057</td>
</tr>
<tr>
<td>Sr</td>
<td>0.001</td>
<td>0.001</td>
<td>0.003</td>
<td>0.002</td>
<td>0.000</td>
<td>0.003</td>
</tr>
<tr>
<td>Ce</td>
<td>0.001</td>
<td>0.001</td>
<td>0.003</td>
<td>0.000</td>
<td>0.000</td>
<td>0.006</td>
</tr>
<tr>
<td>Al</td>
<td>2.970</td>
<td>2.960</td>
<td>2.930</td>
<td>2.966</td>
<td>2.927</td>
<td>2.913</td>
</tr>
<tr>
<td>Fe</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.022</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>S</td>
<td>1.992</td>
<td>2.002</td>
<td>2.026</td>
<td>2.014</td>
<td>2.034</td>
<td>1.967</td>
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<td>P</td>
<td>0.041</td>
<td>0.033</td>
<td>0.025</td>
<td>0.006</td>
<td>0.004</td>
<td>0.092</td>
</tr>
</tbody>
</table>

EPMA data were obtained using a Cameca-SX 100 electron microprobe at the MPI, University of Hamburg.

A NW-SE trending intermediate-sulfidation epithermal mineralization with galena, low-Fe sphalerite, polybasite/pearceite, Ag-tetrahedrite and haematite is the main feature of the Kon- daros-Katsimoutis-Vani area (Alfieris & Voudouris 2005, 2006). The mineralization is hosted mainly by propylitically altered andesite/dacite flow domes. The Kondaros-Katsimoutis system is considered to represent the sub-seafloor feeder zones of the seafloor deposited stratiform Mn-Ba-Pb-Ag deposit at Cape Vani. The presence of micro-chimney like structures composed of various sulphides including the skeletal intergrowths between sphalerite, pyrite and galena (Fig. 2d) is indicative of rapid deposition in a subseafloor environment (Alfieris & Voudouris 2006). A similar situation occurs at the neighbouring Kimolos island, where a NW-SE Ag-rich mineralization overprints NE-SW trending manganese veins. Several As, Sb, Mn mineralized submarine silica sinters have been recognized at Kondaros, Agathia and Koumaria (Fig. 1), accompanying subaerial sinters with typical dessication cracks suggesting temporary emergence of the W. Milos area.

5 DISCUSSION

Based on geological information Plimer (2000), Stewart & McPhie (2003, 2006) suggested that the W. Milos mineralization was formed under shallow submarine to subaerial conditions, and that the palaeogeography at the time of mineralization comprised scattered islands flanked by shallow marine areas. This was also verified by Naden et al. (2005) who demonstrated using stable isotope data the involvement of meteoric in addition to seawater in the hydrothermal system. There are several mineralogical evidences that seawater was involved in all studied mineralization and that these were formed in a partly submarine environment: the presence of framoidal pyrite.
(Triades, Galana, Kondaros-Katsimoutis), the presence of micro-chimney structures (e.g. Chondro Vouno, Profitis Ilias, Agathaia, Triades, Kondaros-Katsimoutis), the abundance of barite, the presence of aragonite at Kondaros-Katsimoutis attributed to rapid precipitation rates in a shallow submarine environment (Pichler & Veizer 2004) and finally the secondary copper sulphides within the Cu-rich stockwork telluride mineralization at Profitis Ilias associated with second generation of galena sphalerite, which may suggest interplay between seawater oxidation and renewed hydrothermal pulse(s) (Alfieris & Voudouris 2006). Western Milos mineralization is characterized by the development of a pre-ore submarine hypogene advanced argillic alteration, as documented at the active Conical Seamount/Lihir isopiste and the transitional submarine to submarine epithermal Pueblo Viejo/Dominican Republic deposit (Kesler et al. 2005). Ore minerals were introduced at western Milos by later fluids of both intermediate- and high-sulphidation character. The presence of precious metal tellurides in the Profitis Ilias deposit is an indication of a magmatic origin of tellurium transported by magmatic vapours as suggested by Jensen & Barton (2000). The elevated content of Mo, W and Bi in the Triades-Galana-Kondaros, the hypogene advanced argillic alteration, and also the high activity of sulphur (as suggested by the very low Fe-content in sphalerite), is an additional evidence that magmatic fluids may have played a role in the evolution of the western Milos hydrothermal system(s). At least two buried porphyro-type deposits contributing to magmatic gases and possibly metals are postulated beneath the Profitis Ilias-Chondro Vouno and Triades-Galana-Kondaros subareas. Milos mineralization could be comparable to the magmatic-hydrothermal system at Nisyros volcano at the eastern edge of the south Aegean volcanic arc, where a deep porphyry-type potassic alteration overprinted by porphyry-related anhydrite veins, grades upwards to epithermal quartz-adularia veins with base-metal sulphides (unpubl. Voudouris & Alfieris 2007).

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
Karakasi mines, Hermione, evolution of a Cyprus-type Cu-Zn deposit, Argolis, Greece.

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ABSTRACT: The Hermione Cyprus-type Cu-Zn deposits, Argolis, Greece, are hosted in Miocene ophiolites overlain by terrigenous turbidites with intercalations of limestones and manganiferous iron formations. The ore deposits form irregular lenticular or stratiform ore bodies, and veins. These ore bodies are associated with marginal volcanic activity in an arc-related Miocene palaeocontinent. Late N- to NNE-trending, sinistral, milky quartz-pyrite-calcite veins cut the host ophiolites. Alteration haloes of quartz-calcite, albite-sericite-chlorite, and chalcedony-epidote-clay minerals envelop the veins or develop in the lavas as concentric shells. The tellurium-bearing Cu-Zn mineralization is developed in two successive stages followed by a supergene stage. The Co-pyrite-chalcopyrite geothermometer defined two stages of sulphide equilibrium: 310° to 375ºC (Stage I), and 220° to 260ºC (Stage II). The calculated δ¹⁸O and δD compositions of the waters reflect the dominance of a magmatic component. The calculated δ³⁴S_H₂S fluid values also reveal a magmatic source for the sulphur, with minor contribution from submarine sediments, whereas tellurium is proposed to be derived from a mafic-ultramafic source. The physicochemical conditions of the hydrothermal fluids in the Hermione system were $T=250^\circ-300^\circ C$, $P \approx 450$ bars, $pH = 4.1$ to 5.0, $f_{S_2} = 10^{-11.6}$ to $10^{-12.4}$, $f_{O_2} = 10^{-35.5}$ to $10^{-38.3}$, $log_{10}(aS_2^{aq}) = 10^{-3.7}$ to $10^{-4.0}$, and $log_{10}(aS^{aq}) = 10^{-2.6}$ to $10^{-3.4}$.

KEYWORDS: Cu-bearing pyrite, Cyprus-type ores, ophiolites, Miocene arc-related rift, Karakasi mines, Hermione, Argolis.

1 INTRODUCTION

The Karakasi mines at Hermione, Argolis, Hellas were famous for the mining of pyrite at the beginning of the 20th century. The production of the mines reached up to 30,000 t, and was used for the production of sulphuric acid. Exploited Cu-bearing pyrite mineralization was first studied by Aronis (1951) who believed that the mineralization formed on or just beneath the ocean floor. In this study, we report the results of a detailed investigation of paragenetic and stable isotope characteristics of the mineralization and use them to constrain the thermo-chemical conditions of ore formation.

2 GEOLOGICAL SETTING

The geology of Hermione consists of a carbonate platform of Upper Triassic neritic limestones (Dostal et al. 1991). This formation is overlain by a turbidite formation (“Shale-sandstone formation” of Varnavas and Panagos, 1989), which consists of shales, cherty limestones, interbedded with sandstones that are intercalated with pillow lavas, iron formation and pyrite ores (Sideris & Skounakis 1987). This unit is overlain by sandstones, limited shales, and conglomerates. Ophiolite was tectonically emplaced in the turbidite and consists of massive metabasalts that are overlain by pillow lavas cut by diabase dykes representing the lava feeders (Robertson et al. 1991); and blocks of dunite, pyroxenite, peridotite, serpentinite, pillowed lava, and thin tectonically emplaced massive sulphide ores (Clift & Robertson 1990). The Hermione area is characterized by a conjugate system of N-trending, sinistral and W-trending, dextral, strike-slip faults and anticlines with NNE- and WNW-trending axes.

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The different rock types and mineral assemblages in the host ophiolites are summarized in Table 1. The secondary minerals are consistent with rock-seawater interaction at lower greenschist facies conditions (\(P \approx 2.5\) kbars and \(T = 200^\circ\)C-300°C).

<table>
<thead>
<tr>
<th>Rock type</th>
<th>Assemblage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peridotite</td>
<td>Olivine, ortho-, clino-pyroxene, magnetite, serpentine, quartz.</td>
</tr>
<tr>
<td>Pyroxenite</td>
<td>Serpentine, olivine, ortho-, clino-pyroxene, magnetite.</td>
</tr>
<tr>
<td>Peridotite</td>
<td>Olivine, ortho-, clino-pyroxene, magnetite.</td>
</tr>
<tr>
<td>Serpentinite</td>
<td>Serpentine, olivine, ortho-, clino-pyroxene, magnetite.</td>
</tr>
<tr>
<td>Basalt</td>
<td>Labradorite, hornblende, augite, olivine, magnetite, ilmenite, biotite.</td>
</tr>
<tr>
<td>Diabase dykes</td>
<td>Labradorite (phenocrysts), metamorphosed glass (chlorite, epidote, calcite, quartz, albite).</td>
</tr>
<tr>
<td>Andesite</td>
<td>Andesine ((A_{24-47})), biotite, hornblende, quartz, diospide, albite.</td>
</tr>
</tbody>
</table>

3 ORE DEPOSITS, ALTERATION, ORE MINERALOGY, CHEMISTRY AND TEXTURES

Exploration of the Karakasi mines revealed that the majority of the pyrite deposits occur as veins within the blocks of peridotites, as veins in the lavas, as lensed at lava tops, and as lenses and layers within the tuffs and tuffaceous iron formations overlying the lavas. A 2-6m layer of Fe-, Fe-Mn-, and Mg-ochre, umber and iron formation covers the pyrite ores. In some occasions the ore deposits lie directly on the lavas. Rarely do they occur as replacement of calcareous sandstones and limestones. These ores are attributed due to remobilization.

The diabase intrusions in the area form a conjugate system of NW-, WNW- and NE-trending dykes with widths \(\leq 50\) m. Late N- to NNE-trending dextral veins of milky quartz, calcite, oligoclase (\(A_{16-13}\)), albite, sericite and pyrite, with widths of \(> 0.5m\), intrude the hosts, or even the ores, but mainly at the contacts with the ore bodies.

Alteration haloes developed around barren and mineralized milky quartz-calcite veins and at the contacts of the ore lenses with the hosts. They form discontinuous borders and shells. The alteration developed in three zones: an inner milky quartz-calcite zone (\(\geq 25cm\)), an intermediate albite-sericite-chlorite zone (\(\geq 15cm\)) and an outer dickite-illite-smectite-hematite, Fe- Mn- and Cu-hydroxide zone.

The pyrite ores display two ore mineral stages, which are followed by a supergene stage consisting of covellite, idaite, limonite, melaniterite, malachite and azurite. Stage I is characterized by subhedral pyrite (pyritohedra up to 1.5 cm) intergrown with pyrrhotite and minor magnetite, Fe-rich sphalerite and chalcopyrite. The pyrite is intensely brecciated, and cements by quartz, calcite, sphalerite and chalcopyrite, or it occurs as disseminations in veins. Pyrite contains up to 2.39 (0.05 \(apfu\)), 0.12, 0.24, 0.56 (0.011 \(apfu\)), and 0.13 wt. % Cu, Zn, Co, Te and As, respectively, and traces of Au and Se. The high Cu contents in pyrite represent chalcopyrite nanoparticles and replacement-related chalcopyrite disease.

In Stage II, the pyrite is more intensely brecciated, veined, replaced and cemented by abundant chalcopyrite and minor galena, freibergite, chalcocite and marcasite (up to 0.09 wt. % Co). Chalcopyrite contains Co up to 0.29 and 0.19 wt. % Te (0.009 \(apfu\)), whereas sphalerite up to 0.39 wt. % Cd. The iron content of sphalerite ranges from 2.53 to 7.82 wt. %, corresponding to 4.41 to 14.92 mol % FeS).

4 PRESSURE-TEMPERATURE CONDITIONS

For estimation of temperature of formation of Hermione ores we used the CuFeS\(_2\)-FeS\(_2\)-Co-contribution geothermometer (cobalt partitioning between co-existing pyrite and chalcopyrite); and of the Al\(^{VI}\) chlorite geothermometer (where T is a fiction of Al\(^{VI}\) and Fe(Fe+Mg) ratio) of Cathelineau (1988) for chlorites in equilibrium with Stage I and II minerals (with Fe(Fe+Mg) = 0.85 and 0.63, and Al\(^{VI}\) = 1.28 and 1.03). The geothermometrical results, when coupled with the ones from Skounakis & Sovatzoglou-Skounaki (1981), defined three temperature intervals for the deposition and equilibration of the Hermione ores. These intervals correspond to deformed (120° to 195°C) versus less-deformed-hydrothermal Stages I and II (310° to 375°C and 220° to 260°C, respectively) pyrite ores.

Sphalerite is compositionally zoned with respect to FeS, with cores containing an average of \(\approx 4\) mol % FeS (with low Cu and high Cd contents compared to rims) and the rims containing an average \(\approx 15\) mol % FeS. The pres-
ence of copper up to 6.45 wt.% in the sphalerite rims that was in contact with hexagonal pyrrhotite and pyrite was not taken into account due to replacement of pyrite after chalcopyrite. Application on the sphalerite geobarometer, for the low-metamorphism developed sphalerite rims, of Hutchison & Scott (1981) yielded a post-depositional pressure of ~ 2.5 kbars. This pressure is higher than those derived from sphalerite hydrothermal cores in equilibrium with pyrite and pyrrhotite of ~ 450 bars. The pressure obtained from the rims reflects pressures of low-grade regional metamorphism.

5 STABLE ISOTOPES STUDIES

Oxygen and hydrogen isotope compositions were obtained from fluids released by samples of chloride and sericite spatially associated with sulphide mineralization, host basalts, diabase, and milky quartz veins. The δ18O and δD values derived from the host lavas range from 12.3 to 18.7 ‰ and from -74.2 to -63.2 ‰, respectively. Average temperatures were obtained from the Co-pyrite-chalcopyrite geothermometer, for the low-metamorphism developed sphalerite rims and galena, representing hydrothermal sphalerite cores, from albite-sericite equilibria (reaction 1).

\[
\begin{align*}
\text{KA}_3\text{Si}_3\text{O}_10(\text{OH})_2(s) + 6\text{SiO}_2(aq) + 3\text{Na}^+(aq) &= 3\text{NaAlSi}_3\text{O}_8(s) + 2\text{H}^+(aq) + \text{K}^+(aq) \\
\text{H}_2\text{O}(l) &= \text{H}_2\text{O}(l)
\end{align*}
\]

(1)

Following the method of Tombros et al. (2007), the calculated log (aNa+/aK+) values are 0.57 and 0.65, respectively. From these values, pH values of 4.1 and 5.0, respectively, are obtained. At 300°C, the assemblage pyrite-pyrrhotite-magnetite buffers the logfO2 values at -35.5 (Barton & Skinner 1971), whereas a maximum value of logfO2= -38.3 at 250°C was derived for a δ34S_H2S of 1 ‰, Σδ34S= 0, and a pH of 5.0. The composition of FeS in Hermione sphalerite, which ranges from ~4 to ~15 mol % FeS, at 250° and 300°C indicates a range of logfS2 values from -11.6 to -12.4 (Kretschmar & Scott 1976).

\[
2\text{H}_2\text{S}(aq) + \text{O}_2(g) = \text{S}_2(g) + 2\text{H}_2\text{O}(l) \\
\text{H}_2\text{S}(aq) = \text{H}^+(aq) + \text{HS}^-(aq)
\]

(2) (3) (4)

Utilizing reactions (2), (3) and (4), yields values of logaH2S(aq) and logaHS(aq) of -3.7 and -4.0, and -2.6 and -3.4, at 250° and 300°C, respectively and a value of logaFe32/aCu(HS)2 = 4.2.

7 DISCUSSION

The geometry, host rock and ore assemblages of the Hermione rocks indicate a formation similar to that of recent mid-ocean ridge black smoker ore deposits. However, the presence of Pb in the ores indicates hydrothermal leaching of more felsic rocks present in the volcanic pile. The ores formed at a maximum temperature of 310° to 375°C for Stage I-pyrite and between 220° and 260°C for Stage II ores. The ores formed at or near the ocean floor at pressures of 165 bars hydrostatic or 450 bars lithostatic, but they were subsequently covered by turbidite and equilibrated to pressures of ~2.5 kbars.

The calculated δ34S_H2S values of the hydrothermal fluid range from -3.2 to 1.4 ‰. Stage I shows typical magmatic δ34S_H2S values, whereas Stage II reveals negative δ34S_H2S values which are consistent with a minor contribution from the submarine sediments. The δ18O and δD values reflect the dominance of a magmatic
component related to volcanic activity in an active arc-related rift (Fig. 1). The lighter $\delta^{18}O$ and $\delta D$ values of vein quartz can be attributed to mixing with seawater, and water-rock interaction.

Given the presence of tellurium in hydrothermal exhalations derived from mid ocean ridge basalts, it is possible that it was derived from leaching of mantle-rocks and then partitioned in the sulphides. Tellurium may have then been re-distributed in conjunction with the release of CO$_2$, as suggested from the fluid inclusion characteristics of vein calcite.

Figure 1. Hydrogen versus oxygen isotope diagram displaying stable isotope systematics of waters from Hermione, Argolis. The calculated $\delta^{18}O$ and $\delta D$ water values were obtained by utilizing the chlorite-water equation of Wenner & Taylor (1971); the muscovite-water equations of O’Neil & Taylor (1972) and Suzuoki & Epstein (1976), and the quartz-water equation of Clayton et al. (1972). Dot lines refer to “Subduction-related vapor, arc and crystal felsic magma.

ACKNOWLEDGMENTS

We thank the European Social Fund (ESF), Operational Program for Educational and Vocational Training II (EPEAEK II), and particularly the Program Pythagoras II, for funding the above work as a grant to KStS and post-doctoral fellowship to S. Tombros.

REFERENCES


Barton PBJr, Toulmin P (1964) Experimental determination of the reaction chalcopyrite+sulfur $\rightarrow$ pyrite+bornite from 350°-500°C. Econ Geol 59: 747-752.


Johnson J, Oelkers E, Helgeson HC (1992), SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5000 bars and 0°F to 1000°C. Comp Geosc 18: 899-947.


Characterization of coal from the Mariovo basin, Macedonia – Insights from organic geochemical and sulphur isotopic data.

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ABSTRACT: Detailed petrographic study of coal from the Mariovo basin in Macedonia suggests circulation of fluids mobilizing metals from different origins (basement, volcanic rocks?) during burial. Sulphur isotopic data on organic matter and pyrite indicate dominantly marine-derive fluids and processes of bacterial reduction of sulphates.

KEYWORDS: Coal chemistry, organic sulphur, metals, vitrinite reflectance, electron microprobe, Mariovo basin, Macedonia.

1 INTRODUCTION

Coal in Macedonia is the main energetic resource for electricity production. The Mariovo basin is located in the southwest part of Macedonia, 46km away from the town Prilep. The basin is constrained within Mt. Selecka, between the villages Vitoliste, Polciste, Besiste and Manastir, between 700 and 1000m above sea level. The exploration was developed with intention towards the prospecting of the coal potential of the basin. The productive coal formation is developed in the eastern and the western parts of the basin. Excluding the most outer parts of the deposit, the productive formation occurs as a main layer of coal, which has sub-horizontal position with variable thickness (between 1.3 and 14.9m) and a relative depth between 7.7 and 279m. The coal from Mariovo basin is represented by lignite with high percentage of ash. The total reserves of coal in the deposit "Mariovo" are around 111 Mt. Informations about the contents, distribution and origin of sulphur and metals are important in coal combustion, because of their consequence on the production and on environment. Few detailed studies have been realized on coals from Macedonia. This work presents new petrographic, chemical and sulphur isotope data on coal, to better characterize organic matter and constrain the deposition conditions.

2 GEOLOGICAL SETTING

Macedonia lies within the Cenozoic Southern Balkan Extensional regime (Dumudzanov et al., 2004). The Mariovo graben is located in central and southern Macedonia, along the boundary between the Vardar zone and Pelagonian Massif.

Figure 1: Major tectonic units of Macedonia. I. Chukali-Krasta zone; II. Western Macedonian zone; III. Pelagonian anticlinorium; IV. Vardar zone; V. Serbo-Macedonian massif.

Most of the basinal infilling has been eroded, one of the best preserved outcrops being close to the village of Vitolishte. The sediments of the graben are divided into four for-
mations from the bottom to the top:
- The Nerezi formation (NeF) is divided into 3 units. The basal unit of ~120m essentially consists of gravels and sandstones of unknown age. The middle unit consists of ~70m of siltstones and silty claystones that grade upward into coal and claystones and finally into a 6-15m thick layer of coal overlaid by marls and claystones. The latter contain planktonic algae association of late Miocene age (Dumudzanov et al. 2004). The upper unit consists of ~60m of siltstones and sandstones followed by a break of sedimentation.
- The Solnje formation (SoF) consists of ~60-80m of gravel and sandstones of Pliocene age.
- The Vitacevo formation (ViF) of Pliocene age (Dumudzanov et al. 2004) begin with stratified tuffs overlain by sandstones and gravels, interbedded with diatomite, tuffs and sandy claystones. Above travertine layers are depoosed, followed by 80 m of tuff and sandstones.
- At the top is the Mariovo formation (MaF). It is ~60-70m thick and contains pyroclastic rocks with nine travertine layers and a 20m thick travertine deposit covering 20 km², indicating a lacustrine environment.

3 SAMPLING

Samples of coal seams and intercalated sediments were collected on three outcrops around the Vitolishte village (~ 21°49.6 E, 41°10.8 N).

The first sample (7B) is from a small outcrop close to the river. The second sample (7K) is from a small outcrop around twenty meters above the river. The coal seam is not more than 50 cm thick with an intercalated siltite layer. The sample 7K is a coal from the upper part of the seam, which also contains vitrinite lenses. The third outcrop (samples 8K, 8M and 8R) is located on the opposite side of the river, at the same level as the second outcrop. It is the most important one, with two coal seams separated by a 15 cm thick layer of siltite containing floated wood fragments. The lower coal seam is 150 cm thick (8M, 8R) and the upper one is 50-70 cm thick (8L). The sediments overlying the coal formation consist of an alternation of hard mica-rich sandstones, soft layers and claystones. The coals are generally of black coal type. Samples 7B and 7K are composed dominantly of clarain with lenses of vitrain, whereas samples 8K, M and R are richer in vitrain.

4 ANALYTICAL METHODS

Samples were observed and analysed using a JEOL scattered electron microscope equipped with an EDS detector. Local analyses of organic matter were performed using a Camebax SX50 electron microprobe with a two stages analytical program. At the first stage C, Si and P are analyzed with a 10 kV acceleration voltage, a current beam of 20 nA and a 4-5 µm beam width. At the second stage Zn, S, Fe, As, Co, Ni, U, V, Ge, Sb, Cr, W are analyzed with a 20 kV acceleration voltage and a current beam of 20 nA. Matrix corrections were made with a ZAF computing program.

Vitrinite reflectance was measured on coal peaces in accordance with standard procedures (ISO 7404/5 1984).

Sulphur isotopes of sulphates and organic sulphur were performed using a CFIRMS system coupled with Flash EA and gas bench.

5 MINERALOGY

A variety of minerals is present in the coal of Vitolishte. The mineral composition is dominated by clays, rare quartz, pyrite, gypsum, iron oxides, and probably calcite. Detrital minerals are represented by clasts of quartz, and by numerous dispersed particles of clay minerals (illite/muscovite, illite, illite/smectite) within organic matter. Pyrite is the major sulphide in the coal of Vitolishte. It is mainly observed as framboids and more rarely as euhedral crystals, occurring along stratified plans or infilling cavities of plant tissues. SEM analyses of pyrite zones show the presence of Si, Al and Ca that strongly suggests the initial co-precipitation of silica, clay mineral and a Ca-mineral (such as calcite) with pyrite.

Gypsum is visible on the surface on the samples; it is one of the major constituent of the inorganic matter. In polished section, gypsum also occurs as fine layers or surrounding pyrite framboids (Figure 2). Gypsum closely connected with pyrite in most of the samples indicates that it is essentially a weathering product of pyrite. However the gypsum in fine layers associated with a calcium phase (calcite) could be due to the crystallization of calcium and sulphate ions dissolved in the pore water during the sedimentation, according to Vassilev et al. (1994). Iron oxides are present as late infilling of fractures, strongly suggesting that they result from the weathering of pyrite. SEM analyses of
pyrite zones and gypsum show the presence of Si and Ca and strongly suggest the initial co-precipitation of silica and a Ca-mineral such as calcite with pyrite.

Figure 2: Backscattered electron image of framboidal pyrite surrounded by secondary products of gypsum.

6 PETROGRAPHY AND GEOCHEMISTRY OF COAL

The contents of sulphur, carbon and trace elements in coal from Vitolishite are given in the Table 1. Major elements are C, Si and Al, whereas minor elements are Ca, Fe, K, S and Ti. Coal from Vitolishite has low total sulphur content, consistent with low-sulphur coal according to Dai et al. (2002). Ash content is high and consistent with previous data. Metal contents in coals from Vitolishite are over the Clarke values for lignites and sub-bituminous coals (Yudovich et al., 1985) for As, Cr, Li, Pb, Sc, V and Zn. They are close to the Clarke values or slightly above for Ba, Co, Cu and Ga.

EPMA analyses and reflectance measurements were realized on macerals to determine the distribution of sulphur and metals (Table 2). Sulphur contents in macerals are high and relatively homogeneous, ranging from 1.2 to 2.3 wt%, whereas iron contents are low, showing that measured sulphur can be attributed to organic matter. Maceral composition of samples 7B and 7K is rather heterogeneous and is composed of alternation of collotelinite layers with desmocolinite and associated fusinite. Collotelinite layers in 7B exhibit rims with higher reflectance than core (Figure 2 and Table 2), and enriched in Si and Sb (280-750 ppm). SEM bulk analyses of collotelinite show homogeneous contents of sulphur, calcium and Fe. Rare light-colored zones in backscattered electron image observed in the core of collotelinite layers are slightly enriched in calcium. Desmocolinite and associated with fusinite in the sample 7B are V-rich (200-1160 ppm).

Table 1: Chemical composition of coal from Vitolishite, compared to Clarke content for lignite and subbituminous coals (Yudovich et al. 1985).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clarke</th>
<th>7K/7E</th>
<th>8 (lower seam)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C tot %</td>
<td>41.4 (40.1)</td>
<td>36.6 (49.2)</td>
<td></td>
</tr>
<tr>
<td>S tot %</td>
<td>1.0 (0.9)</td>
<td>0.8 (0.7)</td>
<td></td>
</tr>
<tr>
<td>N tot %</td>
<td>0.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>H (mgHC/gTOC)</td>
<td>126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (mg CO2/gTOC)</td>
<td>108</td>
<td>136</td>
<td></td>
</tr>
<tr>
<td>Ash yield</td>
<td>27 %</td>
<td>23 %</td>
<td></td>
</tr>
<tr>
<td>Al2O3 %</td>
<td>5.8</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>CaO %</td>
<td>&lt; dl</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>Fe2O3 %</td>
<td>1.8</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>K2O %</td>
<td>0.7</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>MnO %</td>
<td>0.03</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>SiO2 %</td>
<td>13.1</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td>TiO2 %</td>
<td>0.22</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>As ppm</td>
<td>7.4</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>Ba ppm</td>
<td>120</td>
<td>151</td>
<td>104</td>
</tr>
<tr>
<td>Ce ppm</td>
<td>59</td>
<td>42</td>
<td>26</td>
</tr>
<tr>
<td>Cr ppm</td>
<td>4.2</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Cu ppm</td>
<td>15</td>
<td>37</td>
<td>29</td>
</tr>
<tr>
<td>Ga ppm</td>
<td>14</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>Ge ppm</td>
<td>7</td>
<td>8</td>
<td>5.9</td>
</tr>
<tr>
<td>Li ppm</td>
<td>1.5</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Ni ppm</td>
<td>20</td>
<td>26</td>
<td>20</td>
</tr>
<tr>
<td>Pb ppm</td>
<td>9</td>
<td>33</td>
<td>39</td>
</tr>
<tr>
<td>P ppm</td>
<td>220</td>
<td>639</td>
<td>425</td>
</tr>
<tr>
<td>Sb ppm</td>
<td>6.7</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Se ppm</td>
<td>0.82</td>
<td>&lt; dl</td>
<td>&lt; dl</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>2</td>
<td>5.4</td>
<td>3.6</td>
</tr>
<tr>
<td>Tb ppm</td>
<td>130</td>
<td>70</td>
<td>73</td>
</tr>
<tr>
<td>U ppm</td>
<td>2.1</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>V ppm</td>
<td>22</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>Zn ppm</td>
<td>18</td>
<td>46</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 2: reflectance measurements and EPMA analyses of collotelinite (CT) and desmocolinite (D) for carbon, sulphur and iron.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maceral</th>
<th>R0 %</th>
<th>C %</th>
<th>S %</th>
<th>Fe %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8R</td>
<td>CT</td>
<td>0.44</td>
<td>71</td>
<td>1.9</td>
<td>4.5</td>
</tr>
<tr>
<td>8K</td>
<td>CT</td>
<td>0.45</td>
<td>74</td>
<td>1.7</td>
<td>3.0</td>
</tr>
<tr>
<td>8M2</td>
<td>D</td>
<td>0.39</td>
<td>81-82</td>
<td>2.0-2.3</td>
<td>1-1.1</td>
</tr>
<tr>
<td>8M2</td>
<td>CT</td>
<td>0.46</td>
<td>77</td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td>7K</td>
<td>CT</td>
<td>0.52</td>
<td>80</td>
<td>2.2</td>
<td>0.3</td>
</tr>
<tr>
<td>7K</td>
<td>D</td>
<td>0.49</td>
<td>66-68</td>
<td>2-2.1</td>
<td>2-6-4</td>
</tr>
<tr>
<td>7B</td>
<td>CT layer(core)</td>
<td>0.38</td>
<td>81</td>
<td>1.7</td>
<td>0.3</td>
</tr>
<tr>
<td>7B</td>
<td>CT layer(Sb-rich rim)</td>
<td>0.47</td>
<td>62</td>
<td>1.2</td>
<td>1.9</td>
</tr>
<tr>
<td>7B</td>
<td>CT</td>
<td>0.46</td>
<td>76</td>
<td>1.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Figure 2. Micrograph in reflected light of a collotelinite layer from the sample 7K, showing rims characterized by higher reflectance and high Si and Sb contents.

On other hand, samples 8K, 8M and 8R are mainly composed of collotelinite. Its reflectance values are comparable to that of samples 7. This range of values corresponds to that of sub-bituminous coals. However the carbon content of some macerals seems to be high for this rank. Vitrinite from the sample 8K is characterized by prismatic cracks, probably resulting from a thermal influence (M. Yossifova, pers. comm.). However, its reflectance remains rather low, and comparable to that of other samples. Collotelinite in the samples 8K, 8R and 8M are Ni-rich (260-700 ppm) and show important local Ge and Ga contents (up to 350 and 530 ppm, respectively). EPMA analyses of macerals from the coal of Vitolishte also provide evidence of local important contents of Co, Cu, Pb, Sb, Zn and W. The large variety of metals and their distribution in organic matter suggest circulation of fluids during burial, that mobilize metals from different sources (basement, volcanic rocks?).

7 SULPHUR ISOTOPES

Gypsum and organic sulphur was analyzed in different samples of Vitolishte. Gypsum which is the secondary product of pyrite weathering has preserved the $\delta^{34}$S of the syn-sedimentary pyrite. $\delta^{34}$S values of organic sulphur are +5.4‰ and +13.2‰. They are slightly higher than the classical range of organic sulphur signature in low-sulphur coals, which derive essentially from plants (+2 to +8‰; Dai et al. 2002). These data suggest that sulphur was not accounted only for original plants, but introduced into peat after burial. High positive $\delta^{34}$S values of pyrite and organic sulphur could result from the bacterial reduction of additional marine-derived sulphates evolving in a close system. The presence of planktonic algae in clay stones above the coal seam is consistent with an intermittent marine environment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral phase</th>
<th>$\delta^{34}$S$_{\text{sulfate}}$</th>
<th>$\delta^{34}$S$_{\text{vitrinite}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7K</td>
<td>Gypsum</td>
<td>+17.2</td>
<td></td>
</tr>
<tr>
<td>7K</td>
<td>MgSO$_4$</td>
<td>+14.9</td>
<td></td>
</tr>
<tr>
<td>8L</td>
<td>Gypsum</td>
<td>+17.3</td>
<td></td>
</tr>
<tr>
<td>8M</td>
<td>vitrinite</td>
<td>+5.4</td>
<td></td>
</tr>
<tr>
<td>8R</td>
<td>Gypsum and vitrinite</td>
<td>+8.5</td>
<td>+13.2</td>
</tr>
</tbody>
</table>

Table 3: Sulphur isotopic composition of secondary sulphates and sulphur of organic matter.

8 CONCLUSION

New data on the coal from the Mariovo basin confirm the high ash content. Total sulphur content remains low and metal contents are slightly higher than the Clarke values of lignite and subbituminous coals. The detailed petrographic and isotopic studies of organic matter and frambooidal pyrite provide evidence of a relation between macerals and V-Ni-Sb contents, and of bacterial reduction of sulphates, partly of external origin (marine-derived?). Further investigations need to be done to determine the origin of metals.

ACKNOWLEDGEMENTS

This work was financially supported by the ECO-NET program (10161XM) between the BRGM (France), the Geological Institute of Sofia, Bulgarian Academy of Sciences (Bulgaria) and the University of Skopje (Macedonia).

REFERENCES


Chlorides in the Skouries and Medet Porphyry Deposits of the Balkan Peninsula

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ABSTRACT: The Skouries and Medet porphyry Cu-(Mo-Au) deposits belong to the Balkan-Carpathian metallogenic belt of Late Mesozoic to Tertiary age, related to subduction magmatism and exhibit significant precious metal (Au, Pd, Pt) enrichment. The investigation of ores, using SEM/EDS, revealed the presence of abundant fine chloride (KCl) crystals within and/or around decrepitated fluid inclusions, associated with sulphi des and silicates. Mineralogical data may suggest that Cl-rich fluids post-dated the main stage of K-silicates, magnetite-chalcopyrite and chalcopyrite-pyrite deposition, have been trapped in fluid inclusions containing abundant crystals of sylvite. The presented data suggest that the transportation of base/precious metals in porphyry-systems has taken place as chloride complexes even during late stages of mineralization whilst bisulphide complexes are unlikely at any conditions.

KEYWORDS: chlorides, porphyry, platinum, palladium, Skouries, Medet, Greece, Bulgaria

1 INTRODUCTION

Alkaline porphyry deposits in the Skouries, Greece, and Elatsite, Medet, Tsar Assen and Assarel in Bulgaria have received considerable exploration attention due to the attractive resources and elevated Pd and Pt levels in addition to gold, particularly in the Skouries and Elatsite deposits (Eliopoulos & Economou-Eliopoulos 1991; Tarkian et al., 2003).

In the present study we report the first SEM images of chloride (sylvite) crystals occurring around decrepitated fluid inclusions hosted by pyrite at Medet and chalcopyrite at Skouries. These chlorides may provide additional evidence for the transportation of Cu and precious metals by magmatic-hydrothermal fluids as chlorine complexes, e.g. chlorine is a main metal ligand in the hypersaline fluids in porphyry deposits.

2 SKOURIES AND MEDET PORPHYRY DEPOSITS

Late Mesozoic to Tertiary porphyry Cu-(Mo-Au) intrusions located within the metallogenic belt of the Alpine-Balkan-Carpathian-Dinaride orogenic system, are associated with subduction related magmatism following the change from east-west to north-south converge between Africa and Eurasia. The Medet, Elatsite, Tsar Assen and Assarel porphyry-Cu deposits, in the central Srednogorie metallogenic zone are related to multiphase monzonitic-monzodioritic stocks and dikes of Upper Cretaceous (~92 to ~86 Ma, von Quadt et al., 2005) age, while the Skouries porphyry Cu-Au deposit, located at the Chalkidiki peninsula, northern Greece, is of Miocene age.

2.1 Skouries

The defined reserves in the porphyry Cu-Au deposit of Skouries are approximately 206 Mt at 0.54 % Cu, 0.80 ppm Au and 0.08 ppm Pd. Monzonites contain phenocrysts of plagioclase, alkali feldspar and amphibole as well as apatite and titanite microphenocrysts in a fine-grained feldspar-dominated groundmass. Dark-green fine grained xenoliths within mineralized porphyry are mainly composed by orthoclase, phlogopite, and lesser amounts of biotite remnants, fine-grained magnetite, pyrite and chal-
copyrite (Kroll et al., 2002; Economou-Eliopoulos, 2005). Chalcopyrite, and to a lesser extent bornite, contain exsolutions of galena, which commonly has significant concentrations of Se. Minor ore minerals are gold-electrum, clausthalite-galena, hessite and merenskyite-moncheite (Tarkian et al. 1991).

![Backscattered electron images from a drill core sample at Skouries porphyry deposit. Ti-magnetite (Ti-mt) - rutile (rt) intergrowths are closely associated with chalcopyrite (cp) hosting chloride (sylvite) crystals related with decrepitated fluid inclusions. They are found within a matrix of biotite (bi) and quartz (qtz).](image)

The investigation of the Skouries mineralized samples from the drill hole labelled as Sk8 (400m depth), using microprobe (SEM/EDS) analyses, reveals the presence of sylvite (KCl) crystals associated with chalcopyrite in the Skouries deposit (Fig. 1). The drill hole SK8 samples, coming from the peripheral part of the Skouries porphyry stock, are characterized by the frequent association of magnetite and Cu-minerals (bornite and chalcopyrite) with inclusions of thorite, U-bearing thorite, hydroxylapatite and rare earth element (REE)-enriched silicates of the epidote-group (allanite), zircon and rutile. Ti-bearing magnetite-rutile intergrowths with dismembered-corroded chalcopyrite hosting tiny sylvite crystals cut the main stage of the Skouries Cu-Au-PGE mineralization. In general, Ti-magnetite, with titanium content, ranging from 17.5 to 23.5 wt % TiO₂, is commonly associated with rutile, both post-dating the main stage of the magnetite deposition (Economou-Eliopoulos, 2005). Inclusions of albite and orthoclase within chalcopyrite are commonly present. At the deeper parts (670m depth) of the same drill hole dark green fine-grained xenoliths within mineralized porphyry are mainly composed of orthoclase, phlogopite, and lesser amounts of relict biotite, fine-grained magnetite, pyrite and chalcopyrite.

Also, chalcopyrite in places is surrounded by digenite suggesting relatively oxidized fluids with a high ratio of metal to reduced sulphur during the evolution of the mineralized ore forming system.

The average fluorine (F) content of the whole rock is 900 ppm (Eliopoulos and Economou-Eliopoulos 1991), while mica phases contain up to 0.19 wt. % Cl and 2.48 wt. % F (Kroll et al. 2002; Economou-Eliopoulos & Eliopoulos 2001; Economou-Eliopoulos 2005).

### 2.2 Medet

Approximately 244 Mt, grading 0.37 % Cu are the defined reserves in the porphyry Cu-Au deposit of Medet (Milev et al. 1996). The Cu-mineralization of stockwork type, hosted by a quartz monzonite intrusion, is associated with quartz-magnetite and K-silicates. Rutile, ilmenite, Mn-ilmenite, pseudobrookrite, Co-Ni assemblages (carrollite, vaesite), Co- and Ni-bearing pyrites, reaching values up to 17.8 wt%, and 5.3 wt%, respectively. Cu-Sn-V-minerals and micron-sized inclusions of Bi-Ag tellurides (hessite and tetradymite) within chalcopyrite have been described (Strashimirov et al., 2002). The quartz-pyrite association forms veins and veinlets in the middle part of the deposit, while the quartz-galena-sphalerite association only occurs locally at the uppermost and marginal parts of the deposit. The reported precious metal contents in flotation concentrate (at 14.9 wt% Cu) from the Medet deposit indicated up to 50 ppb Pd, 26 ppb Pt and 360 ppb Au (Tarkian & Stribrny 1999).
Abundant fine sylvite (KCl) crystals were identified around decrepitated fluid inclusions from the Medet porphyry deposit (Fig. 2). The trace of the fluid on sulphides (pyrite with inclusions of chalcopyrite) and partly on albite suggest that they have been trapped in fluid inclusions post-dating the main stage of K-silicates and chalcopyrite-pyrite deposition.

3 DISCUSSION AND CONCLUSIONS

A characteristic feature of the Skouries and Elatsite (Bulgaria) porphyry deposits is their significant Pd and Pt potential, over 15 tonnes and 3 tonnes, respectively. Such a potential is considered to be encouraging economic factor for Pd and Pt as by-product, probably along with Au and Cu. Although the analytical data with respect to the Medet deposit are limited there is significant precious metal enrichment too (Eliopoulos et al. 1995; Tarkian & Stribrny 1999).

Experimental, thermodynamic, and fluid-inclusion studies suggest that relatively hot (400° to 700 °C) and saline to hypersaline (up to 70 wt% NaCl equiv) magmatic-hydrothermal fluids transported Cu and precious metals as chloride complexes that were precipitated during the main stage of mineralization with the K-assemblages. The hydrosulphide ion (HS–) may be responsible for PGE transport in hydrothermal systems, but significant transport of the PGE by a bisulphide complex in porphyry systems is unlikely at any conditions (Sillitoe 1993; Jensen & Barton, 2000; Hanley et al., 2005).

With respect to the evolution of the Skouries mineralization the high δ¹⁸O (8 to 10 per mil) and low δD values (-95 to -70 per mil) for fluids in equilibrium with vein quartz/main stage of mineralization, and δ³⁴S values from vein and disseminated sulphides (-2.1 to +0.3 ‰) fall within the typical range of early ore-forming fluids, whereas low δ¹⁸O and high δD values for fluids are linked with the pyrite-chalcopyrite mineralization (Frei 1995). The fluid inclusion study provides evidence for two different fluid types: (i) an early CO₂-rich fluid of an early intermediate salinity, which locally boiled on ascent to shallower parts of the deposit and thereby formed brine and vapour-rich inclusions synchronous with the main stage of mineralization, and (ii) a late low salinity fluid (Frei, 1995). The origin of hypersaline fluids in iron oxide-Cu-Au deposits is controversial. Chiaradia et al. (2006) reported the first chlorine and strontium isotope data combined with Cl/Br ratios of fluid inclusions and concluded heavy chlorine isotope signature of fluids from Fe-oxide-Cu-Au deposits reflecting the magmatic-hydrothermal component of these fluids, in contrast to the near 0‰ δ³⁷Cl values of porphyry-Cu fluids. More research is required to clarify the ligands responsible for precious metal transport during deposition and/or post-ore alteration and metamorphism, and their source, on the basis of chlorine isotope and Cl/Br ratios of fluid inclusions (study in progress) for the Skouries and Medet deposits.

Nevertheless, SEM/EDS analytical data from the Skouries and Medet porphyry deposits, suggest that Cl-rich fluids even at low temperature, post-dated the main stage of magnetite-chalcopyrite and chalcopyrite-pyrite deposition have been trapped in fluid inclusions containing abundant crystals of sylvite (Figs 1 and 2). These data, coupled with the suffi-
ciently oxidizing hydrothermal solutions in porphyry Cu-Au deposits (Halter et al. 2005; Economou-Eliopoulos 2005) may indicate that the transportation of significant amounts of precious metals has taken place as chloride rather than bisulphide complexes.

ACKNOWLEDGEMENTS

The University of Athens is greatly acknowledged for the financial support of this work. Mr. E. Michailidis is thanked for his assistance with the probe analyses.

REFERENCES


Cu-Mo-Au ratios in porphyry-style ore deposits: fluid chemical controls

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ABSTRACT: A series of magmatic and hydrothermal processes involved in the transport and deposition of metals seem to control Cu-Mo-Au ratios in porphyry-type ore deposits and commonly involve three different types of fluids: i) a moderate salinity (2 - 15 wt% NaCl equiv.) aqueous fluid of intermediate density, often trapped in the single-phase field; ii) a high-salinity (35 - >50 wt% NaCl equiv.) aqueous liquid fluid; and iii) a low-salinity (< 5 wt% NaCl equiv.) vapour. In many cases the earliest fluids in porphyry-type ore deposits are of the single-phase type, which separates into coexisting high-density brine and low-density vapour. Cesium (Cs) concentrations in the fluid exsolving from a magma correlate with the timing of fluid exsolution relative to the degree of fractional crystallisation of the magma. Highly fractionated magmas exsolve fluids rich in Cs and metals such as Sn, W and Mo, whereas more primitive magmas saturate in fluids poor in Cs and rich in metals like Cu and Au. Phase separation is responsible for the decoupling of e.g. Cu and Au from Mo. The separating vapour is enriched in Cu and to a minor extent in Au, Ag, Sn and As. On the other hand Mo, W, Pb and Zn do not preferentially partition. Finally, precipitation of ore minerals is temperature dependent and therefore may be of selective nature. Copper and Au commonly precipitate from vapour fluids, but there is evidence that Mo mineralization forms from brine fluids, which is rather immobile compared to the vapour. In summary, magmatic-hydrothermal processes, such as fluid exsolution, phase separation and mineral precipitation have a strong influence on the metal ratios in porphyry-type ore deposits.

KEYWORDS: metal ratios, porphyries, fluid inclusions, LA-ICPMS

1 INTRODUCTION

Economically interesting metals contained in porphyry-type ore deposits - copper, molybdenum and gold - occur in almost every possible abundance combination. Although most of the deposits are Cu-dominated systems with more or less Mo or Au, there exist pure Mo-deposits (e.g. Climax-type), as well as very Au-rich deposits (e.g. in the Maricunga belt). Interestingly, porphyry-type ore deposits occur in spatially very distinct provinces where the deposits are not only similar in their metal endowment but also in their size.

Metal ratios in porphyry-type ore deposits are the product of a long chain of magmatic and hydrothermal processes that are involved in the transport of metals from the source to the depositional site and the precipitation of these metals in a single or in different locations. Which of those processes and to what extent they finally control the metal ratio in the ore is a central question in the field of economic geology.

This paper investigates possible causes for the variety of metal ratios and the provinciality of porphyry-type ore deposits, by comparing fluid chemical data (derived from fluid inclusion microanalysis by laser ablation ICPMS) from 12 different deposits and from one barren hydrothermal system (Klemm 2006 and references therein).

The effects of the different magmatic-hydrothermal processes on the composition of the fluid(s) were identified and their significance for the overall metal budget of the system was investigated. Important processes involved in the evolution of a typical porphyry-type ore deposit include: fluid exsolution from the magma, fluid phase separation, mineral precipitation and remobilisation.
2 MAGMATIC FLUID EXSOULATION

The variable metal ratios of these deposits show a first order correlation with the degree of source magma fractionation and crystallisation as indicated by the abundance of Caesium in the fluids (Audétat & Pettke 2003). With progressive crystallisation of the magma, Cs becomes enriched in the residual melt, from which the fluid eventually exsolves. The data show a systematic distribution of Cs abundances among the various deposits (Fig. 1).

Au-rich deposits have the lowest Cs values and thus are associated with the most primitive magmas, whereas Mo enrichment is associated with somewhat more evolved and Sn-W with the most evolved source magmas, as reflected in high Cs values. The metal ratios in porphyry-type ore deposits are therefore linked to the timing of fluid exsolution relative to the degree of fractionation and crystallisation, which depends on external parameters, such as depth of magma emplacement and cooling rates. In most cases considered in this comparison the magma exsolved fluids in the single-phase field. These fluids preferentially have low- to moderate bulk salinities (2-15 wt% NaCl equiv.) in most of the cases, which seems to be ideal in order to achieve high V/B mass ratios upon later phase separation.

3 FLUID PHASE SEPARATION

Three types of fluids are commonly observed in porphyry type ore deposits: i) a moderate salinity (2 - 15 wt% NaCl equiv.) aqueous fluid of intermediate density (ID), often trapped in the single-phase fluid stability field; ii) a high-salinity (35 - >50 wt% NaCl equiv.) aqueous liquid (“brine” – B); and iii) a low-salinity (< 5 wt% NaCl equiv.) vapour (“vapour” – V). The earliest fluids in many porphyry-type ore deposits are represented by ID-type fluids, which commonly form coexisting B and V fluids upon phase separation. Brine inclusions of all deposits included in this study define a certain range in composition, which is clearly separated from the range defined by (coexisting) V fluids; ID-type fluids plot on an intermediate position between B and V (Fig. 2) consistent with the interpretation that ID is the parental fluid of B and V. The vapour is strongly enriched in Cu and to a minor extent in Au (Fig. 3), Ag, Sn and As, whereas Mo (Fig. 2), W, Pb and Zn do not preferentially partition.

At the bulk composition of the precursor fluid, i.e. the fluid exsolved from the magma, mass ratios between brine and relatively much more mobile vapour are commonly in favour of the vapour phase. Phase separation therefore controls the spatial distribution of metals in the deposit volume with Cu and Au being pervasively distributed by vapour fluids and Mo be-
ing more locally restricted to major fluid pathways and “brine pools”.

Figure 3. Copper versus Gold abundances in ore forming fluids (grey circles – ID; black squares – B; white triangles – V) from various porphyry-type ore deposits.

4 MINERAL PRECIPITATION

Recent case studies of the magmatic-hydrothermal evolution of porphyry-type ore deposits have identified a strong temperature dependence for Cu and Mo deposition (e.g.: Landtwing et al. 2005; Klemm, 2006). Comparing metal ratios from ore grades with metal ratios from fluid inclusions it is remarkable that the Au/Cu ratios in the ore-forming fluids and the bulk ore of the respective deposits generally plot within uncertainty on a 1:1 line (Fig. 4) indicating that Cu and Au precipitate together. Nevertheless, most Au/Cu ratio average values of the fluids tend to lie below the 1:1 line, possibly indicating that the porphyry ore contains less Au than was originally present in the ore forming fluid. Some of the Au may have been lost from the porphyry mineralization to an epithermal environment or it may have been dispersed in the adjacent volume of rock or even vented to the Earth’s surface.

In contrast, the behaviour of Mo in porphyry-type ore deposits seems to be often decoupled from that of Cu and Au. This is implied by the discrepancies between Mo content of fluids and ore. In most cases the fluids are Mo deficient with respect to the ore. This suggests that it precipitated from a different fluid or at a different time. In the case of Climax-type Mo deposits the discrepancy in the fluid is caused by the deficiency of Cu in the ore.

Precipitation mechanisms are selective and therefore responsible for the further decoupling of Cu from Au and from Mo in many cases. Furthermore, remobilisation seems to be a common process in the porphyry environment and might not only be a local feature, which may disturb the initial ore metal ratios.

5 CONCLUSIONS

There is not a single “key” process that controls Cu-Mo-Au ratios in porphyry-type ore deposits. The distinct provinciality observed among porphyry-type ore deposits is most probably caused by the concurrence of many parameters and finally an effect of environmental parameters (e.g. depth and pressure and temperature of fluids and ambient rock units) that control the timing of fluid exsolution, the occurrence of phase separation in space and time, and the efficiency of mineral precipitation and remobilisation.

ACKNOWLEDGEMENTS

ETH Zurich is thanked for funding of the PhD scholarship to the first author. Rio Tinto Iron Ore Atlantic Ltd. gratefully provided financial support for this presentation.
REFERENCES


The Surduc pluton (Upper Cretaceous), Romania: significance for Banatite magmatism

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ABSTRACT: The Surduc pluton, deviates from the standard calc-alkaline composition of Upper Cretaceous Banatite suites of southeastern Europe and represents part of high-K calc-alkaline series with gabbro to syeno-diorite/quartz-diorite, and syenite segregations. No significant geochemical distinction was found between Surduc 1 (S1) and Surduc 2 (S2) types arguing for a similar parental magma. Two high precision U-Pb ages of zircons from (S2) intrusion are at 79.04 ± 0.22 Ma and 78.74 ± 0.31 Ma representing the time of intrusion. 40Ar/39Ar biotite ages are 79 Ma for (S1) and 72.5 ± 0.4 Ma for (S2) representing cooling through ca. 300°C. Sr-Pb-Nd isotope geochemistry supports a regime of a mixed crustal-mantle provenance for the magma, which most probably was derived by processes as magma mingling and mixing not solely due to one magma source. We interpret the Surduc intrusion to have originated either in a post-collisional setting or from a metasomatized lithosphere above a subduction zone.

KEYWORDS: subduction, mantle metasomatism, geochemistry, Sr–Pb-Nd isotopes, U-Pb zircon geochronology, post-collisional granitoids

1 INTRODUCTION

The Alpine-Carpathian-Balkan orogen formed during two major periods of orogenic events related to continental plate collisions, namely early-late Cretaceous and Eocene-Early Miocene (e.g., Csontos & Vörös 2004). Among associated magmatic belts, the so-called Banatite belt (von Cotta 1864) of Late Cretaceous age is particularly important as this belt comprises a high proportion of calc-alkaline rocks, which are often interpreted to represent subduction-related magmatic successions (e.g., Berza et al. 1998; Ciobanu et al. 2002; von Quadt et al. 2005). The L-shaped Banatite belt extends N–S from North Apuseni Mts. through Banat and changes its direction to E–W in the Srednogorie zone of Bulgaria. Russo-Sandulescu et al. (1986a, b) described calc-alkaline and alkaline plutonic rocks including rare syenite segregations from the Surduc Massif of the Banat region (Fig. 1), which is, therefore, critical for evaluation of genetic model of the Banatite belt.

We selected the Surduc pluton for detailed investigations because of (1) missing modern data and (2) the assumed Paleocene age of parts of the suite (S2), and its more alkaline character as reported in the literature. Emphasis is placed on the magma source and the geodynamic setting they have intruded. We present new major trace element analyses along with Sr, Nd, Pb
isotopic data and U-Pb zircon and $^{40}$Ar/$^{39}$Ar mineral ages and focus on distinction between one of the proposed models to explain the geodynamic setting of magma emplacement of the Surduc suite as significant part of the Banatite belt.

2 GEOLOGY OF SURDUC MASSIVE

The Surduc massive is exposed in the westernmost part of South Carpathians (Fig. 1). According to gravity and magnetic anomalies, the body extends ca. 12km in E–W direction, in the west entirely covered by Neogene sedimentary rocks. In the east, the plutonic body intruded low-grade metamorphic phylilitic basement rocks of the Lower Cretaceous Supragetic nappe, which represents the uppermost nappe of the South Carpathian nappe complex (Iancu et al. 2005). Russo-Sandulescu et al. (1986a, b) described two distinct intrusions in the exposed eastern part, (1) (S1) of late Cretaceous age and (2) (S2) of Palaeocene age.

3 GEOCHEMISTRY

In the geochemical classification given by Cox et al. (1979), all samples from Surduc plot in the fields of gabbro, gabbro-diorite, syenodiorite and quartz-diorite, similar to the previous data set of Russo-Sandulescu et al. (1986). The diagram displays the subalkaline nature of these rocks. In that total alkali vs. silica (TAS) diagram (Na$_2$O+K$_2$O) vs. SiO$_2$ diagram), (S1) samples cover a trend between gabbro and syenodiorite, in detail, sample 109A plots in the gabbro field.

![Figure 2. Classification of Surduc magmatic rock on the (Na$_2$O + K$_2$O) vs. SiO$_2$ plot (after Cox et al. 1979).](image)

Figure 2. Classification of Surduc magmatic rock on the (Na$_2$O + K$_2$O) vs. SiO$_2$ plot (after Cox et al. 1979).

The initial age-corrected Sr isotope ratios of the Surduc pluton range between 0.7047 and 0.70493 at Cretaceous time and are similar to previous published initial Sr isotope data from other plutons of the Banatite belt (Berza et al. 1998; Dupont et al. 2002; von Quadt et al. 2005). The calculated $\varepsilon_{Nd}$ values are between -1.0 and -7.7. These data indicates a mixed mantle-crust source of the Upper Cretaceous magmatism of Surduc. Concerning the magma evolution, it may be largely due to mingling and mixing processes accompanied with differentiation and assimilation of crustal fragments. The magma not necessarily derived only from one magma source as underlined by the isotope signature, particularly by $\varepsilon_{Nd}$ values.

In the $^{206}$Pb/$^{204}$Pb vs. $^{207}$Pb/$^{204}$Pb diagram (Fig. 3) the samples indicate moderate distinction, except sample 107 showing a very low $^{207}$Pb/$^{204}$Pb ratio. Since the $^{207}$Pb/$^{204}$Pb ratio can be an indication of crustal contamination or existence of an old-lead component we can estimate that sample 107 is the least “contami-
nated" sample of a mantle origin, whereas the rest of the samples are likely contaminated by an old crustal source consistent with trace element modelling. The samples have distinct ε- Nd(t) values, whereas the Sr_i content is rather similar amongst the samples. All samples plot in the negative ε- Nd(t) field, remarkable is sample 106A with a very low ε- Nd(t) value.

Figure 3. a) 206Pb/204Pb vs. 207Pb/204Pb whole rock plot for the samples of the (S1) and (S2) intrusions; b) ε- Nd(t) vs. Sr_i isotope plot: all whole rock samples exhibit negative Nd values.

5 U-PB ZIRCON AND 40Ar/39Ar DATING

Zircons were separated from two samples of S2 magmatic units. Zircons from sample 106A, define a concordant age at 79.04 ± 0.22 Ma (Fig. 4a). Sample 21 of the S2 intrusion plots on the concordia within their uncertainties and define a mean 206 Pb/238U age of 78.74 ± 0.31 Ma (Fig. 4b). We conclude that these concordant grains indicate the time of intrusion. Within the analytical error both samples 21 and 106A are equal in time, although sample 21 seems to be a little older. The ages show that the (S2) pluton formed within the same time range as several others well dated plutons in Banat und Bulgaria (von Quadt et al., 2005).

A biotite concentrate from sample 107 (S1) displays only a slight disturbed age pattern with a plateau age of 79.4 ± 0.6 Ma, coinciding within error limits with the U-Pb zircon age of (S2). Biotite from the quartz-diorite sample 21 of the S2 intrusion yielded an undisturbed plateau age of 72.5 ± 0.4 Ma. We explain both 40Ar/39Ar ages as geologically significant, representing cooling ages through the appropriate 40Ar/39Ar retention temperature of biotite (ca. 300 °C).

Figure 4. U–Pb concordia diagrams for zircons of sample 106a (a) and sample 21 (b) from the (S2) magmatic intrusion.

6 DISCUSSION

The new U-Pb zircon ages are the first high-precision ages for the Romanian Banatites. They clearly show Campanian intrusion age of 79 Ma for two different rock types of the (S2) pluton. Field and petrographic observations suggest that gabbric and dioritic rocks assigned by Russo-Sandulescu et al. (1986a) to (S1) are older than the main monzogranite/ granodiorite (S2)-suite for which a Palaeocene age was suggested. The 40Ar/39Ar biotite age of 79 Ma of (S1) is close to the age of the (S2) intrusion and can be interpreted as the age of reheating during intrusion of (S2).

The age of 79 Ma for (S2), much older than previously suggested, corresponds to a number of plutons of the western, younger alignment of Banat and eastern Serbia, comprising ca. 90% of all plutons in the Banat region. Their ages range between ca. 84 and 72 Ma (Ciobanu et al.)
Trace element modelling and isotopic data suggests various melt components including 10–15% partial mantle melt and some contamination by subducted sediment or a similar composed crustal source. Available isotopic data from the Panagyurishte region in Bulgaria reveals a similar mantle source. However, the geochemical data clearly suggest consanguinity of nearly all rocks, so that all rocks can be derived from similar parental magmas. Trace element and some isotopic data also show the contamination with crustal material (from subducted sediments or from lower crust).

A number of possible models have been called for the Banatite magmatism, which could explain the high-K calc-alkaline trend: (1) influence of a mantle plume to a subduction zone; (2) metasomatic influence in a fore-arc environment; (3) rift-related magmatism; and (4) slab break-off magmatism. We exclude the rift model because of geological reasons. There are also some palaeo-geographic arguments against continuous subduction zone at ca. 80–78 Ma. The main argument is that there is no convincing argument for an open oceanic seaway during that time, for which the Vardar ocean is often called. If the Vardar ocean extends into the well exposed Mures ophiolite, as generally assumed, then there is no evidence for an open ocean. The Mures ophiolite was obducted before late Cretaceous, and the Banatite belt crossing the Mures ophiolite is convincing evidence against an open Mures-Vardar ocean.

This suggests that rather post-collisional slab delamination or slab break-off could be responsible for the western alignment of the Banatite belt, consistent with our geochemical data. Slab break-off, of a possibly metasomatized mantle, could have resulted in this sort of magma as we found for Surduc. Another reason is that ca. at that time, beginning of Campanian, a sharp subsidence occurred in collapse-type basins, which is explained to result from increased extension due to increased unloading of the subducted lithosphere, similar as postulated for the slab break-off model in general. The timing of extension is the same as postulated for a pulse of upward motion of lower plate units within metamorphic core complexes of the South Carpathians.

A slow cooling, similarly as reported from Bocsa, can be postulated for (S2). The U-Pb zircon and \(^{40}Ar/^{39}Ar\) biotite ages suggest that cooling started at ca. 79 Ma (≥ 750°C) and went through 300°C at ca. 72.5 Ma. Consequently, a cooling rate of ca. 70°C/Ma can be calculated for the (S2) pluton.

ACKNOWLEDGEMENTS

We acknowledge a grant no. P15, 464-GEO of FWF to FN.

REFERENCES


NAMS METALLOGENY

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A Conceptual Magmatic Model for the Genesis of Brunswick-Type VHMS Deposits, Bathurst Mining Camp, Canada

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ABSTRACT: The metals in Brunswick-type, volcanic-hosted, massive sulphide deposits were largely derived from felsic magma that 1) formed by partial melting of lower continental crust; 2) ponded at mid-crustal depths (15-25km) as reduced, “cold-granite” magma (750-800°C and < 6 wt% H₂O); 3) evolved a compositionally zoned, large-volume chamber (by convective fractionation) with a crystal-poor, supersaturated upper part and a crystal-rich (20 – 30%), relatively dry, dominant-volume lower part, including an immiscible liquid-sulphide phase; 4) erupted explosively from mid-crustal depth producing first-phase felsic volcanism; and 5) generated small-volume, upper-crustal (<5 km depth) reservoirs of dominant-volume magma, which underwent decompression melting of phenocryst phases. The upper-crustal magma experienced renewed convection, a rise in oxygen fugacity and separation of sulphur as metal-rich volatile phases, which fed the ore-forming hydrothermal system. Most critically, this magma had to cool in situ without pyroclastic eruption.

KEYWORDS: VHMS deposits, Bathurst, magmatic source, decompression melting

1 TECTONIC SETTING

Middle Ordovician, volcanic-sediment-hosted, massive sulphide (VHMS) deposits of the Bathurst Mining Camp (BMC) formed during the early stages of development of the Tetagouche – Exploits back-arc basin, which was situated on the Ganderian (peri-Gondwanan) continental margin of the northern Appalachians (van Staal et al. 2003). This basin formed behind an ensialic arc analogous to the present day Sea of Japan. The basin closed during the late Ordovician to early Silurian by subduction beneath the arc creating the “Brunswick subduction complex” (van Staal 1994). The rocks were further deformed during the late Silurian Salinic and early to Middle Devonian Acadian orogenies (de Roo & van Staal 1994) creating the present-day geometry of the BMC.

2 CAMP GEOLOGY

In the BMC, the turbidites beneath the volcanic pile are assigned to the Miramichi Group and overlying volcanic and sedimentary rocks are assigned to the Bathurst Supergroup (van Staal et al. 2003). The latter comprises felsic to mafic volcanic and sedimentary rocks of the Fournier, California Lake, Tetagouche and Sheephouse Brook groups, in order of highest to lowest structural level. The latter three groups are more or less coeval and were juxtaposed by thrusting and internally imbricated into thrust nappes during their successive incorporation into the Brunswick subduction complex (van Staal, 1994).

Only the Tetagouche Group is considered here. It comprises the Nepisiguit Falls, Flat Landing Brook, Little River and Tomogonops formations, in ascending stratigraphic order. Specifically, the Nepisiguit Falls Formation, predominantly a felsic volcanic unit, is of interest because it hosts half of the 46 known deposits in the BMC. It is described below:

2.1 Nepisiguit Falls (NF) Formation

At the type locality on Nepisiguit River, this formation is exposed intermittently for approximately 800m and has been described in detail by MacDonald (2001). The lower part, about 200m, comprises coarse-grained, massive quartz-feldspar phryic (porphyry) rock, and the upper part, about 600m, comprises fine- to coarse-grained, quartz-feldspar-rich volcanioclas-
tific rocks (crystal tuffs) that are interlayered with aphyric tuff.

The quartz-feldspar porphyry contains less than 30% phenocrysts (K-feldspar + plagioclase + quartz ± biotite) in a vitreous, cryptocrystalline groundmass, and lacks evidence of reworking. The large crystal size (up to 15mm) is typical of dominant-volume, late-erupted magma rather than crystal-poor, early-erupted magma. The virtual absence of magmatically broken crystals indicates that the emplacement mechanism was non-explosive, but the aspect ratio and lack of carapace breccias and hyaloclastites are atypical of subaqueous lava flows. The genesis of "Bathurst porphyry" has been debated since the 1950s but most recently Downey (2005) has interpreted it as a megacrystic tufflava.

Crystal tuffs that conformably overlie the quartz-feldspar porphyry generally become finer grained and thinner bedded up-section (McCutcheon et al. 2005). They contain abundant (> 30%), commonly broken (slivers), quartz and feldspar (mostly < 5mm) in a very fine-grained granular matrix. They exhibit primary features such as crystal sorting and graded bedding, which are typical of mass flow deposition. These crystal tuffs formed from deep-water, pyroclastic eruptions (cf. MacDonald 2001; Downey & Lentz 2006), which were deposited as cold debris flows after eruption column collapse.

At the top of the section, chloritic and locally magnetic mudstone (silicate iron formation) is intercalated with dark greenish grey, fine grained volcaniclastic rocks. This mudstone/exhalite occupies the same stratigraphic position as exclusively in the nearby Austin Brook and Brunswick 6 deposits (the so called "Brunswick Horizon"). This mudstone is in direct contact with massive rhyolite of the overlying Flat Landing Brook Formation (second-cycle volcanism, e. 465 Ma), indicating that exhalative activity either occurred during the waning stages of first-cycle volcanism or after it was finished.

On Tetagouche River the NF Formation is less than 30m thick. The lower part, about 16m, comprises thin- to thick-bedded, fine- to medium-grained (mostly <1mm), tuffaceous sandstone, locally with pseudomorphed pumice clasts, and the upper part, over 8m, is mainly composed of coarse-grained (mostly >1 mm), tuffaceous sandstone. The fine-grained rocks generally contain less than 30% phenocrysts, whereas the coarse-grained rocks contain over 50% phenocrysts (quartz and feldspar). Quartz-feldspar porphyry is conspicuously absent. This section represents the distal facies of the NF Formation and the one on Nepisiguit River represents the proximal facies. U-Pb zircon dating (Sullivan & van Staal 1996) confirms that these two facies are coeval (c. 470 Ma).

Elsewhere, the NF Formation exhibits lateral variations in thickness and proportions of rock types. For example, a drainage trench east of the Brunswick six open pit exposes a section, about 140m thick, from the depositional contact with sedimentary rocks of the Knights Brook Formation (Miramichi Group) up to and including the massive sulphides (McCutcheon et al. 2005). The entire section comprises fine- to coarse-grained crystal tuffs (no massive porphyry), which show increasing alteration toward the massive-sulphide contact. At the base, crystals are small (mostly <1mm) and sparse (<10%). However, up-section crystals increase both in size and abundance, which is typical of pyroclastic eruptions from large, compositionally zoned magma chambers (McCutcheon et al. 1997). Downey (2005) recognized three lithofacies associations in the NF Formation, as follows: 1) primary pyroclastic, 2) resedimented syn-eruptive, and 3) epiclastic and chemical sedimentary. Downey noted that massive sulphide deposits are spatially associated with megacrystic tufflava (quartz-feldspar porphyry) of the primary pyroclastic lithofacies.

2.2 Massive Sulphide Deposits

The NF Formation hosts 23 massive sulphide deposits, nine with over one million tonnes (Mt) of ore metals including the giant Brunswick 12 deposit, which to the end of 2006 had produced 116.91 Mt grading 3.48% Pb, 8.84% Zn, 0.36% Cu and 102.5 g/t Ag. This deposit is also anomalous in As, Au, In, Sb and Sn as are several others in the BMC (Goodfellow & McCutcheon 2003). At least 12 deposits have an Algoma-type, oxide-iron formation that caps and/or extends laterally beyond the sulphides. Most deposits are zoned vertically and laterally from a high-T, vent-proximal, brecciated-sulphide core to a low-T, vent-distal, bedded exhalite. Many have a well-developed stringer zone and associated hydrothermal alteration zones in the adjacent country rocks.

2.3 Granitic Intrusions

Deformed Ordovician granitic plutons intrude Miramichi Group rocks but rarely cut the overlying felsic volcanic pile (Whalen et al.
1998; McNicoll et al. 2003). These granitic rocks are metaluminous to weakly peraluminous and have Y/TiO₂ versus Zr/TiO₂ ratios that closely resemble felsic volcanic rocks of the NF and Spruce Lake (California Lake Group) formations. Furthermore, U-Pb zircon ages indicate that these intrusions are more or less coeval with the felsic volcanic pile (McNicoll et al. 2003). Gradations to high-level porphyries and the presence of granophyric and aplitic textures in some intrusions indicate a high level of emplacement (Whalen et al. 1998). Ages from xenocrystic zircons combined with neodymium and oxygen isotopic data indicate that these granites were derived by partial melting of Neoproterozoic lower crust of Gondwanan affinity (McNicoll et al. 2003).

3 CONCEPTUAL MODEL

Brunswick-type VHMS deposits require deposition of vast amounts of metal and a magmatic source is inferred for at least some of it (Goodfellow & Mccutcheon 2003). Any magmatic model must be consistent with field observations and other known constraints as outlined below.

1. It is well known that large felsic magma chambers in terrestrial settings have compositional zonation, as evidenced by their pyroclastic eruptive products (Smith 1979). This zonation develops by convective fractionation (Rice 1981), a process that obtains up to about 40% crystallinity in felsic magma. This process can produce a chamber with a high-silica, crystal-poor, volatile- and incompatible-element-rich upper part and a crystal-rich, volatile-poor, dominant-volume lower part.

2. Pyroclastic eruptions are largely driven by the proportion (wt %) and density (molar volume) of the magmatic fluid phase (Lentz et al. 1999), and they can occur from chambers as much as 25km below surface (Stormer & Whitney 1985). In subaqueous settings, water depth is not a limiting factor to pyroclastic eruptions but it influences the eruptive products (Downey & Lentz 2006).

3. Calderas form in response to pyroclastic eruptions from relatively shallow magma chambers (< 5km) that are fed by magma from mid-crustal depths (Stormer & Whitney 1985); large calderas commonly have distinctive intracaldera and exocaldera facies (Lipman 1984). Such facies have not been documented in the BMC.

4. The NF Formation and coeval Ordovician granites contain abundant xenocrystic zircons (Sullivan & van Staal 1996; McNicoll et al. 2003, respectively) suggesting that the parent magma was approximately 750-800 °C (“cold granite” of Miller et al. 2003) and contained < 6 wt% H₂O at mid-crustal depths (cf. Holtz et al. 2001).

5. Brown biotite inclusions in quartz phenocrysts (observed personally) of the NF tufflava indicate that the oxygen fugacity of the magma was at least one log unit above the Ni-NiO (NNO) buffer (cf. Carmichael 1991). This is about at the redox boundary of dissolved sulphur species, S²⁻ and SO₄²⁻ (Carroll & Rutherford 1988) indicating that the magma could have contained a liquid sulphide phase.

6. The size and abundance of phenocrysts in the NF tufflava indicate that it formed from a dominant-volume magma, which was emplaced late in the eruptive cycle. The coarsening upward section east of the Brunswick 6 pit is compatible with this interpretation.

7. The sulphide deposits formed after or during the waning stages of NF volcanism. A two-chamber magmatic model is hypothesized to explain the observations and constraints listed above:

1. Felsic magma was derived by lower crustal melting (probably associated with mica dehydration) and ascended to mid-crustal depths (15-25 km) where it ponded in a large-volume chamber as reduced (sulphur saturated), “cold-granite” (cf. Miller et al. 2003) magma, i.e. initially at 750-800 °C with < 6 wt% H₂O.

2. Slow cooling by convective fractionation produced a compositionally zoned chamber with a crystal-poor, wet, upper part, including a supercritical fluid phase, and a crystal-rich, relatively dry, dominant-volume, lower part, including an immiscible liquid-sulphide phase.

3. Eventually, Pfluid exceeded Plithostatic in this mid-crustal chamber and a pyroclastic eruption occurred, dewatering the magma and depositing the crystal-poor NF volcaniclastic rocks. As the eruption progressed, crystal-rich, dominant-volume magma became involved, and the eruption ended with vent-proximal, largely intrusive emplacement, of tufflava into the early-formed volcaniclastic deposits.
apron.
4. Once the eruption stopped, the relatively dry, dominant-volume magma (with its immiscible liquid-sulphide phase) began to pond in a small-volume, upper-crustal chamber (<5km depth), where decompression melting of phenocryst phases occurred and convective fractionation was renewed.
5. A rise in oxygen fugacity occurred during cooling of this upper-crustal magma, probably due to ingress of water, and sulphur separated as metal-rich volatile phases, which accumulated in the upper part of the chamber and fed the ore-forming hydrothermal system.
6. Most critically, this upper-crustal magma had to have relatively small volume to allow for in situ cooling without pyroclastic eruption; otherwise, the volatiles would have been lost and a caldera complex would have formed.

ACKNOWLEDGEMENTS

Thanks to Dave Lentz for his constructive comments on an earlier version of this abstract.

REFERENCES

MacDonald CAK (2001) Stratigraphy, volcanology and environments of the Ordovician Nepisiguit Falls Formation, Bathurst Camp, New Brunswick. MSc thesis, Laurentian University, Sudbury, 118p
Stormer JC, Whitney JA (1985) Two feldspar and iron-titanium oxide equilibria in silicic magmas and the depth of origin of large volume ash-flow tuffs, American Mineralogist 70: 62-64
van Staal CR (1994) Brunswick subduction complex in the Canadian Appalachians: record of the Late Ordovician to Late Silurian collision between Laurentia and the Gander margin of Avalon. Tectonics 13: 946-962

"Digging Deeper" C.J. Andrew et al (editors)
Spatial and temporal distribution of gold mineralization in the New Brunswick segment of the Northern Appalachians, eastern Canada

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ABSTRACT: The complexity of New Brunswick’s tectonic history related to Appalachian orogenesis is exemplified by the variety of mineral deposit types that occur throughout the province. Gold mineralization occurs within auriferous volcanogenic massive sulphide (VMS), intrusion-related, orogenic, auriferous porphyry copper, epithermal (high sulphidation), and palaeoplacer deposits, each of which contain differing quantities of gold. The genesis of these deposit types can be attributed to the various stages of orogenesis and/or plutonic activity. Although current gold production in the province is restricted to that produced as a by-product from the Brunswick No. 12 Zn-Pb-Cu-Ag VMS deposit, increased understanding of previously known occurrences/deposits combined with current economic conditions may facilitate commercial gold production from other deposit types in the near future.

KEYWORDS: gold, orogenesis, Appalachians, New Brunswick

1 INTRODUCTION

The New Brunswick segment of the Northern Appalachian Orogen comprises four northeast-trending tectonic zones including (from northwest to southeast) the Humber, Gander, Dunnage, and Avalon zones (Fig. 1). These zones were juxtaposed by several accretionary events during Lower and Middle Palaeozoic time, thus producing the present day collage of geological environments hosting a number of gold deposits/occurrences. The syngenetic and epigenetic gold mineralization comprises several deposit types that include volcanogenic massive sulfide (VMS), intrusion-related, orogenic, gold-bearing porphyry copper, epithermal, and palaeoplacer deposits, which can be linked to various stages of orogenesis that occurred between Precambrian and Carboniferous times. With the exception of the VMS and palaeoplacer types, the majority of the deposits/occurrences are closely associated with structural features along and near tectonostratigraphic zone boundaries and/or felsic intrusions. These settings continue to be the main focus of gold exploration in the province.

Currently, the only producing deposit type is the VMS class, from which gold is extracted as a by-product commodity. However, there are several potentially economically viable gold deposits in the province, which may be significant in years to come.

2 STYLES AND DISTRIBUTION OF GOLD MINERALIZATION

Features of several known gold occurrences in the province suggest potential for other deposit types (i.e., iron-oxide-copper-gold, skarn, Carlin-type); however, more comprehensive investigations of these is necessary in order to confirm their deposit classification. The various recognized types of gold deposits and their temporal and spatial distribution throughout the province are described here in more detail.

2.1 Auriferous VMS

Numerous auriferous VMS deposits formed in a back-arc setting during the Middle Ordovician within the Bathurst Mining Camp (Fig. 1). Examples of these include the Caribou deposit, which has relatively high gold grades (average of 1.72 g/t Au; Goodfellow & McCutcheon,
2003), and the Brunswick No. 12 mine, in which massive sulphides contain an average gold grade of 0.67 g/t Au (Martin et al., 2006). Gold-rich gossan zones overlying the Caribou, Heath Steele, and Murray Brook VMS deposits (Fig. 1) were past gold producers.

2.2 Intrusion-Related

Direct genetic relationships between felsic intrusions and gold mineralization have been established for a number of gold deposits/occurrences in southwestern New Brunswick (see Thorne & McLeod, 2003). Examples include those at Lake George, Poplar Mountain, and Clarence Stream, that are associated with Devonian, post-orogenic I-type granitoids. More detailed investigations of occurrences/deposits discovered prior to the emergence of this relatively new class of deposits may add to the list of this deposit type.

The best examples of this deposit type are the Clarence Stream gold deposits that are directly related to intrusions of Early Devonian granite, based on field, geochronological, and isotopic constraints (Thorne, 2005 and references therein). In general, these deposits are characterized by the presence of steeply dipping Au-As-Sb-Bi-bearing fault-fill quartz veins hosted by Silurian biotitized metagabbro and metasediments (proximal deposits; Main Zone) and Au-Sb mineralized stockwork veinng associated with shallow thrusting in sericitized Ordovician metasedimentary host rocks (distal deposits; Anomaly A, Watters et al., 2003). These deposits may be enter commercial production in the near future.

2.3 Orogenic

Various examples of orogenic gold systems occur throughout the province, and are hosted by rocks ranging in age from Ordovician to Carboniferous. For the most part, these types of deposits are associated with major brittle-ductile shear zones where gold is hosted by
quartz ± carbonate veins or disseminated within the host rocks.

In the northern part of the province within the Dunnage Zone, several meso- to epithermal orogenic gold occurrences/deposits lie within an accretionary wedge where extensive back-thrusting has occurred during Early Silurian exhumation of Ordovician rocks. These include the Elmtree and Guitard Brook deposits that are hosted within the Ordovician ophiolitic rocks, and the Middle River deposit (Fig. 1) located within Ordovician volcano-sedimentary sequences. Alteration associated with the Au-As mineralization predominantly consists of chloritization, silicification, and carbonatization (Vetter et al., 2006).

Characteristics of the gold occurrences hosted by the Ordovician volcano-sedimentary rocks of the Annidale Belt (Gander Zone) in south-central New Brunswick (Fig. 1) are consistent with mesothermal orogenic type deposits. Mineralization is generally associated with quartz-carbonate veins along shear zones with varying proportions of sulphides (pyrite ± arsenopyrite ± chalcopyrite ± stibnite). Alteration minerals generally consist of chlorite ± sericite ± fuchsite, depending on the protolith of the host rock. Disseminated mineralization is also common peripheral to structural features, particularly in gabbroic or mafic volcanic host rocks. The timing and relationship of gold mineralization to local felsic intrusions in this area is being investigated.

Immediately south of the Annidale Belt along a terrane-bounding fault between the Gander and Avalon zones, is the Devil Pike Brook deposit that is hosted within a Silurian volcano-sedimentary sequence. Gold associated with pyrite and chalcopyrite is hosted within an en echelon array of northerly-trending quartz veins that occur within mafic volcanic rocks. Drilling of this deposit has revealed three main mineralized zones (Baxter, 16, and Boyd) with assays in excess of >200 g/t Au over 0.5m (Fosters Resources, 1995). The exact timing of the mineralization has yet to be constrained.

The youngest example of an orogenic gold deposit in the province is the former Cape Spencer Mine (Fig. 1), where gold is hosted along shallow thrusts within deformed Neoproterozoic granitoids of the Avalon Zone and Carboniferous sedimentary rocks. These thrusts and associated northwesterly directed folding, are interpreted to be linked to the docking of the Meguma Zone along the southeastern margin of the Avalon Zone. Gold is associated with pyrite in illitic altered host rocks with variable quantities of specularite, chalcopyrite, and ankerite. Watters (1993) established an early Permian age for the mineralizing event.

2.4 Auriferous Porphyry Copper

Two examples of porphyry copper gold deposits in the province occur within the Gander Zone: Connell Mountain, associated with the early Ordovician granodiorite (the largest known deposit of this type in the province), and the Evandale occurrence, associated with an early Devonian granodiorite. Although it is low-grade, there is gold (up to 1.5 g/t Au; Thomas & Gleeson, 1988) associated with chalcopyrite, pyrrhotite and minor amounts of molybdenite and sphalerite at Connell Mountain.

Mineralization at the Evandale occurrence consists mainly of chalcopyrite and minor molybdenite associated with narrow quartz veinlets, as well as in fractured and altered (chloritic and haematitic) granite. Drilling at the deposit intersected a high grade interval that yielded ~15 g/t Au over 0.5m (Dome, 1980).

2.5 Epithermal (High Sulphidation)

Although there are several important high sulphidation epithermal style mineral deposits hosted by similar rocks in Newfoundland, the only known mineralization of this type demonstrated within the Avalon Zone in New Brunswick is the Chambers Settlement occurrence. Here, intensely silicified Neoproterozoic felsic volcanic rocks contain sericite, kaolinite, pyrophyllite, and/or topaz alteration assemblages, but only minor gold. Exploration peripheral to this occurrence is still in the preliminary stages.

2.6 Palaeoplacer

At this time, occurrences of palaeoplacer gold are of little economic significance and are restricted to Carboniferous rocks of southeastern New Brunswick; however, their existence indicates the presence of significant lode gold deposits in the surrounding orogenic belts from which they were derived. One example of this deposit type is the Aboujagane occurrence where historic records indicate that a drill intersection of 6.9 g/t Au over 1.8m was obtained by Dome (1964). A grab sample of sandstone from that same area yielded up to 11.5 g/t Au (Johnson & McLeod, 1998).
3 CONCLUSIONS

Gold mineralization in New Brunswick is not restricted to any specific deposit type, geologic environment, or orogenic event. The majority of the deposits are associated with major structures and/or felsic intrusions. The recent increase in gold exploration in the province has led to the discovery of several new occurrences, further research into new and more comprehensive genetic models, and a better understanding of the mineralizing systems. Development of more comprehensive genetic models is key to successfully exploring for additional resources at known deposits and for the discovery of new economically viable deposits. Given the increased price of gold, escalating exploration activity, and broadened knowledge base of deposit characteristics, the potential for additional economically viable deposits and future gold production is good.

ACKNOWLEDGEMENTS

This publication represents a compilation of documented data collected by several researchers and exploration companies. Thanks to Terry Leonard for preparing the figure.

REFERENCES

Dome Exploration (Canada) Ltd. (1964) Diamond Drill Logs of Norsac Minerals property. NB Dept. of Natural Resources Assessment File 470661.


ABSTRACT: In the Gaspé Peninsula of the Canadian Appalachians, gold occurrences and base metal skarns are spatially associated with the Devonian (Acadian) dextral strike-slip Grand Pabos-Restigouche fault system. Base metal skarns, as well as the Saint-André-de-Ristigouche gold prospect, are enclosed in large halos of argillie hydrothermal alteration. Authigenic illite of the kaolinite clay mineral assemblage was dated at ca. 220 and 130 Ma using K-Ar methods. This suggests that hydrothermal fluid migrations still occurred in the plumbing system of the Grand Pabos-Restigouche fault system during the late Triassic and early Cretaceous at the onset of the Atlantic Ocean opening, 200 to 300 Ma after the Devonian Acadian dextral-slip faulting.

KEYWORDS: K-Ar, clay material, base metal skarns, Mesozoic, Canadian Appalachians

INTRODUCTION

Different styles of gold mineralization and base metal skarns are spatially associated with major faults in the southern Gaspé Peninsula of the Canadian Appalachians (Fig. 1; Malo et al. 2000). Herein, we present new K-Ar ages of alteration clay material in argillie alteration halos around Cu-skarns in the southwestern Gaspé Peninsula (Fig. 2), which also includes the Saint-André-de-Ristigouche (SAR) gold prospect.

1 GEOLOGIC AND METALLOGENIC SETTING OF BASE METAL SKARNS

The Canadian Appalachians consist of Palaeozoic rocks in the Gaspé Peninsula, mainly sedimentary with minor volcanics, which are divided into three temporal rock assemblages (Fig. 1): 1) Cambrian to late Ordovician, 2) late Ordovician to Middle Devonian of the Gaspé Belt, and 3) Carboniferous. The first rock assemblage was affected by both the late Ordovician Taconian and Middle Devonian Acadian orogenies, whereas the second was mainly deformed by the Acadian Orogeny.

The base-metal skarns are hosted by the uppermost Ordovician-lowermost Silurian limestones of the Gaspé Belt (White Head Formation). Felsic dikes and sills of granitic to granodioritic composition are close to the prospects (Fig. 1). The emplacement of the felsic dikes and sills appears to have been structurally controlled since they are perpendicular and parallel to the regional structural trend, but some of the sills, however, predate regional deformation because they are folded. The most common alteration facies in the base-metal skarns is marble hornfels. The calciulite is converted into marble whereas argillaceous limestone and calcareous mudstone are converted into fine-grained calc-silicate hornfels. A metasomatic skarn including garnet, vesuvianite, calcite,
quartz, K-feldspar, phlogopite, and pyroxene also occurs with the marble-hornfels. Secondary clay mineral assemblages that form alteration halos have been delineated around several prospects (see below). Base-metal sulphides are most commonly disseminated and stratabound in different types of limestones and numerous prospects contain mineralized veins. The SAR gold prospect of Carlin-type affinity (Garnier et al. in press) is spatially associated with Cu-skarns in southwestern Gaspé (Fig. 2). It consists of structurally-controlled quartz-stibnite veins hosted by silicified calcilutite of the White Head Formation along the Restigouche fault.

2 ANALYTICAL METHODS

2.1 Clay mineralogy

Clay mineral concentrates were obtained by abrasion of rock fragments in demineralized water. The clay suspension was decarbonated in 1 N HNO₃ under constant agitation. The insoluble clay residue was then separated by centrifugation into < 0.2, 0.2-5 and 5-15 µm size fractions. X-ray diffraction analysis was performed on oriented mounts obtained by sedimentation of clay suspensions onto glass slides and dried at room temperature. Most samples were re-analysed following saturation with glycerol. The composition of illite and chlorite was evaluated by comparing the intensity ratios of their 002/001 and 004/003 reflections. A scanning electron-microscope was used to observe the habitats of the clay material in the host rocks.

2.2 K-Ar geochronology

The separated size fractions were dated by the K-Ar method with an overall accuracy better than ±2%. Some analytical errors are beyond this uncertainty because of the very small K₂O contents. The Ar isotopic results were controlled by periodic measurement of the international GLO-glauconite standard, the ⁴⁰Ar/³⁶Ar ratio of the atmospheric Ar, and the ⁴⁰Ar content of the blank residues of the mass-spectrometer and the extraction line.

3 HYDROTHERMAL CLAY MINERAL ASSEMBLAGE

X-ray diffraction analyses of insoluble residues from White Head limestones show that the mineral assemblages vary according to their distance from the faults or mineralized show-
ings (Fig. 2). In addition to the unaltered clay assemblage, five alteration assemblages are defined by a mineral index or by abnormal proportions of illite or chlorite. The content of feldspar is variable and does not show any relationship with the other minerals or with the location of the sample.

The unaltered assemblage comprises illite, chlorite, quartz, and seldom Na-feldspar and/or K-feldspar. The illite to chlorite ratio is around 70:30 and both are well crystallized. The illite index indicates anchimetamorphic conditions (Kübler 1966). In the five alteration assemblages, the illite index is similar to that of the normal assemblage.

The illite assemblage contains mainly illite with some quartz and sometimes traces of feldspar, chlorite and mixed-layered illite/smectite. In the kaolinite assemblage, kaolinite is accompanied by illite, quartz, and traces of feldspar. Only two occurrences of chlorite were observed. The smectite assemblage contains illite as the major mineral with smectite and minor chlorite, quartz and feldspar. Presence of both kaolinite and smectite characterizes the kaolinite+smectite assemblage, where illite is always present with quartz and traces of feldspar. In the chlorite assemblage, chlorite is more abundant than illite. No other phyllosilicate was usually identified; quartz and rare feldspar are occasionally detected.

The alteration assemblages form zoned halos surrounding two skarns (Fig. 2), which are first surrounded by a chlorite zone, then successively by a smectite, a kaolinite+smectite, a kaolinite and an illite zone. The larger halo is truncated by the Restigouche fault (Fig. 2). The SAR gold prospect is found within the kaolinite assemblage, very close to the kaolinite-smectite assemblage.

4 K-Ar AGES OF THE CLAY MINERAL ASSEMBLAGES

In this preliminary study, we have analysed four samples. SA03-17 was collected in the silicified host limestone close to the SAR mineralized vein. SA03-17B is located in the kaolinite assemblage about 5m away from the mineralized vein. The two other samples were collected in the illite (SA03-15) and normal (SA03-01) assemblages, respectively (Fig. 2). The K-Ar ages were obtained on the three size fractions, 5-15, 0.2-5 and <0.2 µm (Table 1; only two fractions for SA03-17B). The K-Ar ages of the three fractions of the normal assemblage vary between ca. 431 and 447 Ma (SA03-01, Table 1), which is close to the biostratigraphic age of the White Head Formation (Ashgillian to Llandoverian, 449 to 428 Ma). In the illite and kaolinite assemblages, the K-Ar ages of the 5-15 and 0.2-5 µm size fractions are still Palaeozoic, but the finest <0.2 µm fractions are much younger with Mesozoic values (SA03-15, SA03-17 and SA03-17B, Table 1). The K-Ar ages of the 5-15 and 0.2-5 µm size fractions vary from ca. 437 to 396 Ma, which is from early Silurian (Llandoverian) to early Devonian (Émsian). The K-Ar ages of the <0.2 µm size fraction is Late Triassic in the illite (ca. 211 Ma, SA03-15, Table 1) and kaolinite (ca. 222 Ma, SA03-17B, Table 1) assemblages, and Early Cretaceous (ca. 130 Ma, SA03-17, Table 1) close to the mineralized vein.

5 DISCUSSION

Spatial relationship of the alteration clay assemblages with the Cu-skarns, as well as with the Restigouche fault (Fig. 2), suggests a genetic link between alteration, mineralization, and faulting. Regionally, there is a genetic link between the base-metal skarns and the Devonian dyke swarms (Fig. 1), and fluid inclusion data from mineralized skarns indicate that high-temperature (450ºC) and high-salinity (36 wt% eq. NaCl) magmatic fluids were involved in their genesis (Malo et al. 2000). At the SAR gold prospect, the hydrothermal fluids are not of magmatic origin being cooler, less saline and

Figure 2. Geology and alteration zoning around the SAR gold prospect (Au), X sample locality

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mixed with evolved meteoric water (Garnier et al. in press). The chlorite assemblage is very closely associated with skarns and was probably formed by reaction of the wall rocks with magmatic fluids that produced the skarns. The presence of kaolinite and smectite indicates that no significant heating occurred afterwards, and that the fluids were alkali-depleted, so that they most probably formed after the skarns and chlorite, and anchi- to epimetamorphism. These relationships indicate that the clay alteration assemblages resulted from post-Devonian hydrothermal fluid flows unrelated to Devonian igneous activity.

Back-scattered images of limestones show very fine-grained authigenic illite that crystallized on larger illite particles. The authigenic illite of the <0.2 µm size fraction yields younger ages (Table 1). Sample SA03-01 did not record the hydrothermal fluid flows and its K-Ar ages of ca. 431–447 Ma are interpreted to date maximum burial, which is compatible with the late Ordovician-early Silurian age of the White Head Formation. The K-Ar ages of ca. 396–437 Ma for the 5-15 and 0.2-5 µm size fractions of other samples are interpreted to date maximum burial (Acadian metamorphism), and/or late Silurian-early Devonian fluid flows along the Restigouche fault. The K-Ar ages of ca. 211–222 Ma for the <0.2 µm size fraction in the illite and kaolinite assemblages might relate to late Triassic fluid flows along the Restigouche fault and are contemporaneous with the formation of Triassic-Jurassic grabens along the east coast of Canada further south. The youngest age of 130 Ma from the sample within the silicified/mineralized limestone is contemporaneous with rifting of the North Atlantic during early Cretaceous.

6 CONCLUSION

This is the first time that a Mesozoic geological event (fluid flows and formation of authigenic clay associated with argillie alteration) has been reported in the Gaspé Appalachians. This suggests that hydrothermal fluid migrations occurred in the plumbing system of the Grand Pabos-Restigouche fault system during the late Triassic and early Cretaceous at the onset of Atlantic Ocean opening. These fluids were not responsible for base metal mineralization, but might have been partly responsible for alteration of the host-rocks and also for the late gold mineralization at SAR. However, the relationship between the K-Ar ages and the SAR gold mineralization remains unclear and has to be established.

REFERENCES

Garnier V, Malo M, Dubé B, Chagnon A, Beaudoin G, Carlin-type gold mineralization at Saint-André-de-Ristigouche, Gaspé Peninsula (Québec), Canadian Appalachians. Mineralium Deposita (in press)


Table 1. K-Ar ages

<table>
<thead>
<tr>
<th>Sample/Clay assemblage</th>
<th>Size fraction</th>
<th>K2O (%)</th>
<th>Age (Ma ± 2σ)</th>
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<tbody>
<tr>
<td>SAO3-01 / normal</td>
<td>&lt;0.2 µm</td>
<td>0.20</td>
<td>431 (82)</td>
</tr>
<tr>
<td></td>
<td>0.2-5 µm</td>
<td>5.77</td>
<td>443 (11)</td>
</tr>
<tr>
<td></td>
<td>5-15 µm</td>
<td>3.03</td>
<td>447 (13)</td>
</tr>
<tr>
<td>SAO3-15 / illite</td>
<td>&lt;0.2 µm</td>
<td>0.44</td>
<td>211 (51)</td>
</tr>
<tr>
<td></td>
<td>0.2-5 µm</td>
<td>5.19</td>
<td>416 (12)</td>
</tr>
<tr>
<td></td>
<td>5-15 µm</td>
<td>4.36</td>
<td>403 (13)</td>
</tr>
<tr>
<td>SAO3-17 / kaolinite +</td>
<td>&lt;0.2 µm</td>
<td>0.41</td>
<td>130 (28)</td>
</tr>
<tr>
<td></td>
<td>0.2-5 µm</td>
<td>5.74</td>
<td>396 (9)</td>
</tr>
<tr>
<td></td>
<td>5-15 µm</td>
<td>3.94</td>
<td>437 (12)</td>
</tr>
<tr>
<td>SAO3-17B / kaolinite</td>
<td>&lt;0.2 µm</td>
<td>0.38</td>
<td>222 (18)</td>
</tr>
<tr>
<td></td>
<td>0.2-5 µm</td>
<td>5.47</td>
<td>426 (10)</td>
</tr>
</tbody>
</table>
Volcanogenic Massive Sulphide (VMS) Deposits of the Newfoundland Appalachians, Canada: An Overview of their Setting, Classification, Grade-Tonnage Data, and Unresolved Questions

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ABSTRACT: The Newfoundland Appalachians is host to >40 volcanogenic massive sulphide (VMS) deposits with geological tonnages >100,000 tonnes and together an aggregate tonnage of ~112 million tonnes (geological resource) with production and reserves of ~46 million tonnes. Deposits are hosted predominantly by Cambrian-Ordovician volcanic arc, arc rift, and back-arc basin assemblages within the Dunnage zone. Deposits are of three classes: 1) mafic type – Cu(Zn)-rich deposits hosted by ophiolitic rocks (e.g., York Harbour, deposits in the Lushs Bight Group); 2) bimodal mafic type - Cu-Zn-rich deposits hosted by bimodal sequences dominated by felsic rocks (e.g., deposits of the Rambler camp); and 3) bimodal felsic types – Zn-Pb-Cu-rich deposits hosted by bimodal sequences dominated by felsic volcanic rocks (e.g., deposits of the Buchans camp). Some bimodal mafic and mafic type VMS deposits are enriched in precious metals (e.g., Rambler, Ming, Handcamp). Although the Newfoundland Appalachians has experienced significant exploration and VMS deposit research, numerous questions remain unanswered and provide the fuel for many years of research and future exploration.

KEYWORDS: Volcanogenic Massive Sulphide, Newfoundland, Appalachians, Dunnage Zone

1 INTRODUCTION

Volcanogenic massive sulphide (VMS) deposits have been important contributors to the economic development of Canada and the province of Newfoundland. In Newfoundland, numerous VMS deposits have been past producers (e.g., Tilt Cove, Rambler, the Buchans deposits) with some deposits currently in production (e.g., Duck Pond) or with potential to go into production in the near future (e.g., Ming). In this abstract an overview of regional geological setting of these deposits, their classification, relevant grade-tonnage data, and unresolved research questions are presented.

2 GEOLOGICAL SETTING

The Appalachian orogen in Newfoundland is divided into tectonostratigraphic zones based on lithology, age, faunal attributes, geophysical signatures, and metallogeny (Fig. 1; Williams 1979; Williams et al. 1988; van Staal in press). The zones include from west to east (from Williams 1979; Williams et al. 1988; van Staal in...
press) (Fig.1): 1) the Humber zone, which represents the ancient, Neoproterozoic to Ordovician, predominantly sedimentary rocks of the ancient Laurentian margin; 2) the Dunnage zone, which represents a series of Cambrian to Ordovician arcs and back-arc basin assemblages.

The Dunnage zone is further subdivided into subzones: the Notre Dame subzone and the Exploits subzone (Williams et al. 1988). The Notre Dame subzone represents arc and back-arc related rocks with peri-Laurentian affinities (van Staal in press; Waldron and van Staal 2001; Williams et al. 1988), whereas the Exploits subzone consists of arc and back-arc related rocks with peri-Gondwanan affinities (O’Brien et al. 1997; van Staal in press; Williams et al. 1988); 3) the Gander zone, which represents Cambrian-Ordovician sedimentary rocks sourced from the Gondwanan margin; and 4) the Avalon zone, which represents Neoproterozoic arc sequences and Cambrian-Ordovician sedimentary rocks with Gondwanan affinities.

3 DEPOSIT CLASSIFICATIONS AND GRADE-TONNAGE DATA

The Newfoundland Appalachians have over 40 VMS deposits with >100,000 tonnes of massive sulphide (geological resource, not NI43-101 compliant; data from Galley et al. in press). Most, if not all, of these deposits are hosted by rocks of the Dunnage zone or its obducted, ophiolitic equivalents in the Humber zone (Fig. 1).

The deposits of the Appalachians have been classified by previous workers based primarily on their tectonic setting and lithologies (e.g., Evans & Kean 2002; Swinden 1991). The deposits, however, have not been classified until recently (e.g., Galley et al. in press) using modern classifications for VMS deposits (Franklin et al. 2005; Galley et al. in press). Under modern classification schemes the VMS deposits of the Newfoundland Appalachians can be classified into three groups (Fig. 1): 1) mafic type - deposits hosted primarily by mafic rocks of ophiolitic affinity (~ Cyprus-type deposits; e.g., York Harbour, Skidder, deposits of the Lushs Bight Group and Betts Cove ophiolite); 2) bimodal mafic – deposits hosted in bimodal sequences of mafic and felsic rocks but with mafic rocks in much greater abundance than felsic rocks (e.g., deposits of the Rambler Camp and those of the Wild Bight Group); and 3) bimodal felsic – deposits hosted by bimodal sequences dominated by felsic volcanic rocks and lesser mafic rocks (e.g., deposits of the Buchans Camp and Victoria Lake Supergroup).

The aggregate tonnage of all VMS deposits in the Newfoundland Appalachians is ~112 million tonnes (geological resource) (Fig. 2) with total tonnes in reserves and produced roughly 46 million tonnes (results calculated from the database of Galley et al. in press). Shown on Figure 2 are plots of tonnage versus aggregate base metal grade and Au content for the VMS deposits of Newfoundland. This diagram illustrates that aggregate base metal grades are highest in the bimodal felsic-type deposits, but this is partly skewed by data from the Buchans camp, which are some of the highest grade deposits in Canada and globally (Fig. 2). The bimodal felsic deposits are also enriched in Pb and Zn relative to the other deposit classes (Fig. 2).
3). The bimodal mafic and mafic deposits, however, have elevated Cu grades relative to the bimodal felsic systems, as expected (Fig. 3). Gold grades are elevated in some of the VMS deposits in the Newfoundland Appalachians, particularly those of the Rambler Camp (Figs. 1-3; Ming is likely underestimated given new drilling results at this deposit – e.g., Rambler Metals and Mining PLC press release Sept. 8, 2006). Gold grades appear to be highest in the deposits of the bimodal mafic and mafic classes; however, appreciable gold was produced from the Buchans orebodies (Thurlow & Swanson 1981; Neary 1981).

Figure 3. Pb-Zn-Cu (A) and base metal-Au-Ag (B) ternary plots for VMS deposits of the Newfoundland Appalachians. Diagram (B) after Hannington et al. (1999).

4 UNRESOLVED QUESTIONS

Abundant research has been undertaken on VMS deposits of the Newfoundland Appalachians, both historically and recently (Swinden 1991; Evans & Kean 2002; Moore 2003; Squires & Moore 2004). In light of our knowledge of VMS deposits and camps globally, however, a number of unresolved questions exist regarding the setting and genesis of VMS deposits in the Newfoundland Appalachians, including: 1) what are metal inventories, in particular trace metals, in Newfoundland VMS;

2) what is the cause of Au-enrichment in the Rambler camp deposits?

3) classifications of deposits are at a sedimentary level and have to be refined (e.g., Victoria Lake Supergroup deposits have a lot of shales and sedimentary rocks – are they really bimodal felsic or are they siliciclastic felsic?); 4) morphologies (e.g., tabular, pipe-like, mounds) and deposit emplacement mechanisms (e.g., exhalative, sub-seafloor replacement, transported) are only known for a few VMS deposits (e.g., Buchans); 5) are there hybrid-type VMS systems in the Newfoundland Appalachians – e.g., VMS-SEDEX hybrids like Bathurst and Wolverine or VMS-epithermal hybrids like Eskay Creek; 6) regional- to local-scale alteration systems are poorly understood and require detailed mapping and associated work to outline regional (semi-conformable) and proximal (e.g., pipe-like) alteration systems; 7) volcanic, intrusion, and sedimentary facies reconstructions only exist for a few deposits (e.g., Buchans) – reconstructions are required to test what the facies controls on deposit formation are at both the regional and deposit scale; 8) the role of subvolcanic intrusions and intrusive complexes in generating heat for hydrothermal circulation and metal contributions to hydrothermal systems are virtually unknown; 9) lithogeochemistry – much is known about mafic volcanic geochemistry (Swinden 1991) but very little has been done on felsic volcanism and its role in VMS deposit generation and localization; and 10) the role of non-traditional lithogeochemical techniques in finding mineralization (e.g., exhalites, shale geochemistry) has not been tried and its potential as exploration vectors is unknown.

These questions require multi-disciplinary approaches grounded in field geology with contributions from industry, government, and academia. By answering these questions significant insight will be gained into the setting and genesis of VMS deposits of the Newfoundland Appalachians. These insights may help in the discover a new generation of VMS deposits within the Newfoundland Appalachians, and provide insights into the genesis and exploration for similar deposits in other accretory orogens.

ACKNOWLEDGEMENTS

This abstract is based on the work of many others who have laid the framework by doing outstanding work on VMS deposits in New-
foundland, these people deserve special thanks and include: Dave Evans, Baxter Kean, Scott Swinden, and Lawrence Winter. I extend special thanks to the following individuals for discussions regarding Newfoundland VMS deposits: Terry Brace, Roland Butler, John Hinchey, Andy Kerr, Paul Moore, Peter Tallman, Geoff Thurlow, Dick Wardle, Lawrence Winter, Mark Wilson, and Derek Wilton. Steve Piercey’s research is funding by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada (NSERC).

REFERENCES


The regional metallogenic context of Voisey’s Bay: An overview of magmatic Ni-Cu-Co mineralization across Labrador, Canada

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ABSTRACT: The Voisey’s Bay discovery of 1994 led to unprecedented exploration activity in Labrador, and the discovery of diverse magmatic sulphide mineralization. The most promising examples, including Voisey’s Bay itself, are associated with relatively primitive, generally olivine-bearing, mafic plutonic suites of Mesoproterozoic age. In addition to parental magma composition, country-rock contamination (± sulphide addition) appears to be an important genetic control, and dynamic, multistage magmatic environments (e.g., conduit systems) may be crucial for the development of economic deposits. Magmatic sulphides also occur in Mesoproterozoic pyroxenites, anorthosites, and iron-rich intermediate rocks, but for the most part these appear inherently limited in grade, extent and continuity. However, many mafic plutonic suites of Mesoproterozoic age outside a 150 km radius of Voisey’s Bay have received little or no exploration scrutiny, and may have potential for further discoveries. Much remains to be learnt about this rugged and prospective region.

KEYWORDS: Magmatic Sulphides, Labrador, Nickel, Voisey’s Bay, Exploration

1. INTRODUCTION

In late 1993, Albert Chislett and Chris Verbiski discovered nickel-rich sulphide mineralization near Nain, Labrador. In 1994, an intersection grading 2.96% Ni, 1.89% Cu and 0.16% Co over 41 m started the Voisey’s Bay story. Twelve years later, Voisey’s Bay is a producing deposit, with a total resource of at least 100 million tonnes at 1.9% Ni, 1% Cu and 0.11% Co (2003 figures). Unprecedented exploration activity in Labrador and associated Survey research has greatly improved the geological database, although much remains to be learned.

This paper is directed towards the geologic and metallogenic framework of Labrador and the Voisey’s Bay deposits. It outlines the diversity of magmatic mineralization in Labrador, explores potential controls, and highlights potential host suites that remain unexplored.

Ni-Cu (± PGE) sulphide deposits in Labrador are associated with rocks of ultramafic and mafic composition, including Archaean komatiites and Mesoproterozoic plutonic suites (Figure 1). The emphasis of this paper is towards the latter, which contain most of the known mineralization, and are seen as having the highest potential for additional discoveries.

2. REGIONAL GEOLOGY

Labrador (Figure 1) contains sections of the Superior and North Atlantic Archaean cratons, separated by a wide tract of Palaeoproterozoic rocks assigned to the Churchill Province. These are bounded to the south by Palaeoproterozoic and Mesoproterozoic orogenic belts of the Makkovik and Grenville Provinces. Palaeoproterozoic mafic intrusive rocks are most abundant in metasedimentary terranes within the Grenville Province. Mesoproterozoic plutonic suites (1.45 to 1.27 Ga) are abundant in the Churchill and Nain provinces, and transgress major tectonic boundaries (Figure 1). These are composite batholiths dominated by anorthosites and granites, with lesser mafic and intermediate components. The Nain Plutonic Suite (NPS) is considered to be the type example (Ryan, 1998); others include the Harp Lake Intrusion (HLI) and Michikamau Intrusion (MI). Smaller mafic intrusions are abundant in the northern fringe of the Grenville Province and adjacent older terranes, but are mostly not shown at the scale of Figure 1. They include the 1.45 to 1.42
Ga Shabogamo gabbro (SG) and Michael gabbro (MG) suites, mafic sills associated with the 1.27 Ga Seal Lake Group (SLG), and several dyke swarms. Widespread Mesoproterozoic magmatism across Labrador is traditionally viewed in terms of attempted rifting in response to mantle plume activity (e.g., Ryan, 1998).

3. THE VOISEY’S BAY DEPOSITS

Ni-Cu-Co deposits at Voisey’s Bay are associated with the troctolitic Voisey’s Bay Intrusion, an early (1.33 Ga) member of the 1.35 to 1.27 Ga NPS (Figure 1). The intrusion is partly hosted by older paragneisses that locally contain disseminated sulphides and graphite. The intrusion consists of two larger bodies, interpreted as magma chambers, linked by a dyke-like body interpreted as a conduit system, which is generally steeply-dipping, but locally flat-lying. Significant sulphide deposits at Voisey’s Bay are located at the entry point of the conduit system into the postulated upper magma chamber, or are located within and around the conduit system itself (Li & Naldrett, 1999). The Eastern Deeps deposit exemplifies the former setting, whereas the original Discovery Hill deposit and the Reid Brook deposit represent the latter setting. The Ovoid deposit (the richest accumulation) may represent a widened zone in the conduit, or perhaps the intersection of a subvertical feeder with a larger chamber that has now been eroded. Clearly, special circumstances prevailed for 32 million tonnes of massive sulphide to accumulate in such a small area!

Sulphide mineralization in all zones is closely similar, consisting of pyrrhotite, pentlandite, chalcopyrite (+/- cubanite) and variable amounts of magnetite. “Ores” include coarse-grained massive sulphides, disseminated (interstitial) sulphides in troctolites, and complex breccias containing reacted gneiss fragments in sulphide-rich troctolite matrix. These unusual rocks, termed “basal breccia” or “feeder breccia” according to setting, are invariably associated with sulphide accumulations.

Ore grade is essentially a function of the amount of sulphides in a given rock. The sulphide metal contents are typically 3% to 5% Ni, and 1.5% to 2.5% Cu, such that massive sulphide zones contain about 4% Ni and 2% Cu. The immiscible sulphide liquids appear to have been concentrated and trapped in the conduit system, notably where it is widest. The liquids were also pooled where the magmas flowed into larger chambers, perhaps because the flow regimes changed from turbulent to stagnant. The various sulphide deposits likely represent different structural levels within a complex magmatic plumbing system (Li & Naldrett, 1999). Fortuitously, the feeder conduit system is preserved close to the present erosion level.

4. OTHER DEPOSITS ASSOCIATED WITH GABBROIC AND TROCTOLITIC ROCKS

The Pants Lake Intrusions of the NPS (Figure 1) have a setting similar to Voisey’s Bay, and their country rocks include sulphide-bearing paragneiss. The intrusions comprise several discrete sheet-like olivine-gabbro bodies, of at least two ages (~1337 and ~1322 Ma). Magmatic sulphides are widespread at the bases of these intrusions. The mineralization and associated rock types closely resemble those at Voisey’s Bay, and include identical breccias containing reacted paragneiss fragments (Kerr, 2003). Thin massive sulphide zones locally contain up to 11% Ni and 10% Cu, but most contain 1-2% Ni and 1-2% Cu. Sulphide metal contents are more varied than at Voisey’s Bay, but cluster around 2% Ni and 2% Cu; Ni/Cu ratios are typically ~1, versus Ni/Cu ~ 2 at Voisey’s Bay, and Co contents appear higher. Most of the mineralization is disseminated and therefore of low absolute grade, but the total amount of Ni metal at Pants Lake is probably about the same as at Voisey’s Bay. Pervasive metal depletion signatures in the gabbros indicate that even larger amounts of metal are missing (Kerr, 2003). The ~1312 Ma Mushuau Intrusion of the NPS, located near Voisey’s Bay, hosts minor magmatic sulphides near its basal contact. Thin zones contain ~1.4% Ni and 0.6% Cu, and the sulphide metal contents are about 3.5% Ni; reacted inclusions are also reported (Kerr & Ryan, 2000). Minor disseminated sulphides are also known in several other NPS mafic intrusions (Kerr & Ryan, 2000).

Outside the NPS, the ~1.45 Ga Michikamau Anorthosite Intrusion (MI) attracted some attention prior to 1994. Here, a basal layered sequence of olivine norite, troctolite and peridotite hosts disseminated sulphides. Mineralization locally contains up to 0.9% Ni, 0.3% Cu and 0.15% Co, but it is largely disseminated and low grade (<0.5% Ni + Cu). As at Voisey’s Bay and Pants Lake, digested and...
reacted country rock inclusions occur. In western Labrador, part of the ~1.45 Ga Shabogamo Gabbro suite hosts disseminated sulphide mineralization near Evening Lake (Figure 1), near the base of a sheet-like olivine-gabbro body. Sulphide metal contents are modest (~ 1% Ni and ~1% Cu), and absolute grades are low, but these intrusions commonly sit within sulphide-bearing sedimentary rocks, and have wider potential for higher-grade accumulations.

5. MINERALIZATION ASSOCIATED WITH PYROXENITES AND ANORTHOSITES

Disseminated sulphide mineralization occurs in and around irregular pyroxenitic veins and dykes associated with mafic intrusions of the NPS (Figure 1). This contains up to 2% Ni in local massive concentrations, and may be part of a spectrum including sulphide zones hosted by anorthosites (Kerr & Ryan, 2000). The latter are common in leuconorites and anorthosites of the NPS and HLI (Figure 1). Sulphides form irregular semi-massive zones hosted by otherwise barren anorthosites. Sulphide metal contents are variable, but most contain < 1% Ni, with little correlation between Ni and Cu. The sulphides show intrusive contacts with anorthosite, but are commonly spatially associated with gabbroronites containing disseminated sulphides. Kerr & Ryan (2000) suggested that sulphides formed in the mafic residual liquids from plagioclase flotation, and then migrated through partially solid, hot, anorthosite. Disseminated (syngenetic) sulphide zones are also present in HLI anorthosites, but are less obvious in the NPS.

6. MINERALIZATION ASSOCIATED WITH DIORITES AND FERRODIORITES

Disseminated sulphide mineralization occurs in iron-rich intermediate rocks of the NPS in several areas (Figure 1; Kerr & Ryan, 2000). The sulphides are commonly associated with magnetite. The absolute Ni+Cu grades and sulphide metal contents in these examples are invariably low, as are Ni/Cu ratios.

7. CONTROLS ON MINERALIZATION

Labrador illustrates controls familiar from other mafic sulphide districts (e.g., Naldrett, 1999). The more primitive, olivine-bearing suites appear most prospective, reflecting higher initial metal contents. These rocks are a minor component of the NPS, and there is no evidence for any direct link between economic mineralization and the dominant anorthosites. The digested, reacted country-rock fragments seen in the mineralized intrusions of the NPS and MI attest to the importance of contamination, and perhaps sulphide addition. At Voisey’s Bay, there is a spatial link to a magmatic conduit system, and a genetic link to the dynamic, multistage magmatic environment that it represents. Contrasting sulphide metal contents between Voisey’s Bay and Pants Lake may indicate that multistage upgrading processes were less efficient in the latter. The final resting places of sulphide liquids in both were likely controlled by both pre-existing structures and the fluid-dynamic behaviour of the ascending magmas. Analogous conduit systems have yet to be outlined at Pants Lake or elsewhere, and are likely to be small and elusive targets. Amongst other types, pyroxenite-hosted mineralization holds the most promise (Kerr & Ryan, 2000). Beyond a radius of 150km around Voisey’s Bay, many mafic plutonic suites have received only scant attention.

REFERENCES


Figure 1. A generalized geological map of Labrador, showing the most important instances of magmatic sulphide mineralization. Source: Geological Survey of Newfoundland and Labrador.
Greenstone belts in Greenland and related mineral occurrences – possible counterparts in North America and Fennoscandia

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ABSTRACT: The Precambrian geology of Greenland shows geological continuity with eastern Canada and with northern Europe. However, in contrast to its neighbours, Greenland remains under explored in terms of its mineral potential. Greenstone belts in Greenland occur in areas with Archaean and Palaeoproterozoic rocks, and are smaller in volume compared to similar belts in Canada and the Baltic shield. Laurentia and Baltica formed a single continental landmass during Proterozoic times following the amalgamation of Archaean continental nuclei between 1.90 and 1.80 Ga. This presentation will focus on possible similarities concerning crust evolution, style and type of mineralization between greenstone belts in Greenland and proposed counterparts in North America and Fennoscandia. The interest in the greenstone belts in Greenland has so far focussed on their gold rather than base metal potential.

KEYWORDS: Greenstone belts, mineral deposits, Greenland, correlation to Canada and Fennoscandia

1 GEOLOGICAL SETTING

Archaean cratonic fragments make up the Nain-North Atlantic and Karelian provinces of the eastern Canadian-, Greenland- and Baltic-shields (Figure 1). The major crust-forming event of the Archaean in Greenland took place at 3.8–3.7 Ga, 3.1–2.9 Ga and around 2.8 Ga. The Archaean block is surrounded by Palaeoproterozoic mobile belts that were the site of orogenic activity in the period 1.95–1.65 Ga. The Torngat, Rinkian-Nagssugtoqidian and the Lapland-Kola belts flank the western and northern margins of the craton in Labrador, Greenland and north Fennoscandia/northwest Russia, respectively. The composite Rinkian-Nagssugtoqidian belt is interpreted to have formed as a result from the upper plate collision of the North Atlantic Craton with the northern Rae craton (~1850 Ma). This collision carried a south-facing passive margin sedimentary sequence (Karrat Group) towards a south dipping subduction zone. The rocks in the belts are dominated by reworked Archaean orthogneisses incorporating juvenile, calc-alkaline Palaeoproterozoic plutonic magmatic complexes (Conelly et al., 2006; Gaál & Gorbatchev, 1987; Lahtinen et al. 2003; Nironen 1997; St-Onge et al. 2006; van Gool 2002).

In southern Greenland, the Ketilidian orogen is composed of juvenile and evolved crust during northward subduction of an oceanic plate under the Archaean craton. The Ketilidian Mobile Belt in Greenland is correlated with the Transscandinavian Igneous Belt of Scandina-vian that formed during the Svecofennian orogeny. The Makkovik province of Labrador represents the western part of the Svecofennian and Ketilidian orogens. The accretionary growth and extensive granitoid magmatism relate to the geological processes taking place at ~1.8 Ga. The terrains yield a juvenile crustal evolution confirmed by positive Nd isotopes and Pb isotope constraints. The geotectonic scenario that accounts for these observations is an Andean-type collision (Ahl et al., 1997; Culschaw et al., 2000; Garde et al., 2002; Kerr et al., 1997; McCaffrey et al., 2004).

2 MINERAL OCCURRENCE FORMATION

Greenland remains less explored in terms of its mineral potential; however, numerous mineral deposits are recorded in Greenland (Figure

![Figure 1: Summary geological map of North America, Greenland and Fennoscandia Shield, modified from Hoffman (1988) and St-Onge et al. (2006).](image)

2.1 Archaean

No mineable deposits have yet been recognised in the Archaean of Greenland, but there have been significant indications of precious- and base-metals, as well as iron ore in the craton. The Archaean basement hosts banded iron formation (BIF) in Greenland, Canada and the Fennoscandia Shield with the deposits ranging in age from Eoarchaean to Neoarchaean. The Archaean Ni-Cu bearing greenstone belts of the Fennoscandia associated with komatiitic magmatism are absent in Greenland. Gold-bearing greenstone belts are abundant in the Nunavut region (e.g., Baffin Island and western part of Nunavut), Greenland and Fennoscandia: the deposits are genetically related to Orogenic-type gold deposits.

2.2 Archaean - Palaeoproterozoic

An important lineament is the boundary between Archaean and Palaeoproterozoic areas that can be drawn from Lake Ladoga, across the Gulf of Bothnia, and continuing north of the Skellefteå District up to the Caledonian front. This boundary controls the most significant metallogenetic provinces of the Fennoscandia Shield (Gaál & Sundblad, 1990). The metallogenetic diversity along this lineament, e.g., Outokumpu area and Skellefteå district in Fennoscandia, is not duplicated in Greenland.

2.3 Palaeoproterozoic

The Torngat, Nagssugtoqidian and the Lapland – Kola belts are characterised by predominance of Archaean gneisses that were reworked along large subhorizontal crustal movements which, combined with high-pressure metamorphism, is consistent with formation during continent-continent collision. Supracrustal rocks seem to be of both Archaean and Palaeoproterozoic origin. Mineral occurrences of the type from the famous Palaeoproterozoic Pechenga area from the northern Fennoscandian shield are not recognised in Greenland. During this period the Nagssugtoqidian, Rinkian and Torngat orogeneses begins with rift-drift supracrustal sequences around the border to the North Atlantic Craton. Mineral occurrences comprise of VMS, SEDEX and MVT base-metals, orogenic-gold, and graphite deposits. During subduction and formation of calc-alkaline magmatism and volcaniclastic sediments minor occurrences of Fe-Ti-V, Cu-Ni-PGE and Au are known.

The Andean-type collision of the Ketilidian orogen gold occurrences are related to a NE-SW striking zone along the southern rim of the Julianehåb batholith and to regional deformation and metamorphism of the Ketilidian orogen. The Ketilidian/Makkovik orogens and Transscandinavian Igneous Belt are known for their gold, uranium, molybdenum and base metals. The Ketilidian orogen of south Greenland comprises the only active gold mine in Greenland (Nalunaq GoldMine). The northern rim of the Julianehåb batholith has Cu-Fe-Au occurrences similar to the deposit found in the Norrbotten Fe-Cu-Au province.

3 CONCLUSIONS

The best proposed geological correlations between Greenland and adjacent North Atlantic regions are the evolution of the Makkovik-Ketilidian Orogen and the Transscandinavian Igneous Belt. The are accretionary growth and extensive granitoid magmatism in these three areas occurred around 1.8 Ga.
The northern flank of the North Atlantic Craton comprises the trans-Atlantic Palaeoproterozoic collisional orogenic belt extending from west with the Tornqat orogen, the Nagssugtoqidian orogen and the Lapland–Kola belt in east on the northern Baltic Shield.

REFERENCES


Figure 2: Mineral occurrence map of Greenland.
An overview of gold mineralization in the Caledonides of Great Britain and Ireland: insights from placer gold geochemistry

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ABSTRACT: Placer gold occurs throughout most of the Caledonides of Great Britain and Ireland but the relatively small number of in situ occurrences has precluded assessment of the gold mineralization on a regional scale. Microchemical characterization of gold grains from sites worldwide using alloy compositions and opaque inclusion assemblages has identified generic signatures from different styles of mineralization, which have been compared to data describing 7552 gold grains from 198 sampling sites in the study area. Signatures of epithermal and intrusion-related gold have been identified in addition to widespread orogenic gold. This study shows how important information can be gained from studies of placer gold at an early stage in the exploration process.

KEYWORDS: Placer gold, Great Britain, Ireland, gold mineralization

1 INTRODUCTION

Gold mineralization is widespread in the Caledonides of Great Britain and Ireland and has been exploited historically from in situ occurrences in North Wales, and from placer localities Scotland and Ireland. The identification of many new placer gold localities during a proliferation of exploration activity in the 1980s also lead to the discovery of a few sites of in situ mineralization of economic potential. (see overview in Chapman et al., 2000a). However, the source mineralization of most placer localities, including the historically important sites in Leadhills and Sutherland (Scotland), and Wicklow (Ireland), remained undiscovered.

In order to study gold mineralization on a regional scale and to illuminate any important characteristics of the source mineralization contributing to then major placers, it was necessary to gain information from the placer gold grains themselves. The technique of ‘microchemical characterization’ developed by the British Geological Survey (BGS) was a major refinement to previous approaches (which considered only alloy compositions of gold grains) because it also included a systematic record of the opaque inclusion species, which in many cases were diagnostic for a particular mineralizing event (see discussion in Chapman et al., 2000a). The signature produced by combining these data has been shown to be indicative of the mineralogy of the source mineralization (Chapman et al., 2000a) and can be used to infer the nature of the placer source even if this remains undiscovered.
METHODS

Table 1 provides details of the sample locations and sample sets considered in this study. Sample sets from previous studies have been used together with some new data. The full experimental procedure for microchemical characterization is described in Chapman et al., (2000a). Briefly, the grains are mounted according to size, set in resin and sections revealed by polishing. Alloy compositions are determined by electron microprobe and mineral inclusions are identified by scanning electron microscopy.

Alloy compositions of different populations are compared in plots such as Figure 1. In a few cases, the Hg or Cu contents of the alloy may also contribute to the signature. The number of grains containing each opaque inclusion species is recorded and the assemblage is characterized according to the proportions which correspond to the various mineral classes. Figure 2 is an example of how these data may be represented graphically.

Table 1: sample localities and sample sets

<table>
<thead>
<tr>
<th>Sample set/Locality with reference</th>
<th>Component localities</th>
<th>Grains studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scotland</td>
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</tr>
<tr>
<td>1. Leadhills</td>
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</tr>
<tr>
<td>2. Glengaber/R. Tweed</td>
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<tr>
<td>3. Ochil Hills type 1</td>
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<tr>
<td>4. Ochil Hills type 2</td>
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<tr>
<td>5. Sutherland</td>
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<td>6. Eas Anie Vein</td>
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<td>8. Back Burn</td>
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<td>36. Deepford, Pembroke</td>
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Figure 2. Truncated triangular diagram showing compositional fields of inclusion assemblages. Sample numbers relate to Table 1: Fields 1 and 2: sample sets 1, 2, 6-15, 17-19, 21-26, 32-35. Field 3: sample set 3, Field 4: Orogenic gold from the Klondike, (Chapman & Mortensen 2007), Malaysia, and Australia (Chapman et al., 2002). Field 5: Epithermal and intrusion related gold from the Klondike, (Chapman & Mortensen, 2007), Equador, (Potter & Styles, 2003), Fiji, (Naden & Henney, 1995). Field 6: sample set 5.

3 MICROCHEMICAL SIGNATURE AND STYLE OF GOLD MINERALIZATION

Studies of lode and placer gold from various occurrences worldwide have permitted the correlation of styles of gold mineralization with Table 1 sample localities discussed in the text the microchemical signature, although it is recognised that the data base for epithermal and intrusion related gold is in the early stages of development. Nevertheless, some generic features of the different styles of mineralization are already clear. Orogenic gold from an individual mineralizing event normally exhibits a relatively narrow range of Ag (e.g., gold sam-

"Digging Deeper" C.J. Andrew et al (editors)
samples from veins, Figure 1), and Cu and Hg are usually negligible or absent. Gold derived from epithermal mineralization commonly exhibits a wider range of Ag contents and at some localities many grains contain elevated Hg. The compositional field of inclusions within orogenic gold is close to the S-As axis (Figure 2) whereas gold derived from the igneous–related mineralization styles exhibits a Te signature, often in association with Bi. The inclusion species found within epithermal gold are often polymetallic sulphides or sulphotellurides, which may exhibit exsolution textures, whereas those of orogenic gold comprise simple sulphides, and sulpharsenides sometimes with minor contributions from tellurides and sulphosalts.

4 INTERPRETATION OF SIGNATURES OF PLACER GOLD

Figure 1 shows the Ag ranges typical of populations of vein and placer gold from different styles of mineralization. Orogenic vein gold exhibits a limited Ag range although the signature of gold from Eas Anie suggests two different alloy types. Placer samples generally exhibit a higher range of Ag, reflecting variation in the alloy composition throughout the eroded mineralized system. Placer populations from Shortcleuch and the Glengaber Burn (Scotland) exhibit the two main Ag ranges found in gold from the Southern Uplands terrane, (Figure 3). The small Ag range of these two placer samples suggests that they are derived from a single, small, mineralizing event. The wide range of Ag contents of placer gold from localities in the central Ochil Hills (Scotland), is typified by the sample from the Water of May. Consideration of the alloy compositions, (variable Ag, elevated Hg) together with the stability fields of specific mineral inclusion species indicates a low-sulphidation epithermal source (Chapman et al., 2007).

The majority of sampling localities in Great Britain and Ireland are within the metasediments and turbidites of the Caledonides so it is unsurprising that the microchemical signature of most of these populations conforms to the orogenic style, (Figure 2). Deviation from this signature may correlate with information from other geological, mineralogical and geochemical sources, e.g., the Bi–Te signature at Curraghinalt, Northern Ireland (Earls et al., 1989), and a Mo signature in placer gold from Glen Lednock, (Scotland) the Afon Las (Wales) both of which are adjacent to porphyry mineralization (Chapman et al., 2000a,c). The similarity between signatures of Curraghinalt gold and the Cabry River placer (Figure 2) suggests that Curraghinalt style mineralization is also present in north Donegal. A pronounced Te-signature was also recorded from a vein sample from the Clogau Mine and a placer sample from the Afon Wen in the Dolgellau Gold Belt, (North Wales). Mason et al. (2002) characterized this mineralization as orogenic (‘lode gold’) and suggested that the source of the metals was the underlying volcanic formation, an association which may have influenced the resulting signature. A similar signature was obtained from two samples from south east Ireland, also close to igneous lithologies (Chapman et al., 2007), although these occurrences may also be associated with minor intrusions such as that at Balwoges, Donegal, Ireland (Chapman et al., 2000a). Placer gold from south Wales is mainly of the orogenic type, but the signature of the sample from Deepford (Figure 3), which also contained sulpho-tellurides, also suggests an igneous association.

The origins of the placer gold at Kildonan Burn, Sutherland have proved elusive despite
many attempts to identify the source. The gradients of the Ag curves from 34 sample sites in this area are shown in Figure 1. Only grains of rough morphology were analysed to emphasize local variation in the microchemical signature. The inclusion assemblage is dominated by pyrite, with a minor, but consistent Te component (Figure 2). Polymetallic Bi-sulphides were also observed, some exhibiting exsolution textures. On this evidence, a low-sulphidation epithermal source can be inferred, which is consistent with the discovery of epithermal feeders by Crummy et al. (1997) in the vicinity of other Devonian outliers.

5 LOCAL AND REGIONAL VARIATION

Locally distinct signatures (particularly of inclusions) may correlate to high abundance of placer gold within an auriferous region: e.g., As-bearing minerals in gold at the ‘Red Hole’- (the site of the 1795 gold rush) in Wicklow, Ireland (Chapman et al., 2007), Sb-bearing minerals in gold from Glengaber Burn, Scotland (Chapman et al., 2000b), the distinctive Bi-Te inclusion signature of gold from Borland Glen, Ochil Hills, Scotland (Chapman et al., 2005) and Bi-S inclusions near sites of placer workings at Kildonan, Scotland.

On a regional scale, Chapman et al., (2000a, 2007) reported the correlation of microchemical signature of orogenic gold with terrane, and noted increasing Ag content of alloys from the south to north within the Irish and Scottish Caledonides, although this trend is not evident in Wales. A summary of characteristics of gold mineralization studied is presented in Figure 3.

6 CONCLUSIONS

Most placer gold localities within the British and Irish Caledonides are derived from orogenic mineralization, but there is evidence for epithermal gold in Sutherland. Regionally atypical styles of mineralization may be recognized from the signatures of the placer gold, and evidence for an igneous association may be inferred where Te-bearing inclusions are observed. In many cases deviations from the regional placer signature correlate with increased abundance, facilitating identification of the most attractive exploration target. The approach provides an efficient method for assessing the nature of gold mineralization in areas of poor exposure.

ACKNOWLEDGEMENTS

I am indebted to various co-authors who have contributed to the studies reported here, particularly Dr Robert Leake. Dr Eric Condliffe and Robert Marshall provided expertise in analysis and sample preparation respectively. Many individuals helped with sample collection, and the National Museum of Ireland, The Ulster Museum and the British Association contributed to some field work costs.

REFERENCES


ABSTRACT: A wide variety of mineralization styles occur in England and Wales ranging from late Precambrian barite veins to Jurassic MVT-style lead/zinc (Figure 1). No metal mines are currently being worked. The most important deposits, in terms of metal production, have been the tin-copper fissure veins of south-west England. These are followed by the Lower Carboniferous carbonate-hosted lead-fluorite-barite-zinc veins of the Northern and Southern Pennines, North Wales and the Mendips. There are also a number of base and precious metal deposits and prospects which have been discovered in the past forty years, at least one of which may enter production in the near future.

KEYWORDS: England Wales mineralization prospects

1 INTRODUCTION

England and Wales have a long history of mineral production dating back to the Bronze Age. Copper, tin, lead and iron have been won from many thousands of small mines and numerous larger operations. More recently, the complex surface and mineral rights ownership position has been seen as a disincentive to modern mineral exploration. Nevertheless, company and Government exploration has found a number of prospective areas including two potentially economic deposits.

2 GEOLOGY

2.1 Precambrian

Only small areas of late Precambrian sedimentary and volcanic rocks occur in central and western England. A few barite veins have been worked in the Longmyndian sedimentary rocks of Shropshire.

2.2 Lower Palaeozoic

Lower Palaeozoic formations in Wales and the Lake District consist of basic to acid volcanic and volcaniclastic rocks with thick basinal greywacke turbidites and co-evol shelf sedimentary rocks. Mineral deposits formed during the Lower Palaeozoic include the Coed-y-Brenin porphyry copper deposit in Cambrian diorite, the Parys Mountain Zn-Cu-Pb volcanogenic massive sulphide deposit in Ordovician/Silurian volcanic and sedimentary rocks, stratabound iron and manganese deposits and widespread minor Cu-Pb-Zn volcanogenic vein mineralization in Snowdonia and the Lake District.

2.3 Caledonian orogeny

Closure of the Iapetus Ocean was complete by late Silurian to early Devonian times along the line of the Iapetus suture in northern England. The main effect in the Lake District and Isle of Man was the development of a pervasive slaty cleavage. The Caledonian orogeny is associated with a period of intense metalliferous mineralization. Granite-associated Cu, Au, Mo and W mineralization occurs in the Lake District. Sediment-hosted Pb-Zn+Cu+Ba vein mineralization occurs in central Wales, Shropshire, the Lake District, and the Isle of Man. Turbidite-hosted gold mineralization occurs in Wales and the Lake District.

2.4 Upper Palaeozoic

The Upper Palaeozoic Devonian to Permian successions were mainly deposited on a stable platform and consist predominantly of elastic and carbonate sedimentary rocks. Local extensional basins, such as those of Craven and Solway-Northumberland, developed in the early
Carboniferous. Widespread continued subsidence led to the deposition of thick deltaic mudstones and sandstones with associated workable coals in the late Carboniferous (Westphalian). These were followed in Permian times by red-beds containing thick evaporites.

In south-west England block and basin limestones and shales, basalts and turbidite deposits were laid down in an extensional basin developed at the western end of the Rhenohercynian zone. Shallow-water clastic sedimentary rocks were deposited in north Devon, which lay on the northern margin of the basin.

Contemporaneous mineralization includes salt, gypsum and potash deposits of Upper Permian age in northern England. Minor syn-sedimentary Zn-Pb mineralization occurs in the early Carboniferous of the Craven Basin and around the Devonian/Carboniferous boundary in south-west England. The Craven Basin mineralization shows some similarities to the important early Carboniferous Zn-Pb deposits in the Republic of Ireland, such as those at Navan. Disseminated and vein-style gold mineralization occurs close to the unconformity of Permian red-beds and associated alkaline basalt lavas with older rocks in south-west England.

2.5 Variscan orogeny

The Variscan orogeny from late Devonian to early Permian times was caused by a complex series of movements and collisions between Europe, Africa and North America. The main areas affected in Britain were the Variscides in southern England and South Wales. The orogeny caused deformation and tectonism and culminated in the emplacement of the high-heat-flow, Cornubian batholith which extends for 230 km from the Scilly Isles to Dartmoor. The batholith is exposed as a series of large bosses and minor cupolas with which the major Sn-Cu-W vein-style mineralization of south-west England is associated. More gentle folding and faulting occurs to the north of the Variscan front where Dinantian carbonates host major Pb-F-Ba mineralization in the Northern and Southern Pennine orefields, North Wales and the Mendip Hills. Replacement hematite deposits formed near the contact of Dinantian carbonates and overlying Triassic sandstones in the western Lake District and South Wales.

2.6 Post-Palaeozoic

Post-Palaeozoic formations consist mainly of shallow-water, marine clastic rocks and limestones devoid of significant mineralization. The principal exceptions are Permo-Triassic basins containing red-beds with thick evaporites and extensive Jurassic sedimentary ironstones in the English Midlands. Minor red-bed copper mineralization occurs in the Triassic rocks of the Cheshire Basin. The whole country, apart from the extreme south-west, was affected by Quaternary glaciation. This caused deep erosion in upland areas and left widespread superficial deposits of sands and gravels which are exploited in many areas.

3 TYPES OF MINERALIZATION

3.1 Mineralization associated with acid magmatism. Porphyry Cu (Au)

Hosted in Cambrian turbidites and diorite intrusives the Coed y Brenin deposit in North Wales has resources of about 200 Mt at 0.3% copper with minor gold. Several small Cu/Au breccia pipes occur in the same area (Rice, 1993).

3.2 Volcanogenic Massive Sulphide (VMS) mineralization

The Parys Mountain deposit is hosted in hydrothermally altered acid and basic volcanics and sediments of Ordovician and early Silurian age. Massive bedded sulphides and dissemi-
nated 'feeder' veins and stockwork mineralization occur over a zone 2 km long and up to 500 m wide. The property is currently being explored by Anglesey Mining plc. Current drill-indicated reserves are 4.8 Mt at 1.5% Cu, 3.0% Pb, 6.0% Zn, 57 g/t Ag and 0.4 g/t Au. Recent exploration has shown additional mineralization adjacent to the Morris Shaft which was sunk to 300m in 1990 (Tyler 2003).

3.3 Sedimentary Exhalative (Sedex) mineralization

Stratabound Pb-Zn-Ba mineralization occurs in Devonian and Carboniferous sedimentary and volcanic rocks at several sites in south-west England. A 1-2m thick black shale horizon in Devonian rocks with about 2% Pb-Zn occurs at Egloskerry near Launceston.

3.4 Mesothermal lode gold mineralization

The Dolgellau Gold Belt occurs within Middle and Upper Cambrian sediments with numerous intrusions of basic to intermediate volcanic rocks on the southern and eastern flanks of the Harlech Dome. Massive north-east trending mesothermal quartz veins up to several metres wide and several kilometres long contain small sporadic, high-grade deposits. At Clogau St. David's mine gold occurs in small, rich, steeply-dipping shoots associated with pyrite and pyrrhotite together with galena and bismuth tellurides. The veins are often auriferous where they cut graphic shales of the Clogau Formation but not where the host rocks consist of non-graphitic arenites (Shepherd & Bottrell, 1993).

3.5 Mineralization associated with Lower Palaeozoic greywackes

There are a number of Pb-Zn±Cu±Ba veins in Lower Palaeozoic sediments with oreshoots up to 10 m wide in places. The main producing areas were Central Wales, north-west Wales (Llanwrst), the Lake District, Shropshire and the Isle of Man. Mineralization shows a spatial association with underlying granites in the Lake District and the Isle of Man, and with volcanic rocks in North Wales and the Lake District, but in Central Wales there is no indication of magmatic involvement. The Central Wales mineralization occurred in two main episodes at 390 Ma and 360 Ma. (Fletcher et al. 1993). The earlier mineralization contains a complex, fine-grained series of Pb-Zn-Co-Ni sulphides, while the later episode is composed of open-space filling, coarse-grained, brecciated, simple Pb-Zn sulphides.

3.6 Upper Palaeozoic fissure veins associated with acid magmatism

In south-west England over 2.5 Mt of tin, 2 Mt of copper and substantial amounts of zinc, tungsten and arsenic has been produced from quartz-tourmaline veins associated with Variscan granites which intrude Devonian metasedimentary rocks – locally known as killas. There are several styles of mineralization including skarns, pegmatites, greisen veins, replacement deposits in calc-silicates, vein swarms, stockworks and pipes as well as the most important and ubiquitous mainly east-west striking fissure vein deposits. Later ‘cross-course’ mineralization was dominated by lead- and barite with minor uranium. Recently operating mines were South Crofty, which worked a fissure vein swarm, and Wheal Jane, which worked an unusual deposit of cassiterite in very fine-grained sulphides, with sphalerite and minor chalcopyrite. The Wheal Jane deposit occurred at the sheared contact of a shallow-dipping felsite dyke ‘elvan’ and killas. The granite-hosted Hemerdon sheeted-vein deposit near Plymouth contains around 42 Mt @ 0.2% tin/tungsten (Alderton, 1993).

3.7 Carbonate-hosted lead-zinc-fluorite-barite (copper) (iron) mineralization

Major Pb-Zn±F±Cu±Ba vein mineralization occurs in Lower Carboniferous limestones in the Northern and Southern Pennine Orefields, Halkyn-Minera in North Wales and the Mends (IXer & Vaughan, 1993). Fluorite is restricted to the Pennine orefields where it may be related to contemporaneous or later basic alkaline volcanism. Important replacement (flat) deposits were worked at some localities. Two copper-dominant deposits occur at Ecton in Staffordshire and Llandudno in North Wales. The major West Cumbrian haematite deposits are also hosted in Lower Carboniferous limestones where they are unconformably overlain by Triassic sandstones.

3.8 Sandstone-hosted red-bed mineralization

Several small deposits of sulphide and oxide copper mineralization occur in Upper Triassic sandstones in the Cheshire Basin, especially at Alderley Edge. These were formed by oxidising brines circulating in the basin (Plant et al. 1999).
3.9  *Unconformity-hosted gold mineralization*

Following the discovery of widespread gold grains with an unusual palladium-rich chemistry in south Devon, the source was traced to mineralization within Triassic sandstones in the Crediton Trough associated with alkaline Permian basalts (Leake *et al.* 1997).

4  **CONCLUSIONS**

Britain has a substantial base metal mining history spanning many centuries with total production of around 7 Mt lead, 2.5 Mt copper and 2.5 Mt of tin. However, despite some promising discoveries in the past 40 years, there are no operating base or precious-metal mines. The most promising and advanced prospect is the Parys Mountain VMS deposit in Anglesey.

**ACKNOWLEDGEMENTS**

Paul Lusty and Gus Gunn are thanked for valuable comments on the draft text.

**REFERENCES**


Mineralization related to orogenic magmatism in the British and Irish Caledonides: A review

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ABSTRACT: The British and Irish Caledonides contain a wide range of mineralization related to orogenic magmatism. The mineralization is linked to two tectonic settings beginning with ocean closure in the Ordovician and succeeded by a protracted oblique collision from the mid Silurian to early Devonian. Mineralizations include orthomagmatic Cu-Ni-PGE, porphyry Cu-Mo-Au, ophiolite-hosted Cr-PGE, volcanogenic massive sulphide (VMS) Cu-Pb-Zn, granite-related Sn-W-Mo-Li-U, epithermal Au and mesothermal Au and base metal veins. Ordovician arc-related deposits have been of most historical importance for a variety of metals. Currently, meso- and epithermal gold veins may have the most potential.

KEYWORDS: Mineralization, magmatism, Caledonian Orogeny

1 INTRODUCTION

The Caledonian orogeny spans the period from the Ordovician to the early Devonian and is marked by a series of tectonic events related to the closure of the Iapetus Ocean (McKerrow et al. 2000). On both margins volcanic arcs, including back arcs, were developed during the Ordovician and porphyry Cu, Au and base metal veins, magmatic Cu-Ni-PGE and VMS deposits were formed (Fig.1). Accretion of these arcs resulted in obduction of oceanic crust and preservation of podiform Cr-PGE deposits. By the mid-Silurian the ocean had effectively closed and tectonic activity was dominated by a complex zone of sinistral strike-slip movement until the end of the early Devonian and the onset of the Acadian Orogeny. By this time the various terranes comprising the British Isles were in place and represent a complete transect through the orogen (Fig.1).

Final collision between Laurentia and Avalonia in the mid-Silurian was marked by the Scandian orogeny. This resulted in uplift, the onset of ORS facies sedimentation and the emplacement via strike-slip faults of granitic magma of mainly I-type composition, especially in the Grampian Terrane, and alkaline igneous rocks in the Northern Highlands Terrane. In the late Silurian andesitic volcanism began and continued until the early Devonian. Associated with the granitoids are numerous porphyry Cu-Mo-(Au) deposits.

During the early Devonian granitoids of mainly S type composition and reaching batholithic dimensions were emplaced on both sides

Fig. 1  Mineralization related to magmatism and terranes in the British Isles (terranes after Woodcock, 2000.)
of the suture. These are the final granitic magmas produced during the Caledonian orogeny and are associated with Sn-W-Mo-Li-U and mesothermal Au-As-Sb mineralization. Epithermal Au mineralization related to andesitic volcanism and gold-bearing mesothermal quartz veins of possible late Caledonian age were emplaced along major faults.

Despite widespread and varied mineralization only one mesothermal Au deposit is in production, and exploration for orthomagmatic Cu-Ni-PGE deposits and mesothermal Au deposits are ongoing.

2 PORPHYRY CU-MO-(AU)

Porphyry Cu-Mo-(Au) mineralization is mainly found in the Grampian Terrane associated with mid Silurian granitoids. However, the most economically important example is of Ordovician age and located in north Wales at Coed y Brenin. The mineralization is hosted by an arc-related diorite complex and shows classic concentric zoning of mineralization and alteration (Rice & Sharp 1976). It contains c. 200 Mt of 0.3% Cu. The Silurian porphyry deposits seem to be more prospective for Au, e.g., the Kilmelford intrusive suite near Oban on the Great Glen Fault contains weak porphyry Cu (Mo) mineralization at Beinn nan Chaorach and significant Au and Ag mineralization in a large diatreme at Lagalochan (Harris et al. 1988). Placer gold is also present in this area.

3 EPITHERMAL AU

Epithermal (hot spring) Au mineralization is preserved in a small pull-apart basin containing Early Devonian sediments and volcanic rocks at Rhynie in the Grampian Terrane (Rice et al. 1995). The hydrothermal activity may be linked to andesitic magmas. Most of northeastern Scotland is located close to the early Devonian landsurface and recent discoveries in Sutherland indicate the potential for epithermal Au mineralization (Crummy et al. 1997). Late Caledonian basins in the northern part of Ireland containing Devonian sediments and volcanic rocks may also be prospective.

4 MESOTHERMAL AU-BASE METAL

Important quartz vein-hosted gold mineralization occurs in the Sperrin Mountains of Northern Ireland (Curraghinalt and Cavanacaw) and at Cononish near Tyndrum, Scotland. The Curraghinalt and Cavanacaw deposits contain respectively 0.9 Mt at 11.66 g/t Au and 2 Mt at 6.9 g/t and Cononish 0.45 Mt at 11.3 g/t Au. In both localities mineralization has been controlled by major faults along which Caledonian movement has occurred. These include the Omagh Thrust (Sperrin mountains) which may be the along strike equivalent of the Highland Boundary Fault and the Tyndrum Fault in the Grampian Terrane. The gold mineralization is believed to be linked to magmatic activity and that at Cononish may be of Devonian age (Parnell et al. 2000; Pattrick et al. 1988).

Gold-bearing quartz veins spatially related to intrusions are also found in south Mayo, Western Ireland (e.g., Cregganbanua) (Young et al. 1989).

There are numerous occurrences of Au-As-Sb veins which are largely restricted to the N. Belt of the Southern Uplands Terrane. This mineralization usually shows a close association with Devonian granitoid complexes (e.g., Glenhead Burn).

Abundant Cu-As veins of historical importance occur in the Lake District and may be genetically related to Ordovician igneous activity (Millward et al. 1999). Similar veins are spatially associated with early Devonian granitoids in the Southern Uplands and Leinster.

5 GRANITE-RELATED W-SN-MO-LI-U

This mineralization is mostly found associated with early Devonian S-type granitoids. These include Carrock Fell in the Lake District and the eastern margin of the Leinster granite in Ireland. A close spatial relationship with batholiths is common. Glen Gairn in the Grampian Terrane may be a late-stage differentiate of the Silurian Cairngorm batholith. The mineralization may be in veins, skarns, shear zones or pegmatites. Common ore minerals are wolframite, scheelite, cassiterite and molybdenite and alteration assemblages are dominated by muscovite (greisen). Ore fluids vary from dominantly magmatic to dominantly meteoric (Shepherd et al. 1976; Gallagher 1989).

Granite-related U mineralization is the most widely distributed in space and time. It may be formed at the time of intrusion or long afterwards. The style varies from uraninite-bearing late-stage pegmatites emplaced along active shear zones within the Donegal pluton to pitchblende veins of Jurassic age filling faults.
in the aureole of the Criffel granodiorite (O’Connor 1986; Gallagher et al. 1971).

6 ORTHOMAGMATIC CU-NI-PGE

Copper-Ni-PGE mineralization is found in layered basic rocks of Ordovician age at Knock and Arthrath in northeastern Scotland. The plutons were emplaced during the Grampian Orogeny beneath a volcanic arc on the northern margin of the Iapetus Ocean. The mineralization, present mainly as disseminated sulphides, is hosted by gabbro and norite cumulates. At Knock it occurs in a structurally complex contact zone, whereas at Arthrath it is found in a dyke-like apophysis to the Arnage basic mass. The sulphides are dominantly pyrrhotite with minor chalcopyrite and pentlandite (Fletcher and Rice 1989; Fletcher et al. 1997). At Knock 2 Mt of 0.52% Ni and 0.27% Cu have been identified. PGEs are associated Cu-Ni-Fe sulphides and reach 418 ppb Pt (Knock) and 458 ppb Pd (Arthrath), McKervey et al. in press. There is evidence of hydrothermal mobilisation of PGEs at Knock. It has been suggested that separation of sulphide liquids was caused by assimilation of country rock (Fletcher et al. 1989) whereas McKervey et al. (in press) propose that mixing of a primitive magma with the cumulate pile was responsible.

7 OPHIOLITE-HOSTED CR-PGE

Significant mineralization occurs on the Unst ophiolite in the Shetlands. Here podiform chromite bodies yielded c. 50 000 t of chromite until production ceased in 1944. The chromite pods are found within hartzburgite and dunite units at the base of the ophiolite sequence. The basal dunites contain thin (<1m) horizons which are enriched in PGMs (Prichard et al. 1981). Whereas some of the PGE enrichments are related to magmatic processes others are related to later hydrothermal activity.

8 VOLCANOGENIC MASSIVE SULPHIDES

VMS deposits of Ordovician age are found at Avoca in the Leinster basin and Parys Mountain in Anglesey. In the former, massive, disseminated and vein sulphides are hosted by rhyolitic tuffs and the hydrothermal activity is linked to a volcanic centre. Massive ores have chalcopyrite-rich bases and galena- and sphalerite-rich tops. The Avoca mine has yielded 16 Mt of ore grading about 6% Cu (Williams et al. 1986). The VMS deposit at Parys mountain is associated with volcanic rocks, mainly felsic lavas, and shales. Mineralization occurs as massive sulphide lenses and disseminations of dominant pyrite with chalcopyrite, sphalerite and galena (Pointon & Ixer 1980). It has produced about 130 000 t of copper and reserves have been estimated by the BGS at 6 Mt of 6% Zn, 3% Pb and 1.5% Cu.

9 CONCLUSIONS

The mineralizations formed during the Caledonian Orogeny evolve according to changes in the tectonic setting and include examples of all of those that might be expected in a closing ocean rimmed by volcanic arcs and followed by a continental collision. The oldest and the most important in terms of historical production and/or reserves are found in the remnants of volcanic arcs and obducted ocean crust. These comprise deposits of Cr, Cu, Pb, Zn and Ni.

Later mineralizations formed during an extended period (c. 30 Ma) of oblique collision are common and widely distributed but have been of limited economic importance. The most common are mid-Silurian porphyry Cu-Mo-Au deposits which seem to have a low potential for copper but may be prospective for gold. The final magmas were generated during the early Devonian and resulted in granitic batholiths of S-type composition and andesitic volcanism. The granitoids produced W-Sn-Mo-Li-U mineralization, the andesites some epithermal Au mineralization and magmas of unknown composition sourced heat and fluids (and Au?) for mesothermal quartz vein deposits.

Evidence for a terrane control on mineralization is limited to mesothermal Au-As-Sb veins in the Northern Belt of the Southern Uplands Terrane.

Looking to the future the prospectivity of the British and Irish Caledonides for deposits related to orogenic magmatism seems largely limited to epi- and mesothermal Au deposits located along major faults.
Fletcher TA, Rice CM (1989) Geology, mineralisation (Ni-Cu) and precious metal geochemistry of Caledonian mafic and ultramafic intrusions near Huntly, northeast Scotland. *Trans Inst Min Metall*, 98, B185-200


Rice CM and 13 others, 1975. A Devonian auriferous hot spring system, Rhynie, Scotland. *JGS*, 152, 229-250


"Digging Deeper" C.J. Andrew et al (editors)
Mines and ores from Portugal: past, present and future possibilities

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ABSTRACT: Although Portugal is not a major mining country, it has two important metallogenic provinces (Sn-W on the north and centre and Cu-Zn on the south), and presently two world-class mines (Panasqueira and Neves Corvo). In the last 15 years mines have produced Cu, W, Sn, Au, Ag, Fe, Mn, Ti and U. In the last 150 years mines also exploited Pb, Zn, Cr, Sb, Ta, Nb and Mo. This paper presents the location, geology, ore grades, and extracted tonnages for the most important mineral deposits. It also reviews the most promising metallic resources for at least the next 15 years, which may be of future interest for exploration companies.

KEYWORDS: Portugal, metallogeny, mines past present future

1 INTRODUCTION

The relatively small area of Portugal encloses a diversity of ore deposits that have been mined during the last 200 years. Some were already exploited in pre-Roman times (e.g., copper at Aljustrel) or during the Middle Ages (e.g., iron at Moncorvo).

The majority of the deposits are quartz veins and associated disseminations. However, there are also podiform chromites, skarns, placers and massive sulphide deposits. Portugal also includes part of one of the biggest VMS metallogenic provinces in the World, generally known as the Iberian Pyrite Belt. Exploration interest is high in this area, and also in many areas known for gold mineralization.

Present high metal prices and high levels of exploration make Portugal an attractive target area for exploration. The good geological knowledge of the country is a key factor in the implementation of in-depth exploration programs for a range of mineral resource targets.

This communication is intended to be a comprehensive but brief summary about mines and metallic ores from Portugal. The geological knowledge of the country is dispersed in hundreds of article, theses, and other documents. For a general overview about metallogeny the reader should consult the works of Thadeu (1965, 1977) and Schermerhorn (1982).

2 MAIN METALS

The main commodities for the Portuguese mining industry are tungsten, tin, copper, zinc, gold and uranium. All of these were mined until less than 20 years ago. The first four are still mined.

2.1 Tungsten and tin

About 700 small producers of W-Sn in quartz veins are known in a metallogenic province that cross the north and center of Portugal (Goinhas & Viegas 1983). Most of these operated between World Wars I and II. Some important mines (e.g. Borralha) produced until the 1980’s and then closed due to the steep decline of tungsten prices.

There were fewer W mines in skarns. The most important was that of Covas in the Viana do Castelo district. These mines, owned by Union Carbide, worked intermittently after the second World War. Between 1977 and 1980 135 t of scheelite concentrates were extracted from open pits and a 4 level underground mine. The mines closed with much of the 689,000 t of 0.86% WO3, plus 233,000 t of 0.56% WO3 of probable ore, remaining. The skarn of mina de Riba de Alva near the Douro river (Bragança district) produced about 2000 t of WO3 concentrates between 1951 and 1978. Reserves of 380,000 t at 0.51% WO3 remain in place. S.Leocádia skarn deposit (Viseu), which has
never produced, contains about 500,000 t @ 0.30% WO$_3$.

2.2 Copper and zinc

These two metals are found together in the massive sulphide ores of the Iberian Pyrite Belt, which contains 1 700 Mt of ore. Several deposits are known; some of which are still being evaluated (e.g. Lagoa Salgada). Small quartz veins containing copper were also worked in the past in this belt. Zinc occurs in two other situations: 1- associated with Cambrian-Silurian carbonate and metavolcanic rocks as disseminated or massive lenses, in the Alentejo Zn-Fe belt (near Portel village); 2- in quartz veins as at Terramonte (Castelo de Paiva, near Porto). At this latter location, there was an underground mine working intermittently between 1885 and the 1980’s. Ore grades were about 3% Zn, 4-2% Pb and 180-110 g/t Ag. (Ferreira, 1971).

2.3 Gold and silver

In Roman times gold was mined at Três Minas (Vila Pouca de Aguiar), a few kilometers from the Jales Au mine. This mine was active for decades during the 20th century. It closed in 1992 due to the high cost of production below depths of 620m. The mine exploited an Au-Ag quartz vein with an average of 12 g/t gold. The paragenesis includes sphalerite, galena, pyrite and arsenopyrite as main minerals. Gold was also extracted from numerous smaller mines like Freixeda (Bragança).

In modern times the first gold mining was from several small Sb-Au quartz vein mines near Valongo. According to Ferreira (1971), during the 1880’s and 1890’s the gold output from these mines was at such a level that it influenced gold prices on the London Market.

2.4 Uranium

There are more than 100 occurrences of U known in the central part of Portugal. Several were mined during the 20th century. In 1990, 12 mines were still in production. The ores are disseminations in granites or schists, and veins. Cotelo Neiva (2003) proposed that a mixture of magmatic and meteoric waters promoted dissolution of U from the nearby young granites and formed the hypogene ores after a decrease in temperature from 400º to 230-200 ºC.

One of the most important European uranium mines was Urgeiriça (Nelas, Viseu) in the centre of Portugal. From 1915 to 1945 pitchblende-rich ore was mined for radium. 45 g of radium were extracted from 22,000 t of ores up to 1945. After 1945, the mine began production of U$_3$O$_8$ concentrates for the nuclear industry. The underground workings ceased operation when the mine attained the 19th level. Acid leaching was the mining method chosen until the end of production in the late 1990’s.

At the Nisa granite (Portalegre) there are numerous uranium occurrences (quartz veins, stockworks and brecciated rocks). In one area
of around 70 ha there are 6.3 Mt of uranium ore that contains about 3,700 t of U₃O₈, almost half of the 7,900 t known U₃O₈ reserves in Portugal.

3. OTHER EXPLOITED METALS

Several other metals were mined recently in Portugal. The following are those with the most economic impact.

3.2 Iron

There are three main areas where Fe was mined: Moncorvo and Serra do Marão (in the north) and an area between Serpa and Alvito in the south. The mining of an Ordovician ironstone deposit at Moncorvo (NE of Portugal) began in the 18th century. D’Orey (1999) estimates that it contains 1,000 Mt @ 37% Fe. The ore is haematitic and considered detrital.

At Serra do Marão the Fe came from magnetite layers in Ordovician quartzites. The mines were underground and worked until the 1960’s. At Alentejo there were several small mines. Probably the most important was the Orada mine, which worked a magnetite-rich ore.

3.3 Manganese

Manganese-iron ores were mined until the year 2000 at Cercal (a small village not far from the coast of Alentejo). The area covers some 50 x 20 km and the published reserves (Carvalho, 1971) are 4.65 Mt at 8% Mn, 43% Fe and 14% Si. The last production was 11,800 t @ 40.4% Fe and 10.2% Mn. The ore horizon is hosted by a volcano-sedimentary formation of the Iberian Pyrite Belt and has a strike length of 5 km long and a thickness of 18m.

3.4 Lead

The first official mining lease was given in 1836 to the Braçal-Malhada mine (Aveiro district). This mine produced Pb during the 19th century and during the first half of the 20th century. The galena ore was in a quartz vein. Parts of the vein were filled with carbonate. The best year of production was 1899, with 2,900 t at 65% Pb. (Guimarães dos Santos, 1946) The mine also produced zinc. Other small mines of Pb were in production in the north and centre of Portugal during the same period.

3.5 Titanium

Sn-Ti ores from recent placers were exploited until very recently (1990’s) in the Guarda and Viseu districts. At the Nave de Haver basin there were about 20 small mines (Gonçalves, 1966). In 1982 the production was 585 t of ilmenite concentrates (50% Ti) but in 1990 the 5 remaining mines only produced 43 t of concentrates.

3.6 Chromium

During the second World War there were several mines extracting podiform chromites associated with ultrabasic rocks in an area between Vinhais and Bragança. The geology is complicated and the deposits are considered exhausted. Cotelo Neiva (1947) refers to 16 chromite deposits and grades between 20 and 48% Cr₂O₃.

3.7 Antimony

Sb-Au bearing quartz veins were mined during the last decades of the 19th century. They produced several tonnes of Sb concentrate from ores grading 4-10% Sb. Some of the mines attained depths of almost 200 m.

3.8 Tantalum and niobium

Columbo-tantalites from pegmatitic veins located near Cabração (Ponte de Lima, Viana do castelo) were mined during the 1940’s. The mine was underground with four levels. Also at Sabugal (Guarda) there were small Ta-Nb mines in placer deposits, which produced until 1983. The output in this year was 3 t @ 30% Ta₂O₅.

3.9 Molybdenum

The W-Sn-Mo Carris mine (serra do Gerês) produced MoS₂ concentrate as a by-product from subvertical quartz veins enclosed in granite, until the 1970’s.

4 THE JEWELS OF THE CROWN
(PANASQUEIRA AND NEVES CORVO)

The Panasqueira mine (Fundão, Guarda) exploits subhorizontal quartz veins. Since 1896, it has produced more than 30 Mt of ore, which produced 92,800 t of WO₃ concentrates (plus small amounts of Sn and Cu) between 1947 and 2001 (Cavey & Gunning, 2006). Presently, the annual output is about 1,200 t of WO₃ concentrates.

Neves Corvo is one of the highest-grade copper mines in the World with an average grade of 7.9% Cu when it started production in 1988. The mine has produced between 1.6 and
2.1 Mt of ores each year. The tin-rich ores are almost exhausted but the zinc reserves (50 Mt of 6% Zn) went into production during 2006.

5 THE FUTURE

Presently there are twelve contracts for exploration under development in areas ranging from 100,000 ha to 13.5 ha. The list of metals under exploration is long, but the most important are Au-Ag, Cu-Zn, PGE and U.

Gold exploration is current in the following areas: Jales-Gralheira, Penedono- Meda, Moimenta da Beira, São João da Pesqueira, Sernancelhe, Boticas (Chaves) and north Alentejo (Alandroal, Campo Maior, Montemor). At Montemor there is a gold deposit of at least 4.12 M t at 2.74 g/t (10 t Au) with another possible 20 t Au in the surrounding rocks. According to Cotelo Neiva e Neiva (1990), the Jales-Gralheira area could hold total reserves of 78 t gold.

PGE and nickel are being actively prosp ected in basic magmatic rocks in north Alentejo. There are also Pt occurrences in the north (between Vinhais and Bragança) but until now their economic value has not been proven.

Copper and zinc are targets at the SOMINCOR exploration program in the area surrounding Neves Corvo. One of the most promising areas for exploration of Cu-Zn resources is below the Cenozoic cover of the northern part of the Portuguese part of the Iberian Pyrite Belt. It was there that the Lagoa Salgada deposit was found in the 1990’s; the deposit is still being evaluated. Other companies are looking for Cu and Zn same metals at Alandroal and Vila Viçosa.

Uranium is the target for several companies exploring in the Nisa region, which is the most promising unexploited U area in Portugal.

Tantalum and lithium in association with quartz and feldspar pegmatites are under investigation in the old mining area of Cabração (Ponte de Lima, Viana do Castelo).

The Aljustrel mine is scheduled to reopen at the end of 2007 in order to start production of Zn and Pb ores. The announced reserves for the Feitais orebody are 12.2 Mt at 5.67% Zn, 0.22% Cu, 1.77% Pb, and 64 g/t Ag; The Moinho orebody contains 2.15 Mt at 4.49% Zn, 0.54% Cu, 1.82% Pb, and 54 g/t Ag. Most of the zinc ores at Neves Corvo are known to have interesting indium grades and there is potential to exploit this metal as a by-product.

REFERENCES


Mesothermal gold deposits from the Variscan belt: A model for gold deposition based on fluid mixing during exhumation

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ABSTRACT: In mesothermal gold deposits from the Variscan belt, the succession of mineral assemblages and fluid types defines a unique cycle of fluid evolution in most studied deposits. The apparent similarity of the processes at the scale of the whole European province of Hercynian gold deposits provides the opportunity to build up a generalised model based on fluid geochemistry, sources, fluid production and flow regimes during the late uplift stage of a collisional orogen. Dilution, pressure - temperature decrease, and fluid mixing from two distinct fluid reservoirs occurring at a critical time during basement uplift, are favourable factors for decreasing gold solubility and precipitating gold along major fault zones.

KEYWORDS: mesothermal gold, variscan, fluid mixing, exhumation

1 INTRODUCTION

Previous case studies of Au-(As) ore deposits in the Variscan belt of western Europe have shown that they formed under similar conditions during the late stages of exhumation (Boiron et al. 1990; Essarraj et al. 2001; Boiron et al. 2001, 2003). Most mineralized structures are faults sealed by quartz that was deposited from volatile-rich fluids, but experienced a complex evolution combining ductile then brittle deformation during exhumation (Boiron et al. 1996). In contrast with most Archaean Au-lodes (Groves 1993), mineralized quartz faults are characterised all over Europe by a long-lived structural evolution revealed by macro- and microstructures inherited from various superimposed brecciation, fracturing, sealing or healing stages (Bouchot et al. 2005). Thus, crack-seal textures commonly described in Archaean lode deposits are generally lacking in late Hercynian deposits.

This present paper discusses a model based on data from some important crustal structures mineralised in Au and As throughout western Europe: i) in “mesothermal” gold deposit fluids in France (quartz veins in the gold-bearing Saint-Yrieix district (Boiron et al. 1990; 1992; Essarraj et al. 2001), in the Salsigne district (Cathelineau et al., 1993), ii) comparisons with deposits from North Iberia (Galicia) (Boiron et al. 1996, Arias & Martin-Izard 2000), Portugal (Vallance et al. 2003) and the Bohemian massif (Moravek et al. 1989; Boiron et al. 2001).

2 CHEMISTRY AND SOURCES OF THE FLUIDS

Gold precipitation from hydrothermal solutions and the formation of economic gold deposits are the result of variations in the physico-chemical parameters which control the evolution of fluid-rock systems. The main parameters involved in the transport and precipitation of gold are temperature, pressure, oxidation-reduction conditions, pH, fluid salinity, and the concentration of chloride or bisulphide ligands (Gibert et al. 1998; Mikucki 1998; Loucks & Mavrogenes 1999). The parameter variations themselves result from cooling, decompression, immiscibility, condensation, or fluid mixing phenomena, as well as fluid-rock interactions.

Understanding the mode of formation of a given gold deposit requires integrated studies to be carried out. Such studies consist of a detailed description of the local and regional geology, host rocks, and alteration and mineralization parageneses, together with tentative reconstructions of the temperature and pressure condi-
tions, as well as the palaeochemistry and palaeocirculation of fluids responsible for the transport and deposition of gold. Such reconstructions are based on fluid inclusion studies and geochemical modelling calculations.

In late Hercynian gold concentrations, fluids percolating the mineralized faults come from two distinct reservoirs (Boiron et al. 2003): one was a quite shallow reservoir while the other was rather deep-seated. Both types of fluids saw their original composition modified through interactions with host metamorphic formations. Early fluids, present during the primary sealing of the faults by quartz, are considered to have equilibrated with the metamorphic pile and then flowed upwards along the faults. The likely mechanism to precipitate silica was a drop in fluid pressure, as quartz solubility is highly dependent on pressure in the 400-500°C range (Walther & Helgeson 1977). Early fluids are characterized by CH$_4$/CO$_2$/H$_2$O ratios typical of fluids which have equilibrated with graphite, and moderate to medium chlorinities with a high Br/Cl ratio. In any case, we must consider the possibility that scavenging of gold from large crustal volumes was carried out by this type of fluid which then flowed into localized, and very small, crustal domains.

The striking feature of the gold-bearing quartz, is that gold is not synchronous within any quartz deposition, and appears located in late micro-fractures and associated with Pb-Bi-Sb sulphosalts and sulphides. These late stages are characterized by fluids whose salinities decrease to very low values indicating their progressive dilution by waters of surficial origin in the fault system.

The long-lived activity of this fault system favoured the connection between the two distinct fluid reservoirs at a critical time during the basement uplift. The fluids evolved through two main driving mechanisms at the onset of the Au deposition: i) a decrease in temperature accompanying decompression from supra-lithostatic to hydrostatic conditions, which resulted, in some instances, in volatile unmixing in the fault systems, and ii) a mixing of the resulting fluids with shallow waters entering the hydrological system. In this context, dilution and mixing appear to be the most probable factor decreasing gold solubility together with a drop in pressure (Gibert et al. 1998), allowing Au deposition and trapping by early-deposited sulphides. In addition, the presence of micro-fractured sulphides could have enhanced gold precipitation through electrochemical processes (Moller & Kersten 1994).

3 P-T EVOLUTION

The main P-T evolution pathways have already been discussed elsewhere (Boiron et al 1996; 2001; 2003; Essarraj et al 2001) and are only summarized.

The highest pressures (350-450 MPa) were determined for inclusions found in quartz from the wall rocks of the mineralized faults (e.g., Lauriérers) which indicates that this part of the basement was still located at a rather deep structural level (13-17 km) at the end of the Variscan collision stage (Essarraj et al. 2001). In NW Iberia and in Bohemia, pressures for the vein formation were lower but could reach 380 MPa, giving a maximum estimated depth of around 15 km.

One of the specific features of late Hercynian deposits is the relatively long-lived drainage of the same volume of rock, which was either centred on a fault zone, and its immediate boundaries (Lauriéras, Cheni, Fagassièr, Salsigne (Fontaine de Santé fault)), or related to a network of subparallel joints (Mokrsko, Corcoesto, Tomino) formed within the granite at some distance from major faults or shear zones. The fault acted as a trap for several stages of mineralization. The aqueous carbonic fluids associated with the As-S stage were trapped under lower P-T conditions which were respectively 50-180 MPa and 350-450°C. The pressure decrease from the earlier stage documents an uplift of 5 to 10 km (Boiron et al 1996; 2001; Vallance et al 2003; 2004). At this time, apparent geothermal gradients were necessarily high owing to the rather high temperatures (400±50°C) and still recorded in the rock pile for a fluid pressure indicative of rather shallow structural levels.

Such high geothermal gradients probably resulted from the emplacement of syn-tectonic and post-tectonic plutons (aplite body at Castromil, Vallance et al 2003). The latest stage is characterized by the mixing of a moderately saline end member, probably issued from the evolution of fluids from the deep reservoir, with dilute fluids of lower temperature (see above). Fluid mixing yielding to gold deposition is likely to have occurred under hydrostatic pressures, or at a pressure lower than those reached during the preceding stages.
4 CONCLUSIONS

The major geodynamic switch towards generalized extensional tectonics that occurred during the uplift and thinning of the upper crust after the collisional stage may be the key factor controlling Au deposition in the late Hercynian gold deposits. The constancy of the data is indicative of a long but similar fluid history at the province scale. Although granites are present in the surroundings of most studied deposits, they cannot be considered as granite-related gold deposits in the sense of Lang & Baker (2001). The granitoids act as sources of heat that drove thermal convection cells in which fluids scavenged gold and other metals.

REFERENCES


The basement, the source - the surface, the trap: isotope studies in Irish-type ore deposits

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ABSTRACT: A wealth of stable and radiogenic isotope data are available from a spectrum of the carbonate-hosted Irish-type Zn+Pb(±Ba±Ag) deposits and their environs. Radiogenic isotope studies (U-Pb, Rb-Sr and Sm-Nd) point strongly to the involvement of the Lower Palaeozoic and Precambrian basement as a source of metals to the overlying deposits. Recent Rb-Sr work also provides the first radiometric date for an Irish deposit: 360Ma for the Silvermines deposit. S isotope studies have been vital in implicating a surface brine, containing abundant bacteriogenic sulphide, as a trapping mechanism. Without the latter no Irish deposit would have been economic, although the contribution from this source may be variable between the deposits.

KEYWORDS: Irish-type, base-metal, isotopes, basement, bacteriogenic

1 INTRODUCTION

Irish-type base-metal and barite deposits constitute an important class of carbonate-hosted ore deposit. Together, they form the greatest concentration of Zn/km² on the planet (Singer, 1995), with the Navan deposit, at ~100 Mt at ~ 8.4% and 2% Pb, being Europe’s largest Zn producer.


Both radiogenic (U-Pb, Rb-Sr, Sm-Nd) and stable (S, C, O, H, and more recently Zn and Fe) isotope analyses have provided tests for the competing models and, most recently, have provided direct dating of the mineralization (Schneider et al., 2007). Overwhelmingly, these data are more consistent with the SEDEX-type model for the origin of the Irish-type ores.

Here we examine isotopic evidence that elucidates the basement/source – surface/trap for the deposits, highlighting the involvement of metals from the basement and the necessity of surface brines to trap the metals brought towards the seafloor by the hydrothermal exhalative system.

2 GEOLOGY

Deposits in the Irish Midlands (Silvermines, Tynagh, Lisheen, Galmoy) are hosted by brecciated and dolomitized Lower Carboniferous (Dinantian) carbonate rocks, primarily within the Waulsortian Limestone Formation. Mineralization in the northern Midlands (Navan) occurs within the Navan Group, a sequence of variably dolomitized and brecciated carbonates and siliciclastics. At the base of the host sequences lies a thin (<100m) sequence of Old Red Sandstone (ORS) terrestrial/marginal sediments. Like all the carbonates, the ORS is largely Lower Carboniferous in age. The ORS unconformably overlies a thick succession (≤4 km) of Ordovician and Silurian metasediments and volcanics, with unidentified basement below (possibly Lewisian).

Mineralization is texturally complex but mineralogically simple, comprising sphalerite,
galena, pyrite and marcasite with variable barite, dolomite and calcite, and minor quartz. Additional sulphides, such as chalcopyrite, tennantite and other sulphosalts also occur. Orebodies are broadly stratiform but in most cases have been shown to be strictly stratabound and occur as single or multiple lenses hosted by specific horizons.

3 ISOTOPIC EVIDENCE FOR BASEMENT INVOLVEMENT

Whilst there is some evidence from sulphur isotope studies that implicate the basement as a potential source for the deposits (Anderson et al., 1989; Boyce et al., 1993), the best evidence is obtained from radiogenic systems.

The seminal U-Pb work of O’Keefe (1986, 1987), together with others (Caulfield et al., 1986; LeHuray et al., 1987; Dixon et al., 1990; Everett et al., 1999; Fallick et al., 2001) indicated that within a given deposit, the $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios are essentially homogeneous, but variable geographically, becoming more radiogenic to the SE of Ireland. The underlying Lower Palaeozoic basement, and base-metal veins therein, display the same regional geographical variation and are thus strongly implicated as the metal source.

By contrast, Model A specifies the ORS as the primary aquifer and source of metals. Everett et al. (2003) showed this to be untenable through their sequential extraction of Pb from potential source rocks – the extracted Pb being far too radiogenic to be a realistic source. Furthermore, they showed that any Pb in altered ORS rocks proximal to the deposits had Pb ratios similar to the deposits and therefore likely gained the Pb from interaction with mineralizing fluids during Lower Carboniferous ore genesis.

More recently, new Sr and Nd isotope analyses (Wilkinson et al., 2005a; Walshaw & Menuge, 2006) that have reinforced the idea (Russell, 1978) that a surface fluid, derived from Lower Carboniferous seawater, was the primary ore fluid, which penetrated and leached metals from the underlying Lower Palaeozoic basement. In addition this work confirms the idea that basement underlying the Lower Palaeozoic rocks (Lewision/Proterozoic?) was also involved (Mills et al., 1987).

4 ABSOLUTE DATING

Due to the difficulty in obtaining quality samples, which are directly relatable to the ore forming event, no absolute dating of the Irish ores has been published since Halliday & Mitchell’s (1983) clay K-Ar work. In their own discussion, Halliday & Mitchell (1983) indicate that the dates obtained most likely reflect resetting during the Variscan orogeny than being primary dates for the ores.

Ar-Ar step-heating was undertaken on micas in altered ORS by Hitzman et al. (1994), giving ages of 350-337 Ma, suggested to be the age of alteration. This work has never been fully published, and thus cannot be properly assessed.

A new date has recently been obtained from measurement of Rb-Sr isotopes in fluid inclusions from the Silvermines deposit (Schneider et al., This Volume). It gives an age around 360 Ma, which is consistent with the argument of a Tournaisian, essentially syndepositional age for this deposit (e.g., Taylor, 1984; Lee & Wilkinson, 2002; Boyce et al., 2003).

5 SURFACE TRAPPING

The efficiency of deposition of the Irish deposits was a result of several coincidences, with perhaps the most important being mixing of a hot hydrothermal solution, with little contained sulphide, and a cool, surface brine, containing abundant bacteriogenic sulphide. All models agree that bacteriogenic sulphide was vital in precipitation of the Irish ores. The proof of this involvement is derived from S isotope analyses. Classic studies of individual Irish ore deposits were presented by Coomer & Robinson (1976, Silvermines); Boast et al. (1981, Tynagh) Boyce et al. (1983, Silvermines); Caulfield et al. (1986, various); Anderson et al. (1998, Navan); Wilkinson et al. (2005b, Lisheen). Each present strong evidence for the involvement of mixing in the genesis of these deposits. Boast et al. (1981) were the first to demonstrate variation of S isotopes with texture, and this was taken further by Anderson et al. (1998) and Blakeman et al. (2002) who used in situ laser S isotope analyses to further refine our understanding of fluid flow in the fault networks of these systems.

By contrast, Fallick et al. (2001) used samples representing up to a million tonnes of ore to demonstrate that over 90% of the ore at Navan was precipitated from bacteriogenic sul-
phide. Their data implied that no Irish deposit would be economic without a bacteriogenic sulphide source.

6 CONCLUSION

Isotope studies have been critical in our understanding of the genesis of Irish-type base-metal deposits. In particular they have demonstrated that the sub-ORS basement is the source of the metals, and that without a surface brine containing abundant bacteriogenic sulphide, no Irish deposit would have been economic.

ACKNOWLEDGEMENTS

We would like to thank many students, colleagues and friends for innumerable discussions! In particular we would like to thank Tony Fallick, Mike Russell, and the late Kate Everett. Much of this work was sponsored by NERC and Irish companies who are sincerely thanked for their support over the years.

REFERENCES


Fennoscandian Ore Deposit Database: a comprehensive deposit database in the public domain

Eilu, P.
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ABSTRACT: The FODD is a public-domain Geoscience database containing more than 1000 metal mines and unexploited deposits within the Fennoscandian region (Norway, Sweden, Finland and NW Russia). Information on the deposits includes location, mining history, tonnage, commodity grades, geological setting, age, ore mineralogy, style of mineralization, genetic models, and sources of data. The database will be accessible on the Internet, from December 2007, through the exploration pages of Geological Survey of Finland (http://en.gtk.fi/ExplorationFinland/).

KEYWORDS: databases, mineral exploration, Fennoscandia, Norway, Sweden, Finland, Russia

1 INTRODUCTION

Fennoscandia is a significant ore potential and metal producing region on a world scale (Weihed et al. 2005). The shield has a long history of mining and exploration. For example, archaeological evidence shows that copper was produced from the Falun mine in the Bergslagen province (Sweden) in the 8th century (Eriksson & Qvarfort 1996). Statistics on copper production at Falun are available from the mid-16th century until the closure of the mine in 1992. Despite this long history, Fennoscandia is still regarded as underexplored and considered to have good potential for major discoveries, as shown by the new discoveries of metal deposits occurring every year in the region.

Numeric databases covering extensive areas are one of the major working tools for modern exploration. Deposit databases are used in selecting larger areas as targets for more detailed work. Presently, there are single-country deposit databases of variable quality and coverage available from the area, but there is no uniform database covering Fennoscandia as a whole, except those only including major mines of Europe (eg. Juve & Størseth 2000, GEODE 2001), and a few more-or-less global single metal or single genetic type databases (eg. Gosselin & Dube 2005).

To answer this need, the geological surveys of Finland, Norway and Russia are setting up an uniform metal deposit database covering the entire Fennoscandian region (i.e., the Precambrian Shield and the Caledonides). The Fennoscandian Ore Deposit Database (FODD) will present a set of key features, according to uniform guidelines, of mined and unexploited deposits in the area. The database will be accessible in late 2007 through the Internet and will be public-domain. In addition, a Fennoscandian mineral deposit map will be published in 2008. These products will also provide basic information for research in economic geology.

2 STRUCTURE OF THE DATABASE

2.1 Main principles

It is a major challenge to combine data from countries (or any other sources) with different research and exploration traditions. This naturally results in problems in harmonising the data presentation.

To make the data harmonisation possible at all, and to produce information that can be
compared across international boundaries, a number of decisions were made at the outset done for the structure and guidelines of the FODD. The fields in the database are listed in Table 1. When reading Table 1, please, note that it is not possible to include all background discussions nor the options for field definitions here; a comprehensive description of the database will be attached to the FODD when it is published online.

Table 1. Data fields in the FODD.

<table>
<thead>
<tr>
<th>Field name</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>ID no. for a deposit;</td>
</tr>
<tr>
<td>When updated</td>
<td>When the latest info was provided;</td>
</tr>
<tr>
<td>Name</td>
<td>Most common name of the deposit;</td>
</tr>
<tr>
<td>Alternative names</td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Country, latitude, longitude (datum WGS84);</td>
</tr>
<tr>
<td>Geological district</td>
<td></td>
</tr>
<tr>
<td>Metallogenic district</td>
<td></td>
</tr>
<tr>
<td>Status</td>
<td>Mined or unexploited;</td>
</tr>
<tr>
<td>Mining method</td>
<td>Open pit, underground or both;</td>
</tr>
<tr>
<td>When operated</td>
<td>Years when the mine was active;</td>
</tr>
<tr>
<td>Main metals</td>
<td>Metals forming &gt;10% of total value of the deposit;</td>
</tr>
<tr>
<td>Other metals</td>
<td>Metals forming 1-10% of total value of the deposit;</td>
</tr>
<tr>
<td>Main metal group</td>
<td>&quot;Base, precious, ferro, special, or energy metals&quot;;</td>
</tr>
<tr>
<td>Metal subgroup</td>
<td>Further definition to above groups;</td>
</tr>
<tr>
<td>Size category</td>
<td>Minor, major, or very large;</td>
</tr>
<tr>
<td>Tonnage</td>
<td><em>In situ</em> size, in Mt;</td>
</tr>
<tr>
<td>Ore grade</td>
<td>A field for each metal, data only for the commodities of the deposit;</td>
</tr>
<tr>
<td>Ore minerals</td>
<td>Ore mineral list;</td>
</tr>
<tr>
<td>Host rocks</td>
<td>Up to two main hosts;</td>
</tr>
<tr>
<td>Adjacent rocks</td>
<td>Up to four wallrock types;</td>
</tr>
<tr>
<td>Age of host rocks</td>
<td>Name of Geological Period;</td>
</tr>
<tr>
<td>Radiometric age</td>
<td>Rock age, method used;</td>
</tr>
<tr>
<td>Age of mineralisation</td>
<td>Name of Geological Period;</td>
</tr>
<tr>
<td>Radiometric age</td>
<td>Mineralisation age, method used;</td>
</tr>
<tr>
<td>Metamorphic grade</td>
<td>Metam. grade of the deposit;</td>
</tr>
<tr>
<td>Alteration</td>
<td>List of minerals produced by alteration (no comment on process!);</td>
</tr>
<tr>
<td>Genetic type</td>
<td>Control for mineralization;</td>
</tr>
<tr>
<td>Tectonic control</td>
<td>Three fields: Strike, Dip, Plunge;</td>
</tr>
<tr>
<td>Main direction of the deposit</td>
<td>Three fields: Shape, Structure, Textured;</td>
</tr>
<tr>
<td>Form of the deposit</td>
<td>Massive, Semi-massive, Disseminated, Irregular;</td>
</tr>
<tr>
<td>Ore mineral distribution</td>
<td>Free text: anything important that does not fit into other fields;</td>
</tr>
<tr>
<td>Comments</td>
<td></td>
</tr>
<tr>
<td>Bibliography</td>
<td>The most important references on which the information for the deposit is based on</td>
</tr>
</tbody>
</table>

1 compulsory field
2 Only options to be used in the field

Only the metals listed in Table 2 are included in the FODD. Industrial minerals and gems are excluded, because these would need a significantly different kind of approach, and it is more difficult to get these data than for metal deposits. Elements that do not form any known or suspected deposits within the Fennoscandian region are presently excluded.

Guidelines for each data field had to be established so that the same feature is described by the same key word(s) across the entire region. Also, only a small number of data fields are indicated as compulsory (as marked in Table 1). This rule was set to ensure that only confirmed data was included in as many fields as possible, and to avoid entry of unclear or misleading information in the FODD.

From the above, one might think that there is little real information in the FODD; however, this is not the case. For a given deposit, most of the non-compulsory fields do contain information. Note also, that the database includes the field 'Comments' which serves as a place for explanatory notes in cases where there are ambiguous data. This also allows for significant information that cannot be included in the other fields of the FODD (eg. various cut-off grades and alternative resource estimates, variation in the texture, shape, siting, the number of ore bodies, genetic types, etc.).

2.2 Criteria to include a deposit into FODD

The criteria used for a deposit to be included into the FODD are as follows (both criteria must be satisfied):

1) Most of the value of a deposit is defined by one or several of the commodities listed in Table 2. For example, a talc mine with nickel as a minor by-product is not included in the FODD.

2) The amount of at least one of the metals listed in Table 2 exceeds the lower boundary for the size class Minor.

2.3 Deposit size classification

The major issue and greatest potential for problems lie in the definition of deposit size categories. How do we estimate a size class for a polymetallic deposit? How do we compare between deposits with different commodities? These points have been addressed, with variable success, in all previously published deposit databases and metallogenic maps (eg. Bugge 1978, Metallogeny of Karelia 1999, Lafitte 1984, Juve & Grenne 1993, Saltikoff et al.)
After reading all the discussion on the topic one might think that it is better to avoid this issue: so many contradictory opinions and views emerge between workers, and nearly everyone in mining and exploration has an opinion.

However, due to the nature of the FODD, we had to set up a deposit size classification and address the above-mentioned problems. Of course, disagreement remains, and everyone using the FODD naturally is free to set up their own size classes and other categories based on their chosen rules. In order to compare the economic importance of deposits with different commodities and also to summarise the value of polymetallic deposits, a common deposit size classification for the FODD was developed. The deposit size classification for FODD (Table 2), based on previous work by Lafitte (1984) and Saltikoff et al. (2000), simply multiplies the tonnage of the deposit with the grades and average metal prices of 1995-2005.

In practise, this means that we calculate the theoretical in-situ value of the deposits prior to mining. The tonnage figure used includes both documented production and various reserve and resource estimates. The reserve and resource estimates vary in quality from proper calculations in accordance with international standards to very rough estimates. Also, the accuracy of the grades vary depending on the source of information. Average metal prices for the chosen ten-year period have been taken from publicly available sources, mainly the USGS web site and the LME.

The commodity price chosen for the calculations is a compromise between the availability of long-term metal price data and the form in which the commodity is mostly sold to the market in our part of the world. For precious and base metals, we use the metal prices of the refined metals that are listed on the major metal markets around the world. This is also the form in which most metals are sold by companies active within Fennoscandia. The price for precious and base metal concentrates, which could also have been used in the calculation, are not listed on metal markets since they are generally negotiated bilaterally between the buyer and the seller and, hence, are not publicly available.

Our major iron mining companies produce and sell magnetite and haematite concentrates or semi-manufactured products like iron pellets.

Table 2. Metals included into and the deposit size classification used in the FODD. The figures indicate the lower boundaries for each size class. All figures in tons of metal.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Minor</th>
<th>Major</th>
<th>Very large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>10</td>
<td>1,200</td>
<td>10,000</td>
</tr>
<tr>
<td>Au</td>
<td>0.2</td>
<td>19</td>
<td>100</td>
</tr>
<tr>
<td>Be</td>
<td>20</td>
<td>2,000</td>
<td>10,000</td>
</tr>
<tr>
<td>Co</td>
<td>50</td>
<td>4,730</td>
<td>30,000</td>
</tr>
<tr>
<td>Cr</td>
<td>2,000</td>
<td>216,000</td>
<td>2,000,000</td>
</tr>
<tr>
<td>Cu</td>
<td>1,000</td>
<td>100,000</td>
<td>600,000</td>
</tr>
<tr>
<td>Fe</td>
<td>500,000</td>
<td>50,000,000</td>
<td>1,000,000,000</td>
</tr>
<tr>
<td>Li</td>
<td>200</td>
<td>20,000</td>
<td>100,000</td>
</tr>
<tr>
<td>Mn</td>
<td>1,000</td>
<td>1,000,000</td>
<td>25,000,000</td>
</tr>
<tr>
<td>Mo</td>
<td>200</td>
<td>23,100</td>
<td>150,000</td>
</tr>
<tr>
<td>Nb</td>
<td>100</td>
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<td>50,000</td>
</tr>
<tr>
<td>Ni</td>
<td>300</td>
<td>30,000</td>
<td>300,000</td>
</tr>
<tr>
<td>Pb</td>
<td>3,000</td>
<td>363,000</td>
<td>2,200,000</td>
</tr>
<tr>
<td>PGE&lt;sup&gt;1&lt;/sup&gt;</td>
<td>0.2</td>
<td>14</td>
<td>100</td>
</tr>
<tr>
<td>REO&lt;sup&gt;2&lt;/sup&gt;</td>
<td>100</td>
<td>10,000</td>
<td>50,000</td>
</tr>
<tr>
<td>Sn</td>
<td>200</td>
<td>20,000</td>
<td>200,000</td>
</tr>
<tr>
<td>Ta</td>
<td>3</td>
<td>300</td>
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</tr>
<tr>
<td>Ti</td>
<td>8,000</td>
<td>84,000</td>
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</tr>
<tr>
<td>U</td>
<td>10</td>
<td>1,000</td>
<td>10,000</td>
</tr>
<tr>
<td>V</td>
<td>200</td>
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</tr>
<tr>
<td>W</td>
<td>300</td>
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<tr>
<td>Zn</td>
<td>2,000</td>
<td>195,000</td>
<td>1,200,000</td>
</tr>
<tr>
<td>Zr</td>
<td>1,000</td>
<td>100,000</td>
<td>500,000</td>
</tr>
</tbody>
</table>

<sup>1</sup> Total of platinum group metals
<sup>2</sup> Total of rare earth elements + Sc + Y, as oxides

To use the price for pure iron metal in the calculations would hence be strongly misleading. Besides, is no world market price for pure iron since iron is sold in various qualities and alloys. For iron, we have chosen the price for magnetite concentrate FOB ports in Brazil, representing long term price data that is available on the web. Titanium is another metal whose price differs greatly depending on the form in which the product is sold. Since the major titanium producer in the Fennoscandian Shield (Telnes in Norway) is selling ilmenite concentrate, we decided to use the world market price of ilmenite for the calculations on all titanium deposits in the FODD. Similar discussions for all the other commodities included in the database will be given in the final publication of the FODD.

For polymetallic deposits, we summarise the value for all metals in a deposit but, to simplify the matters, exclude those metals that contribute less than 10% of the total value of the deposit.

The reason for using the in-situ value of a deposit, instead of using internationally accepted methods for resources evaluations, like the JORC or the Canadian NI 43-101 codes, is that in most cases we do not have access to the
detailed information necessary for such calculations. Many of the mines included in the FODD have been closed for decades and most of the non-exploited deposits have never been subjected to resource calculations according to modern standards. It has been difficult enough to find reliable figures on grade and tonnage for deposits that are in production today. Furthermore, we have come to the conclusion that it is not the task of a geological survey to produce data for feasibility studies. We have instead focused on producing data that gives an idea of the mineral wealth of the Fennoscandian Shield and the importance of the mining industry to our countries. We note that Lydon et al. (2004) are using a similar approach to compare different deposits in Canada although they have access to more reliable tonnage and grade data than we have for the FODD. Thus, the deposit size classification used for the FODD (Table 2) should not be confused with the resource evaluations made in accordance with the JORC and NI 43-101 codes, or other presently accepted standards.

3 SUMMARY

The new Fennoscandian Ore Deposit Database (FODD) will provide public-domain information on metal mines and major deposits from the whole Fennoscandian region, covering the continental territory of Norway, Sweden, Finland and northwest Russia. The database now contains essential information on more than 1000 mines and deposits across the region. The FODD will be accessible through the Internet, beginning in December 2007 at http://en.gtk.fi/ExplorationFinland/.

The database is set up as a tool for both exploration in northern Europe and for research in economic geology (locally and globally). It is also hoped for that the FODD will serve as a tool for political decision-making, and make the Fennoscandian region even more attractive for investment.

ACKNOWLEDGEMENTS

Special thanks to all our colleagues in the Finnish, Norwegian, Russian and Swedish geological surveys, in the SC Mineral, and to a great number of people who are helping us to set up the FODD.

REFERENCES


Fifty years of progress in the understanding of magmatic Ni-Cu ± PGE sulphide deposits

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ABSTRACT: In the early days of research into magmatic sulphide deposits, the Sudbury camp naturally dominated much of our thinking. As it was later discovered that a meteorite impact was responsible for the generation of the host magmas, Sudbury is an unusual and possibly unique situation. Subsequent research in environments ranging from komatiitic volcanics to feeder conduits to flood basalts and layered intrusions has shown that dynamic rather than static magmatic environments are immensely important in the development of magmatic sulphide deposits that have economically significant amounts of metals. This realization has important implications for the definition of exploration targets and the criteria used in their evaluation.

KEYWORDS: Magmatic Sulphides, Geochemistry, Ore Deposits, Nickel, PGE, Models

Magmatic sulphide deposits are best considered as falling into two groups; those valued primarily for their Ni and those for valued for their PGE. With regard to the first group, prior to the late 1960’s the Sudbury camp had been the principal producer of Ni, and the then understanding of its geology, that deposits occurred scattered widely over the base of a noritic/gabbroic layered intrusion (Figure 1), had dominated the ideas driving exploration for these deposits.

During the 1960’s the prevalence of komatiitic magmatism during the Archaean was recognised and, almost simultaneously, Ni sulphide deposits were discovered associated with these rocks in Western Australia. In retrospect, the detailed studies undertaken by geologists working on the mines, and the recognition that the mineralization occurred in surface, or near-surface conduits through which the major magma flow had been channeled (Figure 2), broke the Sudbury straightjacket and opened our minds to new environments of deposition.

The importance of a dynamic hydraulic regime and the focusing of magma flow as processes leading to the separation and concentration of liquid sulphides from magma, rather than static gravity-driven settling, were appreciated for the first time. Additionally, the importance of the presence of nearby sulphide-bearing sediments became clear. Studies on the Noril’sk deposits in Siberia had suggested that the recognition of chalcophile element depletion in source rocks for magmatic sulphide deposits could aid in exploration (Figure 3).

The precise details of the Noril’sk model have given rise to considerable discussion; Latypov (2002) pointed out that the ores were hosted by olivine-bearing rocks while the Nadezhdinsky and Morongovsky volcanics were too siliceous to be in equilibrium with olivine, Arndt et al (2003) concluded from new Os, Nd and Sr isotopic data that the metals in the ores were unrelated to the metals missing from the Nd volcanics, and Lightfoot & Keays.
(2005) argued for a deep-seated genesis of the mineralization. Figure 4 (1)-(4) shows a scenario in which olivine in ore-bearing intrusions is picked up by magmas passing through partially consolidated cumulates, and Arndt et al.’s principal argument, based on Os isotopes is accounted for by re-equilibration of the sulfides with magma containing less-radiogenic Os.

The discovery and developing understanding of the Voisey’s Bay deposit ten years ago confirmed many of the ideas that had been developing over the previous 30 years. The bulk of the ore is located in the dynamic environment of a dyke connecting a lower intrusion, where sulphides had developed, with an upper intrusion. More than one pulse of magma has passed through the dyke, and the focusing of this flow has enabled later magma to rework, upgrade
and concentrate early-formed, low tenor sulphides. The Ni content of olivines in the Voisey’s Bay troctolites provides evidence of both early chalcophile depletion and the passage of later, less-depleted magma up the dyke. One of the most characteristic features at Voisey’s Bay is the igneous breccia which bears testimony to the interaction of troctolitic magma with the country rocks. The Voisey’s Bay magmatic environment is in stark contrast to that at Pants Lake, 80 km to the south. Here very similar magma has interacted and formed identical breccias with identical country rocks to those at Voisey’s Bay. Magmatic sulphides have been formed, and occur principally at the base of the sills. What is lacking is the focused flow that occurred to the north, and the sulphides remain widely dispersed with low Ni tenors, never having been reworked by later magma pulses.

In conclusion, it is now appreciated that the principal requirements for the formation of a magmatic Ni-Cu sulphide deposit are (i) a primitive (=hot) mafic/ultramafic magma, (ii) country rocks that are sulphide-bearing, (iii) evidence, geochemical and/or geological, of the interaction of the magma with the country rocks, (iv) a structure that has focused magma flow and (v) evidence of repeated magma flow within the structure.

REFERENCES


The relationship between large deep mafic sills, crustal contamination and the formation of Ni-(Cu) and IOCG deposits

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ABSTRACT: The Ossa Morena Zone (SW Iberia) hosts an unusual suite of ore deposits, including magmatic Ni-(Cu) and IOCG mineralization. These deposits are interpreted to have a relationship to a deep mafic sill intruded in the middle crust. Interaction of mafic magmas with crustal rocks produced immiscible sulphide-rich melts and water-rich melts. The latter exsolved large amounts of Fe- and CO₂-rich brines that were responsible for widespread albite-actinolite alteration and IOCG mineralization.

KEYWORDS: Geochemistry, Ni, Cu, Au, Fe, mafic sills

1 INTRODUCTION

In the Ossa Morena Zone (OMZ, SW Iberia), magmatic Ni-(Cu) and iron oxide-copper-gold (IOCG) deposits are contemporaneous with voluminous metaluminous calc-alkaline magmatism of Variscan age. This magmatism is related to the oblique collision between Gondwana and an exotic terrane, represented by the South Portuguese Zone, in late Devonian-Carboniferous times. Classical models suggest that most of the magmas formed overlying a subducting slab in a scheme somewhat similar to that of Pacific-like convergent margins. However, the area lacks significant volcanism and porphyry and epithermal deposits suggesting that the classical subduction-related magmatism and metallogenesis cannot be applied here.

Below the OMZ there is a deep (10-15km) seismic reflector (IRB) (Simancas et al 2003). It probably corresponds to a giant but discontinuous basaltic sill intruded during Variscan times along a detachment zone in the middle crust, and in which many of the structures of the area are rooted. This large intrusion probably controlled both the Variscan magmatism and ore-forming processes in the area (Tornos & Casquet 2005). This magmatic body only crops out in the southernmost OMZ (Aracena-Beja Massif, Fig. 1). Our interpretation is that the IRB controlled Variscan magmatism and hydrothermal circulation, leading to the unusual association of ore deposits.

2 GEOLOGIC SETTING AND ORE DEPOSITS

The geology of the OMZ includes a thick sequence of dark slate, quartzite and amphibolite (Serie Negra) overlain by a syn-Cadomian orogenic sequence of calc-alkaline andesite-rhyolite volcanic rocks, slate and limestone (late Neoproterozoic-early Cambrian) and limestone, slate, sandstone and alkaline-tholeiitic bimodal volcanic rocks belonging to a rift related sequence of Cambrian age. Younger sediments are scarce and are only found in the cores of synclines or in grabens. Magmatic rocks are related to both the Cadomian and Cambrian events, but the more voluminous magmatism is that related to the Variscan orogeny. These plutonic rocks occur as discrete epizonal plutons ranging in composition from ultrabasites to granite but the most common rock types by far are diorite to tonalite.

The area is rich in albite-bearing magmatic rocks. They occur as subvolcanic stocks representing the roots of the Cambrian volcanic systems but are also related to the Variscan rocks.

Variscan deformation in the OMZ is dominated by thick-skinned thrusts and large faults, all of which have an important lateral displacement suggesting that deformation took
The OMZ hosts several hundreds of showings that have made it a leading producer of Pb, Zn and Fe. Nowadays, exploration is mainly focused on Ni-Cu magmatic ores and IOCG deposits.

Ni-(Cu) showings are common in both the Cadomian and Variscan plutonic rocks of the OMZ, but the most remarkable deposit is Aguablanca. This deposit is located in a subvertical, highly discontinuous, irregular body in which massive sulphides cement fragments of ultramafic rocks. This high-grade ore is surrounded by gabbro to norite with disseminated sulphide ore. Fragments in the breccia are heavily dominated by pyroxenite, and only sporadic fragments of other compositions are found. They include host rocks, skarns and some olivine-rich ultramafic rocks. This deposit is interpreted to have formed via the disruption of a deep, layered magmatic complex by injection of molten sulfides to epizonal levels, through a localized pull apart structure in the overall compressive setting (Tornos et al. 2006). Lithogeochemistry and isotope geochemistry trace a major crustal contamination that obliterates the original juvenile values of the magmatic rocks. High $^{87}\text{Sr}/^{86}\text{Sr}$ (0.708-0.710) and low $^{143}\text{Nd}/^{144}\text{Nd}$ (0.512-0.513) values are accompanied by typical crustal signatures of δ$^{34}\text{S}$ (7.4‰), Pb (µ, 9.6-9.8) and Os (γ Os, 40-65) (Casquet et al. 2001; Tornos & Chiaradia 2004; Mathur et al. unpub. data).

Iron oxide deposits, although not large, are widespread in the OMZ. Some of them are exhalative in the Cambrian sequence but others ones are clearly replacive and share many features with the IOCG style of mineralization. They are replacive with respect to the late Neoproterozoic-early Cambrian synorogenic sequence, mainly interbedded calc-silicate rocks and slate; where carbonate rocks are present, they develop large calcic and magnesian skarns. As a whole, they show a vertical zonation. Deep Cu-Au-poor magnetite-rich systems (Colmenar, Berrona, Monchi) are associated with albite-actinolite alteration, and adjacent to

Figure 1. Geologic setting of the most significant Ni-Cu and IOCG deposits of the Ossa Morena Zone, showing the ages of individual deposits and related metaluminous plutonic rocks (in ellipses). Data from Romeo et al. (2006), Stein et al. (2006) and the compilation of Tornos & Casquet (2005). Modified from Tornos & Casquet (2005).
albite-rich magmatic rocks. Shallow systems (Cala) are richer in Cu-Au, have a biotite-sericite-chlorite-ankerite alteration and are apparently unrelated to intrusions. In both cases, the mineralization shows a major tectonic control (Tornos & Casquet 2005; Carriedo et al 2007).

Fluid inclusion and isotope data show that fluids related with the IOCG deposits are very heterogeneous, always hypersaline and sometimes enriched in CO₂-CH₄, and underwent complex processes of unmixing-mixing. Fluids in the deep systems are characterized by relatively heavy $\delta^{18}$O values (9-15‰) and $\deltaD$ (-35 to -30‰) signatures within the metamorphic field but close to magmatic values. In shallow systems they show O-D values that indicate mixing with surficial waters. However, all Nd ($\varepsilon$Nd, -8 to -4; Tornos & Casquet 2005), Pb (µ, 9.6-9.9; Tornos & Chiaradia 2004) and Os ($\gamma$Os, 380; Stein et al 2006) isotopic values are indicative of a large crustally-derived component. Sulphur ($\delta^{34}$S, 3.6 to 20‰) is also mostly derived from the host metasedimentary sequence.

Dating of hydrothermal and magmatic rocks (in progress) shows that most of them are contemporaneous. Variscan mineralization ranges in age from ca. 374 to 340 Ma while magmatic rocks are near 340 Ma (342-338; see a compilation in Tornos et al 2005 and Romeo et al 2006). These ages are also equivalent to those of the mineralization at Aguablanca (Spiering et al 2005; Romeo et al 2006) and those of the deep sill (336±2 Ma; Tornos et al 2006). However, there is not always a direct relationship between magmatism and mineralization. For example, Re-Os dating of magnetite at the Cala orebody show that at least some of the magnetite mineralization predated by the adjacent plutonic rocks some 20 Ma (Stein et al 2006).

3 ORE FORMING PROCESSES IN THE OMZ

Geological and geochemical data on mineralization and related rocks in the OMZ suggest a scenario in which the intrusion of the mafic sill had a critical influence on the ore forming systems. Crustal contamination of deep mafic magmas intruded in the middle crust is responsible of the formation of both IOCG and magmatic Ni-(Cu) deposits in the OMZ. Intrusion of juvenile magmas into water-bearing low grade metamorphic slate produced widespread dehydration of the metamorphic rocks but wa- ter-enrichment in the magma was accompanied by assimilation of large amounts of host rocks.

The contamination was so intense that geochemical signatures of mafic-intermediate rocks are controlled by those of the crustal rocks. Contamination favored the formation of sulphide-rich magmas, the protore of the Aguablanca orebody. However, it also promoted the formation of fluid-rich mafic intermediate magmas that exsolved hypersaline, iron-rich and CO₂-bearing brines. These brines were probably responsible for sodic autometasomatism and formation of albitite on igneous rocks, widespread albitite-actinolite-magnetite hydrothermal alteration and related mineralization (Fig. 2).

4 CONCLUSIONS

The intrusion of the IRB controlled the metallogenic evolution of the OMZ. It inhibited the formation of intermediate, relatively dry, calc-
alkaline magmas but favored the formation of highly contaminated more basic and water-rich magmas. These magmas intruded along major crustal discontinuities to shallow levels and exsolved large amounts of hypersaline, usually CO$_2$-bearing, brines that formed large IOCG-like hydrothermal systems. Crustal contamination also favored immiscibility of sulphide-rich magmas, which used the same channel ways as silicate melts and hydrothermal fluids to ascend to shallow levels in the crust.

Deep sills perhaps similar to those forming the IRB system can be common in transpressional settings, substantially modifying the heat flow, magmatic regime and mineralization in converging terranes. A magmatic-hydrothermal system similar to that proposed here could be important in other IOCG-rich provinces. However, the intense deformation and metamorphism that has affected Proterozoic terranes has probably masked the original relationships.

ACKNOWLEDGEMENTS

The study was funded by the DGI-FEDER project BTE2003-290 and the IGME. We thank C. Conde, L. R. Pevida, H. Stein and C. Maldonado for their help during the realization of this work.

REFERENCES


ABSTRACT: Strong commodity prices in the last few years have led to a remarkable renaissance of uranium exploration in Labrador, focused in a complex and geologically diverse region known as the Central Mineral Belt (CMB). Potentially economic epigenetic U deposits are mostly hosted by supracrustal rocks of Palaeoproterozoic and Mesoproterozoic age, and are difficult to place in the traditional pantheon of uranium deposit types. Recent exploration work implies that structural controls are important in some examples, but there is also empirical evidence for a primary link to U-enriched felsic volcanic sequences. For some, parallels have been drawn with IOCG environments, suggesting a role for magmatic hydrothermal fluids, and at least one example may be associated with a significant unconformity. It seems likely that the Labrador CMB represents a region in which U (and other lithophile elements) were repeatedly and sequentially concentrated by hydrothermal processes. The current exploration boom lends impetus for systematic research studies that may ultimately lead to refined genetic models that may be applicable elsewhere.

KEYWORDS: Uranium, Mineralization, Labrador, Exploration, Epigenetic, Hydrothermal

1. INTRODUCTION

In the last few years, Labrador has become an important area for uranium exploration in the Canadian Shield, second only to the Athabasca Basin of Saskatchewan. Uranium in Labrador is not a new development, for parts of the territory have a long history of such exploration. But as is always the case, renaissance leads to new discoveries and new ideas. This contribution provides an historical overview, outlines the known (or suspected) geological context of deposits, and highlights the most significant exploration results.

2. FIFTY YEARS OF EXPLORATION

Uranium mineralization was first discovered in Labrador in 1954, and the high-grade Kitts deposit was discovered in 1956. Uranium exploration in the area that would later become known as the Central Mineral Belt (CMB) intensified in the 1960s and 1970s. In 1968, British Newfoundland Exploration (Brinex) discovered the Michelin Deposit, which remains the single largest resource in the CMB. In the 1970s, Shell Canada discovered potentially important uranium deposits at Moran Lake.

In the mid-1970s, Brinex moved towards commercial development of Kitts and Michelin. The proposed development failed because the price for U3O8 collapsed dramatically in 1976, and because of environmental concerns. Market conditions halted exploration for uranium in Labrador for the next 25 years. By the dawn of the 21st century, mineral rights to defined deposits such as Michelin and Moran Lake had lapsed, and the lands were open for staking. At this time, there was some interest in grass-roots exploration for iron-oxide-copper-gold (IOCG) deposits in parts of the CMB. As part of a wider land acquisition, Altius Minerals acquired the rights to the Michelin Deposit and Lewis Murphy staked the Moran Lake deposits. The Kitts deposit was by this time part of a land claims settlement with the Inuit people of coastal Labrador (Nunatsiavut).

The acquisition of these areas in a time of low commodity prices proved to be prescient, for a steady increase in U3O8 prices since 2000 has since fundamentally changed the economics of uranium in Labrador.

The initial exploration effort was directed at obtaining more precise resources estimates for known deposits (i.e., to NI 43-101 standards),
and towards expanding resources by drilling at greater depths and along strike. The most impressive results are at Michelin, where exploration by Aurora Energy has increased the total resource fivefold, to 86 million pounds of U₃O₈. Work at the Moran Lake C deposit by Crosshair Exploration has also expanded resources significantly. The most impressive results are at Michelin, where exploration by Aurora Energy has increased the total resource fivefold, to 86 million pounds of U₃O₈. Work at the Moran Lake C deposit by Crosshair Exploration has also expanded resources significantly. The Kitts Deposit remains dormant, but additional resources are likely present at depth, and will be explored when Nunatsiavut opens the area to exploration. Regional geophysical surveys and prospecting have detected several previously unknown uraniferous zones, some of which have now advanced to the stage of formal resource definition. Although some are broadly analogous to known deposits such as Michelin, others are in geological environments that were not previously considered prospective for uranium. These results have expanded the rather arbitrary boundaries of the CMB, and have led to staking in many other parts of Labrador.

3. REGIONAL GEOLOGY

Labrador (Figure 1) contains sections of the Superior and North Atlantic Archaean cratons, separated by a wide tract of Palaeoproterozoic rocks assigned to the Churchill Province. These are bounded to the south by Palaeoproterozoic and Mesoproterozoic orogenic belts of the Makkovik and Grenville provinces, respectively. Uranium occurs in many parts of the territory, in a wide range of environments, but the most important examples are all located within the CMB, a loosely-defined area at the intersection of the Nain, Churchill, Makkovik and Grenville provinces (Figure 1). The CMB is defined mostly in terms of several Palaeoproterozoic and Mesoproterozoic supracrustal sequences containing low-grade sedimentary and volcanic rocks, but it also includes voluminous plutonic suites and older (largely Archaean) basement rocks. The CMB has a very complex evolutionary history and the timing of some important deformational and magmatic events lacks precise definition. Figure 2 provides a general summary of its geology and the setting of U mineralization (after Ryan, 1984; Kerr et al., 1996; Wilton, 1996, Wardle, 2004).

The basement to the CMB is probably composed of Archaean rocks equivalent to the adjacent Nain Province. The oldest supracrustal rocks are mafic volcanics and sedimentary rocks of the 2200-2000 Ma Moran Lake Group and Post Hill Groups (the latter was formerly known as the Lower Aillik Group), believed to have formed as a passive margin sequence following rifting. These were variably deformed, and intruded by granitoid rocks prior to the deposition of the ca. 1860 Ma Aillik Group, which is dominated by felsic volcanic and volcanioclastic rocks. Strong deformation during the main phase of the ca. 1800 Ma Makkovikian Orogeny affected all the above, and this event also generated large volumes of syn- and post-tectonic granites. More local granitoid magmatism occurred ca. 1720 Ma. Voluminous magmatism occurred throughout the CMB at ca. 1650 Ma, forming the Trans-Labrador Batholith (TLB). The sedimentary and volcanic rocks of the Bruce River Group unconformably overlie the older Moran Lake Group, and their ca. 1650 Ma age implies that they are in part a carapace to the TLB.

The youngest supracrustal sequences in the CMB are the ca. 1330 Ma alkaline volcanic rocks of the Letitia Lake Group, and the overlying Seal Lake Group (ca. 1270 Ma), which includes varied (terrestrial) sedimentary rocks and mafic volcanic rocks. The Seal Lake Group is well-known for numerous Cu occurrences. The Letitia Lake Group contains some rare-metal (Zr, Be, REE) occurrences. Both of these younger sequences also host minor U mineralization. The southwestern portion of the CMB lies within the Grenville Province, and was affected by distal deformation related to this 1000-900 Ma orogenic event. However, there appears to be no plutonism or significant metamorphism of this age within the CMB.

4. URANIUM MINERALIZATION

Uranium occurs in practically all major components of the CMB, but the most significant deposits are hosted by supracrustal sequences, notably in the Post Hill, Aillik and Bruce River Groups (Figure 2).

In the Post Hill Group, the Kitts Deposit (~0.17 Mt at 0.7% U₃O₈) and related zones are hosted by graphitic, ferruginous, pelitic metasedimentary rocks. The same unit hosts synmagmatic (but barren) massive sulphides, and the U mineralization is associated with strong hematitic alteration. Early models viewed the U as a synmagmatic component of the protolith shales, but subsequent work suggests that it is of epigenetic hydrothermal origin (Wilton, 1996). Reduction of fluids by carbon and sulphides
provided a quasi-stratigraphic control on U precipitation. Structural complexities suggest that the relatively ductile host rocks are also an important zone of deformation and translation, but the timing of this with respect to the mineralization is less clear. Kitts locally contains exceptionally high-grade material, containing up to 20% U3O8.

In the Aillik Group, the most important U mineralization is hosted by felsic metavolcanic rocks. The largest deposit is Michelin in which low grades (0.1 to 0.4% U3O8) are compensated by large size, continuity and structural predictability. The deposit as a whole is conformable with compositional layering in its strongly-deformed host rocks, and has traditionally been thought of as broadly syngenetic (Gower et al., 1982). The mineralized zone has a remarkably consistent dip and plunge, such that its location may be accurately predicted during deep drilling. The importance of strong deformation in controlling its geometry may have been underestimated in the past, and the uranium may have been introduced syntectonically, in the same way that gold is deposited in typical mesothermal shear-zone environments (O’Dea, 2005; Valenta, 2006). Alteration at Michelin is dominated by sodic metasomatism coupled with locally intense haematization. The relationship between mineralization, alteration assemblages and the strong deformation is a subject of much debate, and this holds the key to future genetic models. Michelin, and nearby mineralized zones of similar character, do not have obvious analogues in the traditional pantheon of uranium deposit types. There are also reports of disseminated U mineralization in alaskitic granitoids within the Nain Province, outside the traditional confines of the CMB. Possible links between U mineralization and evolved granites are also indicated by the association of U with F and Mo in the eastern CMB (Gower et al., 1982; Wilton, 1996). The association between U and felsic volcanism has led to exploration of alkalic flows in the Letitia Lake Group, and in the similar (but younger) alkaline volcanic and pyroclastic rocks of the Nuclavik Caldera north of the CMB. Both areas host Zr, Y and REE.

The basal conglomerate-sandstone sequence of the Seal Lake Group in the western CMB hosts a potential unconformity-style U deposit at Stormy Lake. Here, the underlying Bruce River Group volcanic rocks may represent a potential source of leached uranium. There has been exploration of similar Mesoproterozoic cover sequences elsewhere in Labrador, notably the older (pre-1440 Ma) Sims Formation of western Labrador (Figure 1).

5. GENETIC ASPECTS AND CONTROLS ON MINERALIZATION

Uranium mineralization in the CMB is characterized by a diversity of style and host rocks, and it is naïve to suppose that a single genetic model can explain all its variations. Previous models for deposits such as Kitts and Michelin, suggested that they were deposited from fluids associated with Aillik Group felsic volcanism (e.g. Gower et al., 1982; Wardle, 2004). The importance of structural controls on at least the geometry of some deposits suggests that these concepts need rethinking. However, the timing
of uranium deposition is not necessarily the same as that of shear zone development. Uranium showings are more abundant in the felsic volcanic rocks of the Aillik Group than in any other unit, and these are also regionally enriched in uranium. They likely play an important role as sources of uranium, even if the fluids were not synvolcanic. The presence of U in undeformed plutonic rocks (including some of possible 1650 Ma age) suggests that U was mobilized and deposited in multiple episodes. Similarly, mineralization at Moran Lake must postdate the ca. 1650 Ma host rocks. The mineralization in the basal Seal Lake Group must in turn be an even younger event, possibly Grenvillian. There is independent evidence from U-Pb isotopic studies for widespread mineralization ca. 1740 Ma, with some remobilization ca. 500 Ma (Wilton & Longerich, 1993). Wardle (2004) suggested at least four periods of uranium mobilization and precipitation.

Like many metallogenic provinces in which incompatible (or “lithophile”) elements are important, the CMB of Labrador seems to represent an area in which U has been repeatedly and perhaps sequentially concentrated and locally redistributed. There are possible discrete events of late Archaean (?), Palaeoproterozoic, Mesoproterozoic and perhaps Neoproterozoic-Palaeozoic age. Clearly, much remains to be learnt about the timing and origins of individual deposits. The current exploration boom has reawakened interest in this area and its unresolved metallogenic questions. It is hoped that the resultant diverse research effort including corporate data, university research projects and regional government geoscience will improve our understanding in years to come, and allow concepts from Labrador to be applied elsewhere in the world.

REFERENCES


Valenta, R. 2006. Personal communications.


Uranium deposit models in the Western part of the mid-European Variscan belt

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ABSTRACT: The Western part of the mid-European Variscan belt host numerous uranium deposits of two main types: (i) vein type deposits mainly of Permian age and mostly hosted in uraninite-rich two mica peraluminous leucogranites, rarely in enclosing metamorphic rocks, and also rarely in high-K calcalkaline granites, and (ii) sediment hosted deposits of Permian and Tertiary ages in which U deposition is strongly controlled by organic matter. The last uranium mine has closed in 2001, because of the very low uranium prices, but significant uranium resources are still available.

KEYWORDS: uranium deposits, Variscan, granites, vein type, episyenites, sediment hosted

1 INTRODUCTION

The French Massif Central (FMC) belongs to the Western part of the mid-European Variscan belt. After the resorption of existing oceanic basins by subduction during the Silurian, then during Carboniferous-early Permian the tectonic regime shifted from compressional to extensional. Most uranium deposits were formed in extensional settings during Early Permian (at about 270 Ma) over about 4000 km, from southern Portugal and Spain (Fig. 1) to Erzgebirge (SE Germany and Czech Republic). The Post-Variscan mineralizing events recorded thermal flows in the lithosphere linked with early Alpine events leading to the formation of uranium deposits in siliciclastic sediments with the Lodève deposit, and during the Tertiary as a distal consequence of the Alpine orogeny with the Coutras deposit.

2 PREVARISCAN BEDROCK U CONTENT

Prevariscan bedrock enrichment is evidenced by the very good correlation observed between heat flow and heat production in the western part of the Variscan orogen in Brittany (Fig. 2 and 3) (Vigneresse et al., 1987).

The slope of the correlation indicates that the thickness of the U-Th-K enriched layer is of about 15km, a thickness largely exceeding that the collision between continental blocks during Devonian-early Carboniferous, led to the formation of crustal-scale nappe structures and granite intrusions. Although these granites were enriched in uranium they did not yield significant mineralization at the magmatic stage. of the granitoids (2 to 6km) according to the modelling of the gravimetric data. Therefore, this High Heat Flow Heat Production (HHFHP) Belt corresponds to a segment of the crust 2 to 3 times enriched in radioelements relative to average upper crust. The radioelement enrichment concerns not only the granites but also the whole metamorphic pile. The anomalous heat flow and heat production is caused for more than 50% by U enrichment. It has not been possible to define a similar correlation in the Limousin because heat flow is strongly disturbed there by Quaternary volcanism. However, it seems highly probable that the HHFHP Belt continues at least into the Limousin area.

U contents higher than Clarke values have been also measured in Lower Palaeozoic acidic orthogneisses of high-K calcalkaline origin in the Limousin which may have represented one of the possible sources for the Variscan U-enriched granites (Cuney et al., 1990).

3 URANIUM ENRICHED GRANITES

Two types of granites are enriched in U in the Western part of the Variscan belt: metalu-
minous high-K calc-alkaline granites and muscovite-biotite peraluminous leucogranites. Each of them is characterized by a specific accessory mineral paragenesis of critical importance for the genesis of U mineralization associated with those granites (Cuney & Friedrich, 1987).

3.1 Peraluminous two mica leucogranites.

They are characterized by Al/Na+K+2Ca > 1.1 reflecting the presence of one or several peraluminous minerals: sillimanite, andalusite, topaz, Al-rich biotite, muscovite, garnet, cordierite. With increasing fractionation peraluminosity and U, Sn, W, Ta, Rb, Cs, Li, F, P contents increase, whereas Th, REE, Y, Zr and Nb/Ta ratio decrease. Because of their strong peraluminous character, they are classically related to S-type granites. However, S-type granites present highly variable mineralogical and geochemical characteristics resulting from a large variety of genetic processes. Typically, peraluminous leucogranites form abundant post-torogenic plutons in continental collision belts, as in the mid-European Variscan belt, the SE China Yanshanian belt, the Tertiary high Himalayan leucogranite belt and have a restricted variation of chemical composition. They result from low degree of partial melting of metasediments or acidic metavolcanics, followed by crystal fractionation.

3.2 Metaluminous high-K calcalkaline granites.

They are characterized by Al/Na+K+2Ca < 1.1 reflecting the presence of Ca-rich, Al-poor minerals such as pyroxene, amphibole, titanite.
They have relatively high REE, Y, Zr, Th, Pb contents compared to leucogranites. They correspond to I or A2 granites. They occur in both post- and an-orogenic geotectonic settings.

4 U BEARING ACCESSORY MINERALS

3.1 Peraluminous two mica leucogranites.

Variscan U deposits are spatially and genetically mainly related to U-rich peraluminous leucogranites. U is dominantly hosted by Th-poor uraninite. The low solubility of monazite and zircon in peraluminous low temperature melts produce the early fractionation of Zr, Th and REE from the melts, allowing the crystallization of Th-poor uraninite which represents an easily leachable source of the metal (Cuney & Friedrich, 1987, Friedrich et al., 1987).

4.2 Metaluminous high-K calcalkaline granites.

High K-calcalkaline granites are always enriched both in U and Th (with a Th/U ratio close to 4), but to variable extend in relation with the degree of U enrichment of the source. Higher melt temperature and metaluminous composition compared to peraluminous leucogranites lead to a lower fractionation of high field strength elements. Higher Ca contents of the melts, induce the crystallization of Ca-rich minerals (amphibole, titanite, allanite) able to incorporate large REE proportions together with minor Th and U contents. Then, Th crystallizes together with U in thorite which incorporates up to 30 wt% UO₂. Uranothorite represents a refractory U source for hydrothermal fluids, if they circulate soon after granite emplacement (Cuney & Friedrich, 1987). Thorite as other Th-U-rich silicates may act as U source when they become metamict. The alteration of the silicate structure by α-recoil, allows U to be leached very easily. In the most fractionated facies uraninite may crystallize as well as complex Nb-Ti-U minerals. Hence, high K-calcalkaline granites may be associated with U-deposits but more rarely than leucogranites.

5 URANIUM DEPOSITS

3.1 Peraluminous two mica leucogranites.

U-deposits occur as veins or disseminations (episyenites) within the granites more rarely in the enclosing metamorphics. Episyenites are porous rocks formed by quartz dissolution (Cathelineau, 1986) at 305 Ma (Scaillet et al., 1996). The alteration fluid results from the condensation of vapors deriving from infiltrated meteoric waters (Turpin et al., 1990), heated up to 400°C until boiling (El Jarray et al., 1994). U ore is deposited during a hydrothermal event corresponding to the Permian extension (270 Ma). Locally, older ages have been recorded in deposits enclosed in metamorphic rocks enclosing a peraluminous leucogranites as at Pen Ar Ran. Younger ages also exist but they mainly correspond to U remobilization in response to the opening of the Atlantic Ocean and the Alpine orogenesis (Cathelineau et al., 1990).

The Limousin U district, essentially with the Saint-Sylvestre –Western Marche leucogranite complex (Leroy, 1978; Cuney et al., 1990), is the largest one for this type of mineralization (about 35 000 t U). Late magmatic shear-zones have initially controlled the emplacement of late uraninite-rich leucogranites in the granite complex (Friedrich et al., 1987; Cuney et al., 1990). Highly fractionated melts and fluids, enriched in U, were expelled from these late leucogranites. The shear zones enriched in uraninite, were the most favourable areas for the formation of the major U ore bodies during
Permian. Stable isotopic studies (Turpin et al. 1990) indicate that infiltrated meteoric oxidizing fluids, were able to leach those uraninite preconcentrations, at low temperatures (160°-180°C). Mixing of the meteoric fluids with connate reducing waters issued from presently eroded overlying Permian basins led to the precipitation of U in fractures and episyenites.

4.2 Metaluminous high-K calcalkaline granites.

Some vein type U deposits in Morvan and Montagne Bouronnaise (NE French Massif Central, Fig. 1) are hosted in high-K calcalkaline granites. But, evidences of peraluminous leucogranites intrusions at depth are generally recorded in their vicinity, such as for the Bois Noirs deposit (Cuney, 1978). Therefore peraluminous leucogranites may also represent the main U source for these deposits.

4.2 Permian and Tertiary continental basins.

Deposition in Permian and Tertiary siliciclastic intracontinental basin resulted from the conjunction of large volumes of outcropping U-rich granite which could be leached by oxidizing meteoric waters, the presence of a U-rich silicic volcanic component in some of these basins and the presence of organic matter in the sediments providing a source of reductants for U deposition (Pagel, 1990). The Lodève tonolithologic deposit (southern Massif Central) is the largest sedimentary hosted deposit. It consists of a series of strata-bound and fault-related ore bodies of hydrothermal origin. Significant amounts of an acid volcanic component and eighteen cinerite beds are known in the Lodève basin and they were probably the main source of the U. The main mineralizing stage was linked with the activity of a basin-scale, fault-related low-temperature Liassic hydrothermal system that overprinted earlier concentrations (Lancelot et al., 1995).

The largest U deposit in Tertiary sediments is of tabular type and located at Coutras, north of Bordeaux (Landais & Connan 1980).

REFERENCES


Industrial Minerals in Newfoundland and Labrador, Canada

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ABSTRACT: The industrial-minerals industry is a small, but significant, part of the mineral industry in Newfoundland and Labrador. For 2007, the forecast for 2007 of the value of industrial minerals in the province is C$27.3 million and most of the products are exported to the rest of Canada and the USA. The major components are high-calcium limestone and high-magnesium dolostone that are exported for use in the chemical industry. Some limestone and dolostone is used within the province as agricultural lime, and in the production of fluxed iron-ore pellets for export. Barite is recovered from mine tailings and used as drilling mud in the oil industry. Gypsum is used in the local manufacture of wallboard; and pyrophyllite is used in the ceramics industry and as a filler in paints. High-purity quartzite (>99.5 % silica) is quarried in Labrador and exported for the production of silicon metal. Peat is processed in central Newfoundland where it is converted to an oil-absorbent material mainly for export and also as agricultural peat for export and local use. Not currently in production is the dormant fluorspar mine at St. Lawrence, in southern Newfoundland, which has significant reserves of fluorspar. The provincial Geological Survey has carried out numerous assessments of other potential deposits including dolostone and limestone, silica, talc and fluorspar. Sizeable deposits of limestone, dolostone and silica are indicated. Some of the reports on this research are available on-line via www.nr.gov.nl.ca/mines&en/. A summary report and mining statistics on the mineral industry in Newfoundland and Labrador is found at www.nr.gov.nl.ca/mines&en/mining/.

KEYWORDS: Newfoundland, Labrador, industrial minerals, dolostone, limestone, barite, gypsum, pyrophyllite, silica, peat, fluorspar.

1. INTRODUCTION

Industrial minerals in Newfoundland and Labrador are a small, but significant, part of the province’s mining industry. Much of the production is concentrated in western Newfoundland where there are extensive deposits of limestone, dolostone and also gypsum. Eastern Newfoundland hosts a producing pyrophyllite mine, and central Newfoundland produces barite drilling-mud for the offshore oil industry and peat products for use in oil-spill remediation and agricultural use. Dolostone is quarried locally, and used in the production of fluxed iron-ore pellets in Labrador City, Labrador. A relatively new operation in Labrador City produces high-purity quartzite for use in the production of silicon metal.

Locations of the various producers and potential producers in Newfoundland and Labrador are shown on the attached maps.

2. HISTORIC INDUSTRIAL-MINERAL PRODUCTION

Industrial-mineral production in the last 100 years has included limestone, dolostone, barite, fluorspar, gypsum and silica in now abandoned or dormant mining operations.

Limestone was quarried in western Newfoundland and exported to Canada for use in the production of iron and steel in Nova Scotia. Some limestone was also quarried for agricultural use. The former cement plant at Corner Brook in western Newfoundland used local limestone and shale in the production of Portland cement, mainly for the Newfoundland and Labrador construction industry.
Near-surface barite veins at Colliers Point, in eastern Newfoundland, were mined for the production of drilling mud to be used in the offshore oil exploration programs. However, problems with purity led to the demise of this barite operation.

The town of St. Lawrence, in southern Newfoundland, has a long history of fluorspar production. Mining of the fluorspar veins started in 1933 and was conducted by a subsidiary of Alcan for 44 years. Their operation closed in 1977 (see Howse et al., 1983). A subsequent attempt to restart the mining operation failed after a few years of production. The current owners of the property are Burin Minerals Ltd.

Gypsum mining was carried out near Flat Bay in western Newfoundland for about 35 years, most recently by Domtar Inc. The mine produced around 500,000 tonnes of gypsum annually, until it closed in 1987 due to reported problems with salt in the ore. The gypsum was used locally for the production of wallboard and also exported to Nova Scotia.

Silica (bedded quartzite) was quarried at the Villa Marie operation in eastern Newfoundland for use in the nearby phosphorus operation run by Albright and Wilson Americas. The silica was used as a flux in the reduction of phosphate ore imported from Florida. The phosphorus was then exported worldwide. Fine-grained silica from the operation was also used by the cement plant in Corner Brook. The silica quarry ceased production when the phosphorus plant closed in 1989.

3. CURRENT PRODUCERS

Current industrial minerals produced in Newfoundland and Labrador include high-calcium limestone, high-magnesium dolostone, dolostone, agricultural limestone and dolostone, gypsum for use in the production of wallboard, peat for industrial and agricultural uses, silica for silicon metal, barite for use as drilling mud, and pyrophyllite is currently used as a filler in the paint industry and in the ceramics industry. See www.nr.gov.nl.ca/mines&en/mining/.

The main producer of high-calcium limestone which is exported for use in the iron-ore industry, desulphurisation, lime production and precipitated calcium carbonate. The chemical grade dolostone is used in the production of iron ore pellets, in iron and steel production and dolomitic lime manufacture. The less pure limestone and dolostone are used as aggregate. The company is expected to produce about 2,000,000 tonnes of products in 2007.

Dolomite has been quarried by the Iron Ore Company of Canada at its Leila-Wynn quarry, near Labrador City, from 1992 to 2007. A new quarry, known as the Plateau dolomite quarry, will open in 2007-8. About 200,000 tonnes of dolomite are produced annually for the manufacture of fluxed pellets (DR iron-ore pellets) using the iron ore mined at Labrador City.

About 5000 tonnes agricultural limestone and dolostone are produced in western Newfoundland at Cormack by Island Aggregates and Ready Mix Inc. for use mainly in the farming industry in Newfoundland. This aglime is a by-product of their construction aggregate operation.

Gypsum is quarried in a small operation run by Galen Gypsum Mines Ltd. of St. Georges, Newfoundland. This seasonal operation produces raw gypsum for use in wallboard manufacturing by Lafarge Gypsum in Corner Brook, Newfoundland. It is estimated tonnage that
50,000 tonnes of gypsum will be produced in 2007.

Peat products are manufactured by Hi-Point Industries (1991) Ltd. at a facility that is adjacent, near Bishop’s Falls in central Newfoundland (see http://www.oclansorb.com/). The company produces an oil absorbent material, known as “Oclansorb”, in a variety of forms that are used in oil-spill recovery operations. The company also produces peat moss for agricultural and gardening uses.

High-purity silica is produced from bedded meta-quartzites, near Labrador City, by Shabogamo Mining and Exploration Ltd. This quarrying, screening and cleaning operation produces about 63,000 tonnes of crushed quartzite rock that is shipped by rail to Quebec, where it is the raw material for the production of silicon metal.

Barite is currently being recovered from mine tailings at the former Buchans base-metal mine in Central Newfoundland. Atlantic Barite Ltd. of St. John’s, Newfoundland, reactivated the former barite recovery operation in 2005 and has the capacity to produce 15,000 to 25,000 tonnes of barite annually.

Pyrophyllite ore is quarried by Trinity Energy and Resources Ltd. near St. John’s, in eastern Newfoundland (see www.tre.ca). The pyrophyllite is exported for use as filler in the paint and ceramics industries. The company expects to ship about 95,000 tonnes of pyrophyllite powder and aggregate in 2007.

4. POTENTIAL DEPOSITS

The west coast of Newfoundland contains extensive deposits of limestone and dolostone extending from Port au Port to the tip of the Northern Peninsula, a distance of over 400 km. The Geological Survey has carried out numerous investigations into the industrial potential of these carbonates, e.g., Dickson (2002a, 2003), DeGrace (1976) and Howse (2004). Several areas containing high-purity dolostone, limestone and marble suitable for industrial applications have been described. The Port au Choix dolostone prospect is the largest single deposit and contains an estimated 1 billion tonnes of chemical-grade high-magnesium dolostone (Dickson, 2003).

Silica deposits throughout Newfoundland and Labrador have also been assessed by the Geological Survey. Initially these surveys were designed to obtain a source of silica for use on the island and are summarized in Butler & Greene (1976). Most of the deposits they assessed are relatively low grade (<90 % SiO₂) and also distant from potential users on the island. However, this survey did discover the Villa Marie silica deposit that was used in the phosphorus reduction plant as a flux.

As a follow-up to one of the silica surveys, Dickson (2002b) carried out an assessment of a silica (bedded quartz arenite) prospect on the Northern Peninsula in the Highlands of St. John. The results indicated that the quartz arenite (or quartzite) was of fairly high grade, being generally over 95 % SiO₂, (see Dickson, 2004) with a potential tonnage of over 10 billion tonnes.

Small talc occurrences at Pine Cove are associated with serpentinized ultramafic rocks on the Baie Verte Peninsula, in northwestern Newfoundland, were examined by Howse and Way (2001). These small deposits had been known for many years and assessed by several mining companies. Although the grade was high, Howse & Way (2001) concluded that the known showings are too small for commercial production but indicated that the area had potential to contain more significant deposits.

A detrital garnet deposit in Northern Labrador is in the late-stage of assessment. This deposit is currently held by Freeport Resources
Inc. The deposit is a beach and marine sand deposit. Freeport Resources have taken a bulk sample for testing. Environmental impact studies and market analyses are ongoing. The garnets are suitable for use as an abrasive in sand blasting and sandpaper.

REFERENCES


NEW DISCOVERIES IN AFRICA

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Exploring for diamonds in the Democratic Republic of Congo

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ABSTRACT: Political stability over the last 5 years in Angola, the Democratic Republic of Congo (DRC) and the Central African Republic (CAR) has been accompanied by the introduction of new and more investor friendly mining codes in all three countries. It is estimated that up to 1997 some 853 million carats had been extracted from the DRC valued at some 34 billion US$. The current cumulative production for the DRC would be well over 1 billion carats. Diamonds in central Africa are found in both primary (volcanoclastic sequences associated with kimberlite craters) and secondary deposits (eluvial and alluvial sediments linked to the present and palaeo-drainage network).

KEYWORDS: Democratic Republic of Congo, diamonds, exploration, kimberlites, alluvial sediments

1 INTRODUCTION

The focus of diamond exploration in Africa has very much shifted to central Africa in recent years. Political stability over the last 5 years in Angola, the Democratic Republic of Congo (DRC) and the Central African Republic (CAR) has been accompanied by the introduction of new and more investor friendly mining codes in all three countries.

The growing gap between demand in diamond jewellery and the supply of rough diamonds has also made this part of African a major target for diamond exploration. And although central Africa has been subjected to exploration campaigns by the French (CAR and DRC), Belgians (DRC and Angola) and Portuguese (Angola) from the early 1900’s until the mid-1960’s, central Africa has seen very little application of modern exploration techniques. The end of unstable governments and post colonial wars has resulted in increased access to this region.

This has resulted in an influx of major and junior exploration companies into the region for various commodities. A slow but steady increase in the production of diamonds from existing alluvial and kimberlite resources, and the discovery of new deposits have been evident.

2 DISCOVERY BACKGROUND

The first diamond in central Africa was found in 1903 in the DRC. This led to the discovery of several barren kimberlites in the south eastern part of the DRC. However the first diamond linked to economic deposits was found in 1907 and this developed into the discovery of the Tshikapa alluvial diamond fields that started producing in 1912. Diamonds around Mbuji Mayi were only found in 1918 and mining there started in 1920. The Belgium company Forminière who was responsible for these discoveries also found the first diamonds in Angola in 1912. The first diamonds in the CAR were found in 1913 but diamond production only really started in the 1930’s.

Although the bulk of the diamonds have been extracted from the Mbuji Mayi deposits in East Kasai, these are of inferior quality. Interestingly it was only in 1948 that kimberlite was first described from these deposits and it was realised that most of the overlying ‘alluvial’ deposits had actually been highly weathered volcanoclastic material. There are big differences between diamonds from Mbuji Mayi, based on present market conditions valued at between 15 and 20 US$ per carat, and better quality diamonds derived from West Kasai.
around Tshikapa which are valued at between 200 and 300US$ per carat.

It is estimated that up to 1997 some 853 million carats had been extracted from the DRC valued at some 34 billion US$. The current cumulative production for the DRC would be well over 1 billion carats. Production of diamonds in the formal sector peaked at some 20 million carats per year in the 1960’s but this has steadily declined over the years. The majority of these diamonds were however generally of low value and mostly were probably derived from the primary resources at Mbuji Mayi.

The annual production in the CAR, all out of alluvial deposits, has been estimate at approximately 0.5 million carats per year over the last 15 year. In total the CAR has produced some 20 million carats of good quality diamonds of between 180 and 250 US$/carat.

Angola’s production has been steadily increasing over the years and particular with the opening of the Catoca kimberlite mine which alone is aiming to produce 5 million carat per annum. In addition to the Catoca mine there are several other kimberlites that have been producing diamonds and these include Camatchia, Camutue and Camagico. Angola’s total production since the early 1900’s is estimated to be around 105m carats. The value of the Angolan production, although varied is much higher than the DRC and in 1997 the value of its total cumulative production of 79 million carat was estimated to be around 12 billion US$.

3 KIMBERLITES

Diamonds in central Africa are found in both primary (volcanoclastic sequences associated with kimberlite craters) and secondary deposits (eluvial and alluvial sediments linked to the present and palaeo-drainage network).

The development and application of more advanced airborne remote technology has been instrumental in making central Africa more accessible for diamond exploration particular with improved geological models. The challenge to discover kimberlite pipes under substantial thicknesses of Cretaceous and Tertiary cover...
has been overcome both in Angola and DRC where several new kimberlite clusters have been found.

Dating of kimberlites in the DRC and Angola has identified four distinct intrusion ages and these are: 322, 133, 71 and 35 million years (Davis 1977, Fourie & Kiviets 2001).

The oldest known kimberlites in central Africa outside Gabon are the Carboniferous intrusions of Bas Congo, followed by the early Cretaceous kimberlites in the northeast Angola. Kimberlites with ages of around 70 million years are associated with the Mbuji Mayi cluster in southern DRC whilst the youngest group of kimberlites are in the Kundelungu cluster in southeast DRC. The kimberlites in Bas Congo are dykes and a small blow and these suggest that substantial erosion has occurred since the Carboniferous. The other kimberlites are well preserved with crater facies either in the form of volcanoclastic sediments or even crater lake sediments with fossils suggesting that very little erosion has in fact taken place since the Early Cretaceous.

4 Mesozoic/Cainozoic Cover and Alluvial Diamonds

Because the infill of the Congo basin has been ongoing whilst the kimberlites were emplaced, the history and relationship of the post-Gondwana stratigraphy and the Cretaceous intrusions is fundamental in the search for other primary sources. The Mbuji Mayi kimberlites for instance clearly cut across the Lower Cretaceous but have in places been overlain by Upper Cretaceous sediments. Similarly older kimberlites have been found under both Lower and Upper Cretaceous cover sequences in Angola. Examples of these various settings will be illustrated.

Although, the Congo basin has a record of sedimentary infill since the Proterozoic it is the late Mesozoic events that have a direct bearing on the distribution of the diamonds weathered out of the primary host rocks in northern Angola and the DRC.

The improved understanding of the post-Gondwana stratigraphy has produced upgraded geological models for the various alluvial settings (Pybus & Spaggiari 2006). For instance Cretaceous conglomerate are mineralised proximal to primary sources but upgrading under tropical weathering conditions during the Cainozoic has produced higher grade sediments in successive younger deposits. This is the reverse in southern Africa where the older terraces generally have higher grades (de Wit 1996).

Several authors have tried to correlate Mesozoic sediments across the basin from Angola in the south to the CAR in the north (Censier 1991) but the absence of suitable datable material makes this more speculative than factual.

More recent research has shown, based on palaeontological evidence, that the basin was submerged below sea level throughout the upper Mesozoic (Stankiewicz & de Wit 2006). The presence of similar fossils along the east coast of Africa and their absence along the west coast suggest that marine conditions were linked to the east. This implies that the Congo River drained into the Indian Ocean until the uplift of the East African Highlands in the Oligocene or Eocene. The central basin then became landlocked until it was captured in the Miocene by a river system draining into the Atlantic Ocean (Stankiewicz & de Wit 2006). This is supported by seismic studies of the offshore Congo Fan which suggests that during most of the Tertiary the sediment supply was only from small catchment areas in Congo Brazzaville and Gabon. It was only from the Early Quaternary that the Congo River has been the dominant source of sediment to this fan (Uenzelmann-Neben 1998). The change in the focus of the sediment accumulations is also reflected in the main basin where younger sediments occur progressively to the west.

The understanding of this regional switch in drainage direction and the relationship between stratigraphy and the timing of the various kimberlite intrusions are geological factors that will result in new discoveries of both primary and secondary deposits in the region.

REFERENCES


Fourie L.F. and Kiviets G.B. (2001). 40Ar/39Ar dating of phlogopite and kelyphitised garnet from the...
Tengo Kimberlite, Kundelungu cluster, DRC. GSC report KR01/0024.


The Tongon Deposit, Côte D’Ivoire – Randgold Resources Latest Discovery In West Africa.

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ABSTRACT: The Tongon Project is located in northern Côte d’Ivoire in the centre of the Senoufo greenstone Belt, some 628km north of the capital Abidjan within the 671 km² Nielle permit. Tongon is at the feasibility stage and benefits from nearby access to relatively well-developed transportation, telecommunications and power systems. The total inferred resource base is 35.96 million tonnes at a grade of 2.69 g/t Au for more than 3 million ounces of gold. The mineralization at Tongon occurs within two zones, the Northern and Southern Zones (NZ and SZ), over a cumulative strike length of 3.5km. The NZ Mineralization is found within a single zone, hosted in the immediate hangingwall of a 2 kilometre-long continuous graphitic shear zone which trends 250° to 260° and dips 80° to 70° northwest. This gold mineralization grades between 1.5g/t and 4.5 g/t over widths of 3 to 24m, and is associated with increased silicification, sulphidation and fine brecciation. The SZ mineralization is more complex and consists of multiple bodies, between 5 and 50 meters in width and grading 2 to 9 g/t over 1.5km of strike length. The mineralization is associated with a broad envelope of biotite-silica-tremolite-diopside-sericite-carbonate alteration within which occur brecciated and sheared bodies of disseminated arsenopyrite-pyrrhotite-pyrite-gold. In both zones, the mineralization is still open along strike and at depth. As part of the re-entry strategy in the northern zone of the country, an 8 hole (1,992 m) tactical diamond coring programme was completed at the Tongon project, from June to August 2006. A 30,000m diamond drilling programme started in March 2007 to form the basis for the final feasibility study which will allow a production decision and financing arrangements to be made within 2 years. Another 10,000m RAB programme will test the potential for the 10 other targets of the Nielle permit.

KEYWORDS: Tongon, Côte d’Ivoire, +3Moz, Northern Zone, Southern Zone

1 INTRODUCTION

The Tongon Project is located within the 671 km² Nielle permit (PRA 92) in central northern Côte d’Ivoire, some 628km north of the capital Abidjan and about 200km south-east of Morila Gold Mine (Mali). Randgold Resources Ltd, together with its country partner New Mining CI, owns 100% of the rights of Nielle permit. This area has historically been a zone of ancient prospectors’ activity with numerous small pits throughout it. BHP under Joint Venture with government agency Sodemi has carried out Regional work and limited detail exploration over an eight-year period (from 1988 to 1995). The original 1000 km Randgold Nielle Exploration Permit was granted by De-
cree No. 96-922 on the 29 November 1996. Randgold exploration activity on the project has occurred in several phases (Table 1) with total expenditures amounting to US$ 7.2 million from October 1996 to December 2006.

Since its initial appointment, the permit has been renewed on two occasions, and the second renewal granted on the 24 January 2002 for three years from the 1 December 2001 in which time Randgold Resources was required to complete a Type IV Feasibility and commit minimum expenditure of 1.4 billion CFA (US$2 million). Drilling was interrupted in September 2002 by the political conflict in the country.

<table>
<thead>
<tr>
<th>Method</th>
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<td>Rab</td>
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<tr>
<td>Ddh</td>
<td>59</td>
<td>12,095m</td>
</tr>
<tr>
<td>Aircore</td>
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</tr>
<tr>
<td>RC</td>
<td>28</td>
<td>2,556m</td>
</tr>
<tr>
<td>Water bore hole</td>
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<td>75m</td>
</tr>
<tr>
<td>Exploration pit</td>
<td>339</td>
<td>1,176m</td>
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</tbody>
</table>

Table 1: Work completed at Tongon grid

<table>
<thead>
<tr>
<th>Zone</th>
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<th>Mt</th>
<th>g/t Au</th>
<th>Moz</th>
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</thead>
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<td>NZ</td>
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<td>0.49</td>
</tr>
<tr>
<td>SZ</td>
<td>Inferred</td>
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<td>2.65</td>
<td>2.61</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>35.96</td>
<td>2.69</td>
<td>3.11</td>
</tr>
</tbody>
</table>

Table 2: Tongon mineral resources

A stand still agreement is presently in force with respect to the expiry of the permit. In 2005, following encouraging moves towards a resolution of the conflict, all aspects of the Tongon project were reviewed, updating the June 2002 pre-feasibility parameters to reflect December 2005 market conditions. An Inferred Resource of 35.96 Mt at a grade of 2.69 g/t for 3.11 Moz has been estimated at the Tongon project (Table 2) using polygonal wireframe estimate (NZ) and ordinary kriging and inverse distance squared methods (SZ).

<table>
<thead>
<tr>
<th>Drill line spacing</th>
<th>deepest mineralized intersections</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ 50m and 100m</td>
<td>200m below surface</td>
</tr>
<tr>
<td>NZ up to 300 meters</td>
<td>120m below surface</td>
</tr>
</tbody>
</table>

Table 3: Data spacing at Tongon grid

For the feasibility drilling programme, inter-hole spacing will be reduced to 50 m x 50m for both the SZ and NZ, and mineralized intersections will regularly reach 150mBS for the NZ and 200mBS for the SZ. The RAB programme will test the potential of the 10 other targets of the permit.

2. REGIONAL GEOLOGY

Côte d’Ivoire is situated entirely within the Leo Rise of West Africa. The western edge of the country is underlain by the 3.1 – 2.7 Ga. Archaean Man Domain whilst the remainder of the country comprises Palaeoproterozoic Birimian lithologies of the Baoule-Mossi Domain, which was affected by a major tectono-thermal event around 2.1 Ga.

The Ivorian Birimian consists of NE-trending litho-structural domains (Ashanti, Bondoukou, Bouake, Korhogo, Syama, and Odienne) separated by metasedimentary belts (‘overlap sequence’) and affected by 3 main episodes of deformation. The D1 fabrics, probably developed during NE-SW to N-S shortening, were later rotated anti-clockwise during D2. The complex D2 event is responsible for the main NNE trend and overall geometry (with NE to ENE thrust faults) and has involved major WNW - ESE shortening, which resolved at times into dextral transpression (for example, associated late N-S trending folds). The ‘overlap sequences’ shows evidence for D2 deformation only.

The Senoufo belt is a more than 200km long zone of NNE-trending greenschist grade supracrustal lithologies that extends across the country border into Burkina Faso. The belt which is bounded on either side by variably tectonised granitoid and gneisses has a distinct change in the S-N direction from 045° to 030°. Syn to late Birimian felsic to intermediate intrusive bodies occur throughout the region. The plutons may have intruded dilation zones (flexures in second order structures or at extensional intersections between first and second order structures).

Within the Tongon grid, the contact of the host rocks with the intrusive bodies is a classic intrusive cooling margin or is sheared, generally striking 230° in the SZ and 250° in the NZ, with 45° to 75° dips. Minor interbedded intermediate and mafic extrusions are mapped in the lower half of the belt.
3. NIELLE PERMIT GEOLOGY

On Landsat/Spot and airborne geophysical data, the dominant feature within the permit is a NNE trending Central Linear Belt (CLB) which is characterised by a relatively uniform magnetic low signature running along the axis of the Birimian package. A NNE to NE trending fabric is prevalent throughout the CLB while linear magnetic high margins are bounding the CLB both to the east and west. These are a series of regional first order belt bounding dextral shears that horsetail into and away from the contact with the surrounding granitoids and gneisses, particularly along the western margin of the belt. In the centre and south of the permit, the belt margins deflect around prominent elliptical magnetic highs termed the Magnetic Bodies (Figure 2), which acted as more competent rigid packages. The competent bodies are strongly dissected by anastomosing NE to ENE second order structures which splay into and away from the principal NNE shears. A late stage post-Birimian structural activity is thought to be associated with the presence of abundant NW trending cross-cutting faults which have resulted in minor sinistral dislocation.

For the presence of gold mineralization at Tongon grid, it is thought that a period of oblique structural reactivation may have occurred and preferentially localized along the pre-existing NE belt parallel first order structures. Progressive dextral shearing may have caused some clockwise rotation in the centre of the belt. This re-activates and step across the ENE second-order structures resulting in them adopting a more E-W orientation. Best dilations occur where ENE structures run at the margin of pluton due to contrast competency.
4. TONGON GRID GEOLOGY

The NZ and SZ gold mineralization is located in a dislocated segment of the component core zone in the centre of the Senoufo Belt. Gold mineralization shows a spatial relation with the sheared margins to the intrusives. Various regolith domains occur in the Tongon grid and outcrops are limited. An erosional domain is mapped on the northern portion (with minor outcrop, subcrop and residual soils) while the south is dominated by masking transported material (clays, silts and gravels, up to 10m-thick) associated with the Badeni River.

The Northern Zone mineralization locates on the immediate hanging wall of a strongly foliated graphitic shear, and is associated with increased silicification, sulphidation and fine brecciation. The main shear zone is represented by wide zones of pervasively foliated and altered mafic volcaniclastics, now transformed into sericite schist, and variably altered black shale and graphite. Within the highest strained zone the main foliation (250°-260° / 080°-070° dip) is itself folded on a small scale and contains folded quartz veins. Prominent structures include quartz veins (trending 240° to 250° with 70° to 80° dips), graphitic shears (260° to 270° with 70° to 80° dips) and silicified shears, of which the quartz veins and graphitic shears are dominant.

4. PETROGRAPHIC STUDIES

Several petrographic studies (thin sections and polished blocks) have been undertaken from 1998 to 2002 from selected diamond core samples of the Tongon ore body and host rocks.

The dominant sulphide, arsenopyrite, appear as individual crystals or composite arsenopyrite-pyrrohotite-chalcopyrite grains. This second type shows distinct overgrowths over an early anhedral phase, and often contains inclusions of silicate material and the higher percentage of occluded gold. Pyrite is sporadic and appears late. Oxide phases include ilmenite, rutile, leucoxene and magnetite.

A high percentage of the observed gold grains (approximately 80%) are between 1 to 200 microns and occur within individual arsenopyrite crystals or within the composite grains or at the contact between the two phases of arsenopyrite. About 17.5% of the gold grains are free (average size of 16 microns, with large grains up to 50 by 40 microns) and occur in the gangue immediately adjacent to arsenopyrite grains.

About 2% of the observed grains are found in veins and fractures and are also free with the maximum grain size being 10 by 5 microns. The balance of the breakdown corresponds to very fine gold, generally less than 1 micron observed within the alteration silicates.
5. CONCLUSION

Since Randgold Resources acquired the Nielle permit in 1996, it has discovered and partially defined a significant gold deposit at Tongon.

To date this discovery is considerably larger than any other gold deposit discovered in Côte d’Ivoire and potential exist to further add to the size of the deposit. Subject to a positive outcome of the bankable feasibility study and the current political process, the Tongon deposit will be developed as the company’s third gold mine in West Africa.

ACKNOWLEDGEMENTS

The writer acknowledges Randgold resources for permission to publish this extended abstract and also to all previous Randgold staff who have contributed to the understanding of the deposit.

REFERENCES

- Report on Tongon Prefeasibility Type 2 - June 2002
- Internal Monthly, Quarterly, and Annual reports and presentations
ABSTRACT: The Lumwana basement hosted Cu-Co (U) deposits, of NW Zambia are large tabular low-grade disseminated ore bodies hosted within the Mwombezhi Dome Region of the Lufilian Arc. The host rocks to the Lumwana deposits are migmatitic gneisses to amphibolite which grades into kyanite schists. The host rock to the ore bodies are dominated by two mineralogically similar but texturally distinct rock types, a granitic to pegmatic gneiss and a banded to augen gneiss that both comprise quartz-feldspar ± biotite/phlogopite ± haematite. The ore bodies are a muscovite-phlogopite-quartz-kyanite-sulphide schist, although mineralization can be observed locally within the weakly mineralized internal gneiss units. Kinematic indicators such as s-c fabrics and pressure shadows on porphyroblasts suggest a top to the North shear sense and sulphides are deformed by the S1 fabric and overprinted by kyanite which formed at peak metamorphism; indicating that copper was introduced to the basement either syn or pre-peak metamorphism. Post S1 metamorphism with associated quartz-muscovite alteration has remobilized sulphides into low strain zones and pressure shadows around porphyroblasts. \( \delta^{34}S_{\text{SULPHIDES}} \) give values of +2.3 to +18.5‰ within the range of values observed in the Copperbelt of -17 to +23‰. The transitional contacts observed at Lumwana are due hydrothermal alteration which removed feldspar from ore horizons. These new data suggest that the deposits represent metasomatically altered, mineralized and sheared basement, rather than mineralized Neoproterozoic sediments with amphibolite grade metamorphism.

KEYWORDS: Zambia; basement; alteration; copper; cobalt

1 INTRODUCTION

The neo-Proterozoic Katangan Central African Copperbelt that straddles the border between Zambia and the Democratic Republic of Congo is host to one of the world’s greatest concentrations of stratiform copper-cobalt mineralization. Understanding the mechanism and timing of ore formation and associated wallrock alteration of the Lumwana deposits has implications for the role of pre-Katangan basement in the genesis of the Zambian Copperbelt.

The Lumwana deposits are located 220km northwest of the Copperbelt, and 65km from the provincial capital of Solwezi in the North Western Province of Zambia. The Lumwana Prospect is a small settlement with the largest known Zambian copper resource outside of the Zambian Copperbelt and will rank as Africa’s largest copper mine when mining commences in 2007 (Equinox Annual Report 2005).

The origin of the host rock and mineralization at Lumwana is ambiguous with transitional contacts from unmineralized quartz-feldspar±phlogopite basement gneiss to Cu±Co mineralized quartz-phlogopite-muscovite-kyanite-sulphide “Ore Schist”. This paper presents new petrographic, stable isotope analysis (\( \delta^{34}S \)), whole rock geochemistry, and electron microprobe analysis of ore and host rock assemblages in an attempt to better understand the origin of this significant mineralized system.

2 GEOLOGIC SETTING

The Lumwana deposits are located in the Mwombezhi Dome of the Domes Region of the Lufilian Arc, an orogenic Pan-African fold-
thrust belt approximately 900km in length that hosts the Central African Copperbelt (Cosi et al. 1992) (Fig. 1). The Lufilian fold belt consists of four distinct, convex-north zones. From north to south these are: I) the external fold and thrust belt that host the Congolese Copperbelt deposits, II) the Domes Region that host the Lumwana deposits, III) the Synclinorial Belt, and IV) the Katanga high (Porada 1989) (Fig. 1).

The Mwombezhi Dome is interpreted as one of several basement inliers within the Lufilian Arc that represent antiformal stacks above mid to lower crustal ramps (Daly et al. 1984) and are separated from the overlying Katangan Supergroup sediments by a major decollement (Cosi et al. 1992; John et al. 2004) (Fig. 2). Whiteschist assemblages in the Mwombezhi Dome basement indicate peak metamorphism of 750°C ± 25°C and 13 ± 1 kb corresponding to burial depths of approximately 50 km (Cosi et al. 1992; John et al. 2004).

In the Domes Region unconformable relationships between older basement and the younger Katangan Supergroup sediments are preserved and metamorphic grade varies from upper greenschist to upper amphibolite facies (Selley et al. 2005). Basement rooted recumbent folds, nappes and juxtaposed thrust blocks of contrasting metamorphic grade have been described (Cosi et al. 1992; Key et al. 2001).

The age range and lithological make up of the basement rocks of the Domes Region have a strong similarity with the basement rocks of the Kafue Anticline and have been interpreted to collectively belong to the Lufuub Metamorphic Complex which is interpreted as a Palaeoproterozoic magmatic arc terrane (Rainaud et al. 2005).

The Lumwana basement hosted copper ± cobalt deposits Chimiwungo and Malundwe, are large tabular low-grade disseminated ore bodies, each approximately 4km in length with a gentle dip to the south and west respectively. The host rocks to the Lumwana deposits are migmatitic gneisses to amphibolite that grades into kyanite schists. The host rock to the ore bodies are dominated by two mineralogically similar but texturally distinct rock types, a granitic to pegmatic gneiss and a banded to augen gneiss that both comprise quartz-feldspar ± biotite/phlogopite ± hematite. The ore bodies are a muscovite-phlogopite-quartz-kyanite-sulphide schist, although mineralization can be observed locally within the weakly mineralized internal gneiss units (Fig. 3).

The Malundwe and Chimiwungo deposits are host by separate thrust sheets. The Chimi-
The primary sulphide mineralization at Lumwana commonly occurs in mineral pairs of copper sulphides, which exhibit a weak down hole zonation. The sulphide pairs consist of pyrite (FeS2) – chalcopyrite (CuFeS2), chalcopyrite – carrollite (CuCo2S4) (Chimiwungo only) and chalcopyrite-bornite (Cu9FeS8). Bornite and chalcopyrite are replaced by digenite (Cu6S5) and chalcocite (Cu5S4) then covellite (CuS). Quartz veins which cross-cut both the mineralization and the barren internal gneiss units are commonly host to pyrite, chalcopyrite and/or bornite. Common accessory minerals in the ore schist are ilmenite, graphite and REE minerals allanite,apatite and monazite. Minor uranium mineralization occurs locally cross-cutting the Cu-Co mineralization.

Post S1 metamorphism with associated quartz-muscovite alteration has remobilized sulphides into low strain zones and pressure shadows around porphyroblasts.

4 GEOCHEMISTRY

A representative sample suite of ore and host rocks were analyzed including stable isotope analysis (δ34S), whole rock geochemistry, and electron microprobe analysis, in order to assess the timing and style of mineralization and associated wall rock alteration.

The sulphide mineralized zones at Lumwana are highlighted by a depletion in Na and Ca and relatively higher Al due to an alteration event associated with the mineralization that removed feldspar from ore horizons resulting in the transitional contacts.

δ34SSULPHIDES give values of +2.3 to +18.5‰ which fall within the range of values observed in the Copperbelt of -17 to +23‰ (McGowan et al., 2004, 2006). Sediment-hosted copper deposits exhibit a wide range of δ34S values from -22‰ to +12‰ at White Pine and -44‰ to -2‰ at the Kupferschiefer and indicate that bacteriogenic reduction of sulphate is an important mechanism for ore formation. (fig. 4).

The mechanism of ore formation at Lumwana was dominated by thermochemical sulphate reduction (TSR), indicated by the relatively heavy δ34S values and the absence of the light δ34S values.

The Lumwana sulphides exhibit variations in δ34S values within individual hand specimens suggesting that these results are not the result of metamorphic homogenisation.

In contrast, electron microprobe data of mus-
covite, phlogopite and chlorite show little variation between early and late mineral phases indicating that metamorphic homogenization of silicate assemblages occurred.

![Diagram](image)

Fig. 4. $\delta^{34}S$ (‰) values for sediment hosted copper deposits and the Lumwana basement hosted copper deposits.

5 CONCLUSIONS

The origin of the protolith to the Cu±Co mineralization is ambiguous at Lumwana with transitional contacts from unmineralized quartz-feldspar± phlogopite basement gneiss to Cu±Co mineralized quartz-phlogopite-muscovite -kyanite-sulphide Ore Schist. The presence of transitional contacts and structural controls on distribution of the mineralization suggests that these deposits represent metasomatically altered, mineralized and sheared basement, rather than mineralized Neoproterozoic sediments with amphibolite grade metamorphism. This hypothesis is supported by petrographic analysis, stable isotope analysis ($\delta^{34}S$), whole rock geochemistry, and electron microprobe analysis of ore and host rock assemblages. The transitional contacts observed at Lumwana are due to an alteration event associated with mineralization that removed feldspar from ore horizons resulting in depleted Na and Ca and relatively higher Al components. Sulphides are deformed by the S1 fabric and overprinted by kyanite which formed at peak metamorphism. This indicates that copper was introduced to the basement either syn or pre-peak metamorphism. Post S1 metamorphism with associated quartz-muscovite alteration has remobilized sulphides into low strain zones and pressure shadows around porphyroblasts.

REFERENCES


Cassiterite mineralization in vein-type deposits of the Kibara orogen (Central Africa): Nyamiumba (Rutongo area, Rwanda)

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ABSTRACT: The Central African Kibara orogen forms a metallogenic province that hosts different types of granite-related mineralization. The belt contains numerous deposits rich in cassiterite, niobotantalite, tungsten, gold, monazite, amblygonite and beryl. The mineralization predominantly occurs in pegmatites and quartz veins. The quartz vein mineralization hosts cassiterite and postdate granite and pegmatite consolidation. The Nyamiumba Sn-mineralization in the Rutongo mining area consists of massive quartz veins associated with an intense alteration: silicification, tourmalinization, greisenization and muscovitization. Cassiterite itself is associated with muscovite in the quartz veins. Sn mineralization is followed by the precipitation of arsenopyrite, pyrite, chalcopyrite and galena. Cassiterite mineralization resulted from the circulation of fluids with a H2O-CO2-(CH4-N2)-NaCl composition, which have a metamorphic isotopic signature.

KEYWORDS: Kibara orogen, Central Africa, Cassiterite, Quartz veins

1 INTRODUCTION

The Central African Kibara orogen extends from Katanga in the south to southern Uganda in the north. It forms also a large metallogenic province, which contains numerous granite related ore deposits, which are rich in cassiterite (SnO2), niobotantalite (i.e. coltan, (Nb, Ta)2O5), wolframite ((Fe, Mn)WO4), beryl (Be3Al2Si6O18), spodumene (LiAlSi2O5), amblygonite (LiAlFPO4), monazite ((Ce, La,Y, Th)PO4), gold (Au), etc.

These minerals are present within different types of mineralisation, as primary mineralization in quartz veins and pegmatites, but also as secondary mineralization in alluvial or eluvial deposits. Historically, the secondary deposits have been favourably exploited due to the ease of extraction. However, this contribution, focusses on the quartz vein-type mineralization. By integrating the existing geological and historical mining data with new observations and geochemical, petrographic techniques, a preliminary metallogenic model is proposed.

Figure 1. Geological map of Rwanda

The cassiterite vein-type deposit studied occurs at Nyamiumba, in the Rutongo area (Figure 1), and is representative of tin mineralization in the northern part of the Kibara Belt (Rwanda, Burundi and D.R.Congo).
2. GEOLOGICAL SETTING

The Kibara orogen formed and evolved between two pre-Mesoproterozoic domains: the Archaean-Palaeoproterozoic Congo craton to the west and the north, and the Archaean- and Palaeoproterozoic Tanzania craton and Bangweulu Block to the east and the south. The Kibara belt consists of two distinct segments, separated in the DRC by the northwest extension of the Palaeoproterozoic Ubende belt (SW Tanzania) across Lake Tanganyika. The "Northern" (Rwanda, Burundi, Uganda, Tanzania, Kivu and Maniema in the DRC) and "Southern" (Katanga in the DRC) segments should be viewed as two separate – albeit coeval – orogenic belts (Tack et al., 2002).

3. PETROGRAPHY

In the Rutongo area, the emplacement of the quartz veins was associated with an intense alteration of the host-rock (Figure 2). The quartz grains in the Mesoproterozoic host-rock are intensively deformed and fractured. Tourmaline and muscovite crystals can be found in these fractures. Intercalated phyllites layers in the quartzites are often completely altered to tourmaline (the so-called “tourmalinite” rocks). The quartz veins are bordered with a dark rim of tourmaline, which passes into dispersed tourmaline and muscovite further away from the vein (sericitization, silicification and muscovitization).

The cassiterite mineralization within the quartz veins is concentrated in certain zones associated with large muscovite crystals (i.e. the so-called “poches de greisen”) in the centre or at the margin of the quartz veins. The cassiterite mineralization shows fractures which have been filled with arsenopyrite, pyrite, chalcopyrite and galena. Recent weathering resulted in the formation of haematite and goethite in fractures.

4. FLUID INCLUSION MICROTERMOMETRY

No primary inclusions can be found within double polished thin sections of quartz and cassiterite from the vein-type mineralization at Nyamiumba. The inclusions in the quartz crystals occur in secondary trails that are directed towards the cassiterite mineralization and are thought – therefore - to be representative for the fluids responsible for the mineralization. Fluid inclusions in the cassiterite crystals are randomly distributed or occur along cleavage planes. Where cleavage planes are developed, the randomly distributed fluid inclusions are decrepitated, which indicates that the randomly distributed inclusions are an earlier generation.

Fluid inclusions studied in secondary trails in quartz are > 15 µm and two-phase (L+V), with a large gas volume (> 50%). TmCO₂ occurred between -63°C and -62.3°C, indicating an additional gas component to CO₂. Raman analyses have been carried out by Pohl (1991) on mineralized quartz veins at other locations in the Rutongo area and indicate the presence of important fault systems (unpublished map SOMIRWA).
minor traces of CH\textsubscript{4} and N\textsubscript{2}. The first melting of the inclusions was only visible in a few inclusions at around -20°C, indicative of a H\textsubscript{2}O-NaCl system. The temperature of the final melting of ice varies between -12.7° and -4.4°C. Tm\textsubscript{Clathrate} values are between 15 and 19°C. The total homogenisation temperature is between 280° and 300°C. So, the fluid inclusions in the secondary trails directed towards the cassiterite crystals in the quartz veins have a H\textsubscript{2}O-CO\textsubscript{2}-(CH\textsubscript{4}-N\textsubscript{2})-NaCl composition.

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<td>Greisen Rongi</td>
<td>11.0</td>
<td>-57.86</td>
</tr>
<tr>
<td>SD6</td>
<td>Quartz</td>
<td>Greisen Rongi</td>
<td>10.8</td>
<td>-65.02</td>
</tr>
<tr>
<td>SD7</td>
<td>Quartz vein</td>
<td>Rutongo</td>
<td>14.0</td>
<td>-29.90</td>
</tr>
<tr>
<td>SD8</td>
<td>Quartz vein</td>
<td>Rutongo</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>SD9</td>
<td>Cassiterite</td>
<td>Quartz vein Rutongo</td>
<td>6.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Results of stable isotope investigation of quartz veins, granites and pegmatites in the northern part of the Kibara orogen.

Fluid inclusions that are randomly distributed in the cassiterite crystals are < 10 µm and two-phase (L+V), with a small gas bubble (~ 10 %). Tm\textsubscript{CO\textsubscript{2}} is not observed due to the small size of the inclusions. The first melting of the inclusions occurred around -20.5°C, which is indicative for a H\textsubscript{2}O-NaCl composition. The temperature of the final melting of ice (Tm\textsubscript{Ice}) varies between -13.2° and -6.5°C. Tm\textsubscript{Clathrate} is between 1.7 and 14.9°C. The Tm\textsubscript{Clathrate} above 10°C indicates another additional gas component next to CO\textsubscript{2}. Total homogenisation of the inclusions starts from 224°C and decrepitation occurs at ~ 270°C. Randomly distributed fluid inclusions in the cassiterite have a H\textsubscript{2}O-CO\textsubscript{2}-(X)-NaCl composition.

Fluid inclusions along cleavage planes are < 8 µm and two-phase (L+V), with a gas volume of ~10 %. The first melting of the inclusions is around -22°C, indicative for a H\textsubscript{2}O-NaCl-KCl composition. The temperature of the final melting of ice varies between -10.7° and -6.2°C. Tm\textsubscript{Clathrate} is ~8.9°C. The homogenisation temperature is between 183° and 208°C. Fluid inclusions along cleavage planes in the cassiterite have a H\textsubscript{2}O-CO\textsubscript{2}-NaCl-KCl composition.

Although no primary fluid inclusions have been found in the cassiterite crystals, the fluids in the trails towards the mineralization in the quartz crystals and the randomly distributed inclusions in the cassiterite crystals, are considered representative as ambient fluid for the cassiterite mineralization. Therefore, cassiterite precipitation possibly occurred from a H\textsubscript{2}O-CO\textsubscript{2}-(X)-NaCl fluid with Tm\textsubscript{Ice} values between -12.7° and -4.4°C and a minimum formation temperature between 280° and 300°C.

5. STABLE ISOTOPES

Two quartz and one cassiterite sample from a mineralized quartz vein from Nyamiumba (Rutongo in Table 1) were selected for stable isotope analyses to determine the origin of the mineralizing fluids (Table 1). To calculate the $\delta^{18}$O value of the ambient fluid, the precipitation temperatures of the quartz has to be known. The minimum precipitation temperature of the quartz can be estimated from the homogenisation temperature of the fluid inclusions.

![δ\textsuperscript{18}O and δ\textsuperscript{D} isotopic plot for the calculated fluid composition of quartz veins, granite and pegmatites in the northern part of the Kibara orogen (Dewaele et al., this volume).](image)

The calculated oxygen isotopic composition of the ambient fluid for the quartz vein falls between + 7.9 ‰ and + 9.8 ‰ V-SMOW. By combining the $\delta^{18}$O and δD isotopic composition of the fluids, we can observe that the isotopic composition of the fluids responsible for the cassiterite mineralization falls in the field for metamorphic waters.

6. DISCUSSION AND CONCLUSION

In the Kibara orogen, the main granite generation G1-3 intruded at 1380 +/- 10 Ma in the Palaeo- and Mesoproterozoic rock (U-Pb
SHRIMP zircon). At 980 +/- 8 Ma (U-Pb SHRIMP zircon), the so-called Kibara “tin-granites” were emplaced. Recent investigations demonstrate that these G4 granites are not associated with Sn mineralization. After consolidation of the G4 granites, pegmatites were emplaced at 968 +/- 8 Ma (Brinckman et al., 2001). The pegmatites are crosscut by quartz veins (Varlamoff, 1956). The emplacement of the cassiterite mineralized quartz veins has been dated at 951 +/- 18 Ma in Burundi (Brinckman et al., 2001). The mineralized quartz veins are associated with an intense alteration of the host-rock: silicification, tourmalinization, sericitization, muscovitization. The cassiterite mineralization itself was formed during a later phase in the vein development and occurs in fractures filled with large muscovite crystals. The main cassiterite mineralization in the Rutongo area occurs along fault systems, which could have acted as fluid pathways. Cassiterite precipitated from a fluid with a H₂O-CO₂-(X)-NaCl composition, Tmₑₑ values between -12.7°C and -4.4°C and a Tₑₑ between 280°C and 300°C. The stable isotope composition suggests a metamorphic origin of the fluids.

ACKNOWLEDGEMENTS

We would like to thank Jean-Claude Defleur and Gilbert Chartry for stimulating discussions on various aspects of the Sn-Nb-Ta ore deposits in Rwanda and the DRC. Herman Nijs and Rene Boyen kindly prepared the numerous thin and polished sections and the doubly-polished wafers.

REFERENCES


Anomalous High Field Strength Element (HFSE) enrichments in the Gamagara and Mapedi Formations: implications regarding Fe- and Mn-ore genesis in the Transvaal Supergroup, South Africa.

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ABSTRACT: The late Palaeoproterozoic Mapedi/Gamagara Formation in the Northern Cape Province, South Africa, unconformably overlies (largely) sedimentary rocks of the Transvaal Supergroup. Commercial, epigenetic ores of both Fe and Mn variously occur below this unconformity. There is increasing geochemical evidence from several localities in the broader Northern Cape area, that Transvaal Supergroup rocks may have suffered at least some degree of alkali metasomatism. We postulate that such metasomatic overprinting is likely to have affected the Mapedi/Gamagara shales as well, possibly via fluid-flow focused at or close to the regional unconformity with Transvaal strata. The widespread and stratigraphically well-constrained anomalous enrichment of the Mapedi/Gamagara Formation in HFSEs reported here, and perhaps even the development of some BIF-hosted Fe- and Mn-ores, may also be explained through such fluid events.

KEYWORDS: Palaeoproterozoic, shales, metasomatism, haematitic iron-ore, fluid-flow

1 BACKGROUND

The Kaapvaal Craton in southern Africa hosts exceptionally well-preserved late Archaean to Palaeoproterozoic sedimentary successions. In the Northern Cape Province (formerly known as the Griqualand West region; Beukes & Smit, 1987) extensive occurrences of Palaeoproterozoic carbonates (Campbellrand Subgroup) and banded iron-formation (BIF: Asbestos Hills Subgroup), along with lesser siliciclastic sediments (Koegas Subgroup) diankite (Makganyene Fm) and continental flood-type volcanic rocks (Ongeluk Fm). These collectively make up the largest part of the wider Transvaal Supergroup (2.7-2.2 Ga). World class high-grade Fe-ore deposits occur in association with the Transvaal BIFs, whilst the uppermost portion of the Transvaal Supergroup hosts a unique association of manganese-rich rock intercalated with BIF, in the form of three discrete sedimentary cycles constituting the Hotazel Formation in the so-called Kalahari manganese field (Tsikos et al., 2003).

The ca. 2.2 Ga Mapedi/Gamagara Formation represents the basal portion of the late Palaeoproterozoic Olifantshoek Group, and rests on Transvaal Supergroup rocks along a regional unconformity which essentially develops across the entire Northern Cape area. Palaeoweathering profiles (palaeosols) are extensively developed below this unconformity (e.g., Wiggering & Beukes, 1990; Gutzmer & Beukes, 1998; Beukes et al., 2002). The Mapedi/Gamagara Formation consists predominantly of red shales intercalated with lesser, pale green shales, subordinate organic-rich black shales and fine- to medium-grained quartzites. Traditionally, the term Gamagara Formation applied with specific reference to the shale succession that immediately overlies massive haematitic iron-ore deposits like those seen at Sishen and Beeshoek. These deposits appear to have formed in sinkholes at or below the unconformity, as a result of solution collapse, slumping and meteoric/hydrothermal leaching of Asbestos Hills iron-formation from the lower parts of the Transvaal Supergroup (Beukes et al., 2003). The term Mapedi Formation has been widely used with direct reference to the shale succession that lies directly on top of the uppermost portion of the Transvaal Supergroup, i.e. the manganiferous Hotazel iron-formation in the Kalahari manganese field. Although direct stratigraphic correlation between the Gamagara and Mapedi Formations has been a contentious
issue in the past, they are currently considered to represent lateral equivalents (e.g., Yamaguchi & Ohmoto, 2006), albeit on no well established stratigraphic criteria.

The Mapedi/Gamagara Formation has recently become the focus of much detailed research (e.g., Evans et al., 2002; Yamaguchi & Ohmoto, 2006), as it preserves a record of palaeo-environmental conditions during the critical time interval 2.4-2.2 Ga. Here, we place more emphasis on the likelihood that the geochemistry of these rocks may have registered fluid-rock interaction processes of metallogenic significance in terms of the origin of underlying haematitic iron-ores.

2 THE MAPEDI/GAMAGARA FORMATION

We selected two approximately 80m-long diamond drill-core intersections, located roughly 100km apart, for detailed sampling of the Mapedi and Gamagara Formations: the former was sampled from a core recovered in the N‘chwaning mine area of the Kalahari manganese field, whereas the latter was captured in a core drilled in close proximity to the Beeshoek iron-ore mine. Thin sections of all samples were examined under transmitted light, whilst corresponding powdered samples were analysed using x-ray diffraction (XRD) for determinations of bulk mineralogy, and X-ray fluorescence (XRF) for major, minor and trace elements.

Macroscopically, the cores exhibit closely comparable litho-stratigraphic patterns, with a crude transition from a ca. 40m-thick basal portion dominated by red shale, through a quartzite unit in the middle, to an upper portion with red and green shale intercalations (Fig. 1). A minor black shale unit is also present in the uppermost part of the Beeshoek core.

Mineralogically, the red shales are dominated by a very fine-grained assemblage of quartz-sericite-haematite; by contrast, the green shales are characterised by the complete lack of hematite and the abundance of chlorite. In terms of major element geochemistry, all shale samples are dominated by essentially four oxide components. Regarding the Beeshoek core, the range of values for SiO$_2$ is 50.1-64.8 wt%; for Al$_2$O$_3$ it is 7.3-22.6 wt%; for total Fe-oxide (as FeO) it is 3.2-33.5 wt%, and for K$_2$O it is 2.0-6.4 wt%. Similarly, samples from the N‘chwaning core exhibit similar ranges for SiO$_2$ (54-67.3 wt%) Al$_2$O$_3$ (14-20.3 wt%) total Fe-oxide (as FeO: 2.8-20.9 wt%) and K$_2$O (3.6-6.2 wt%). All other major oxides are at levels at or very near the limit of detection, with the exception of MgO (around 1 wt%).

However, the most notable bulk geochemical attribute of both cores is the anomalous enrichment, as well as striking distribution across the stratigraphy, of some of the high field strength elements (HFSEs), specifically Ti (as TiO$_2$), Nb, Zr and Y. As clearly demonstrated in Fig. 1 on the basis of the above four elements, both the Mapedi and the Gamagara Formations can be further subdivided into three distinct units:

- a basal portion with relatively low HFSE contents (Beeshoek core: TiO$_2$: 0.41 & 0.65 wt%; Nb: 7 & 12 ppm; Zr: 192 & 264 ppm; Y: 16 & 24 ppm; N‘chwaning core: TiO$_2$: 0.72-0.83 wt%; Nb: 13-15 ppm; Zr: 226-274 ppm; Y: 18-21 ppm);
- a lower portion with relatively high HFSE contents (Beeshoek core: TiO$_2$: 1.91-4.84 wt%; Nb: 67-173 ppm; Zr: 512-836 ppm; Y: 21-46 ppm; N‘chwaning core: TiO$_2$: 2.19-3.76 wt%; Nb: 82-147 ppm; Zr: 446-735 ppm; Y: 29-46 ppm); and,
- an upper portion with HFSE contents intermediate to those from the lower parts of the stratigraphy (Beeshoek core: TiO$_2$: 1.05-1.24 wt%; Nb: 22-33 ppm; Zr: 212-373 ppm; Y: 23-28 ppm; N‘chwaning core: TiO$_2$: 0.91-1.49 wt%; Nb: 19-47 ppm; Zr: 191-584 ppm; Y: 22-35 ppm).

In particular, the very strong co-variation between Nb and TiO$_2$ as shown on Fig. 1, would suggest the preferential enrichment in the lower portion of the Mapedi/Gamagara Formation of a Ti-phase such as rutile or ilmenite, although the low relative abundances of the latter and the very fine-grained nature of the shales did not permit verification of these phases via XRD and conventional petrography.

3 HFSE ENRICHMENTS: PROVENANCE OR FLUIDS?

A comparison of the major element chemical composition of the Mapedi/Gamagara shales with that of PAAS (Table 1) reveals that the former are particularly enriched in both TiO$_2$ and total Fe-oxide. Fe-enrichments in the Mapedi/Gamagara rocks should not be regarded as surprising, considering that Transvaal BIF is
a prime source-rock candidate. On the other hand, the stratigraphically well-constrained enrichment in TiO$_2$ (and other HFSEs; Fig. 1) carries obvious value for firm lateral correlation between the Gamagara and Mapedi Formations, yet it is also more problematic to decipher.

It is possible that the source of HFSE enrichment may be through re-working of weathered Ongeluk lavas on a regional scale, as the latter also exhibit substantial residual Ti-enrichment (Table 1). Ongeluk palaeosols, however, are also known to be particularly enriched in K, and these enrichments have been tentatively attributed to fluid metasomatism (Wiggering & Beukes, 1990). As potassic metasomatism in shales is not an uncommon feature (see, for example, Fedo et al., 1997, for shales of the Huronian Supergroup:), the possibility emerges that the relatively enriched character of both the Ongeluk palaeosols and the Mapedi/Gamagara shales in K is related to later fluid event/s. Furthermore, the traditionally-held view that HFSEs behave as conservative elements in most geological settings has been increasingly challenged by several workers who advocate high HFSE mobility in a variety of environments via highly alkaline fluids (e.g. Hole et al., 1992; Jiang et al., 2005). The above, in conjunction with other recent evidence for fluid metasomatism in the uppermost Transvaal Supergroup (Tsikos & Moore, 2005) add value to the contention that large-scale, alkaline fluid-flow may be responsible for many geochemical characteristics and possibly ore-forming processes variously observed in rocks of the Transvaal Supergroup and Olifansthoek Group.

Table 1: Mean, bulk major element data for broad lithologic subdivisions of the Gamagara/Mapedi shales (this study), compared with those of Ongeluk palaeosol and parent andesitic volcanic rock (Wiggering & Beukes, 1990) and that of post-Archaean average shale (PAAS: Taylor & McLennan 1985)

<table>
<thead>
<tr>
<th></th>
<th>upper shale</th>
<th>lower shale</th>
<th>basal shale</th>
<th>paleosol fresh</th>
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<tr>
<td>Gamagara</td>
<td>n=16</td>
<td>n=9</td>
<td>n=3</td>
<td>n=3</td>
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<tr>
<td>Mapedi</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>PAAS</td>
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</tr>
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<td>4.93</td>
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<tr>
<td>P$_2$O$_5$</td>
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<td>0.26</td>
<td>0.05</td>
<td>0.13</td>
</tr>
</tbody>
</table>

All values in wt %; *total Fe/Mn as FeO/MnO, respectively

ACKNOWLEDGEMENTS

We wish to thank Mr A. Pretorius, Mr M. Burger and Mr S. van Niekerk, all of Assmang Ltd, for providing us with unconstrained access to drill-core material from their Fe- and Mn-ore mine premises (Beeshoek and N’chwaning respectively) in the Northern Cape, South Africa, for the purposes of this study. Professor Goonie Marsh (Rhodes University) is thanked for facilitating the acquisition of the bulk rock XRF data. Most of the results presented in this paper were also included in two unpublished Honours dissertations carried out by the co-authors J. Kalumbu and F. Shivute at Rhodes University, during the second half of 2006.
REFERENCES


Fluid evolution and conditions of ore deposition of a shear zone-hosted gold mineralization, Barramiya Mine, SE Egypt

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ABSTRACT: The Barramiya mine area is a tract of deformed Neoproterozoic ophiolitic mélangé sequences comprising metamorphosed volcano-sedimentary-serpentinite rocks in the central Eastern Desert of Egypt. The gold mineralization comprises a number of narrow anastomosing lodes of massive and brecciated gold+ sulphide-quartz and quartz-carbonate veins. These veins are hosted by, or directly associated with highly deformed carbonaceous serpentinite and volcanoclastic schists along east-trending shear zones, commonly exhibiting pinch-and-swell and boudinage structures. Hydrothermal alteration is pervasive throughout the shear zones, with a common assemblage of chlorite, ankerite, sericite, ±calcite, ±magnetite, ±graphite. Gold/electrum inclusions are common in pyrite coexisting with arsenopyrite and pyrrhotite, mostly where chlorite and carbonate are abundant, whereas free-milling gold appears as tiny grains along micro-fractures in the vein quartz or disseminated in the adjacent wallrocks. Inclusions of C-O-H fluids, mainly mono-phase carbonic (CO₂±CH₄±H₂O) and two/three-phase aqueous-carbonic (H₂O-NaCl-CO₂±CH₄) inclusions along intragranular trails and aqueous (H₂O-NaCl±CO₂) inclusions along transgranular trails are common in the auriferous quartz veins. The aqueous-carbonic inclusions were most likely entrapped during gold deposition and represent the ore fluid. Estimated pressure-temperature conditions for ore deposition based on arsenopyrite thermometry and using the isochores for aqueous-carbonic inclusions range from 1.2 to 2.5 kbar at 309–377°C, consistent with brittle-ductile transition. Gold deposition from a dilute aqueous-carbonic ore fluid with significant concentrations of CH₄ added via interaction with the carbonaceous wallrocks may have been triggered by a sharp decrease in fO₂, caused by the CH₄ enrichment of the fluid and precipitation of carbonate.

KEYWORDS: Barramiya, Egypt, shear zone-related gold, faulting, fluid inclusions

1 INTRODUCTION

The central Eastern Desert of Egypt has long been known for historic gold deposits, e.g. Barramiya, Atud, Fawakhir, El-Sid, Sukari, Um El-Rus etc, where gold is dominantly confined to quartz-mineralised shear zones formed during compressional or transpressional stages late in the Pan-African Orogeny (El Gaby et al., 1988; Loizenbauer & Neumayr 1996; Botros, 2004). These shear zones cut sequences of ophiolitic and metasedimentary rocks or occur along their contacts with granitoids. The Barramiya district, in the central Eastern Desert, contains several gold deposits, e.g. Barramiya, Dungash, Um Samra, in which the gold-bearing quartz veins are mostly situated along an east to east-northeast trending ductile-brITTLE shear zones associated with the Idfu-Mersa Alam shear system. This system cuts across a late Precambrian (~560Ma) pink granite with a dextral offset of ~1.5km. The Barramiya gold deposit is a vein-type, gold-pyrite-arsenopyrite mineralization, occurring adjacent to chromite, magnesite and scheelite ores (Sabet & Bondonosov, 1984). It is located midway between the towns of Idfu and Mersa Alam (Fig.1). Mining activities started most probably in the pre-Dynastic times and was abandoned completely in 1948 (Kochine & Basyuni, 1968). Between 1903 and 1915, the mine produced 46,330 ounces Au from approximately 39,800 short tons, at an average of 35.5 g/t (Gabr a, 1986). The mineralization was worked out from several quartz veins scattered over an area of 24 km², underlain mainly by carbonaceous schists. The major
auriferous quartz veins were stopped out to depths ranging from <40 to 76m through several vertical and inclined shafts. Although gold is present in the hydrothermally altered wallrock, the bulk of mine workings is confined to the quartz and quartz-carbonate veins.

2 GEOLOGY

The Barramiya district is underlain by a Neoproterozoic ophiolitic mélangé of allochthonous rafts and clasts of serpentinite, tectonically incorporated and intermixed with an intensively deformed matrix of psammitic to pelitic and calcareous-schists, locally with intercalations of quartzite and black marble. The psammitic schist is a finely banded sericite-actinolite ± chlorite ± haematite-bearing rock, with carbonaceous material in places. This rock is commonly crumpled into synclinal folds. The psammo-pelitic schist is represented by different varieties of quartzo-feldspathic slate, graphitic slate, metagreywacke and metab-conglomerate, with lithic and quartz pebbles. Locally, discrete elongate bodies of tonalite and granodiorite intrude into the mélangé rocks along the pre-existing structural fabrics. Several sub-rounded to elongated bodies of syn-orogenic granodiorite-quartz-diorite and post-orogenic granite-alkali granite and granite porphyry intrude into the metasedimentary and serpentinite rocks, commonly in the mine area.

Regional deformation involved an early folding (D1=F1; N67-80°E/58-69°NW) preserved mainly in the low-strain metasediments. D2 is manifested by a series of NW-SE open folds and related ductile shear zones mostly accommodating a sinistral offset. S1 and S2 are superimposed by a series of local F3 folds with NE-SW axial planes and SE-dip (D3). A late deformation increment produced an extensively developed crenulation cleavage (S4) that is commonly sub-vertical and trends approximately NNW-SSE. Consistent asymmetry of the differentiated crenulations suggests an east-side-up sense of shear. Finally reactivation of early faults and formation of fault and fracture sets crossing the major tectono-stratigraphic contacts is interpreted to have taken place late during D4 and re-oriented D1 and D2 structures. The development of kilometer-scale low displacement, east-trending ductile-brittle shear zones was most likely the last ductile deformation in the area.

3 MINERALIZATION STYLE

The Barramiya deposit comprises four major veins, striking in east-northeast to east, west-northwest and northeast directions. In addition, smaller intersecting and parallel veins form a separate system 18 to 20m thick, giving rise to an ore zone of considerable thickness if compared to the veins. The gold-bearing reefs consist of two main phases of silica injection. This is commonly attested by a brecciated auriferous milky to bluish-grey quartz-carbonate sealed by barren clear white quartz. Beside the quartz and quartz-carbonate veins, zones of carbonatization and silicification are widely developed in the adjacent carbonaceous schist. Petrography of the altered wallrocks suggests that the carbonaceous matter was gen-

Figure 1. Geological map of the Barramiya district.

Figure 2. Geologic map of main Lode at Barramiya Gold Mine. Inset shows structures associated with strike-slip faults and orientations relative to a single main displacement zone (D): R Riedel shears, R’ antithetic Riedel shears, P shears, T tension fractures, and N normal faults.
Road. Generally, this shear system and associated quartz veins cross cut $S_3$ foliation (N54°E/67°NW) at variable angles and are either deformed by or wrapped around $S_4$, are also considered post-D3 and pre- to syn-D4. Evidence of syn-kinematic quartz veining is expressed in abundant dextral asymmetries and intense quartz crystal plasticity (Fig. 3a).

The ore zone is confined to intensively tectonized graphite and actinolite schists, yellowish brown cavernous talc-carbonate, listwaenite and quartz lenses. The auriferous quartz veins are characterized by stylolitic structures and elongate slivers of carbonaceous wallrocks. Ore minerals are mainly pyrite, arsenopyrite, subordinate chalcopyrite and pyrrhotite ± gersdorffite, and rare galena. Gold inclusions are common in pyrite coexisting with arsenopyrite ± pyrrhotite, mostly where chlorite and carbonate are abundant (Fig. 3b). Gold concentrations were recorded in quartz veins (5-18 g/t) and adjacent wallrocks. The sulphidized graphite schist, thickly seamed by quartz veinlets, has the highest gold value ($\leq 7$ g/t) in the mineralized wallrocks (El Shazly, 1977).

Figure 3. (a) Elongated quartz ribbons with dominant bulging recrystallization, undulose and patchy extension. Carbonate forms a network along fractures. (b) Large pyrite crystal coexists with arsenopyrite and pyrrhotite and contains chalcopyrite and gold inclusions.

4 FLUID INCLUSIONS

Nine representative vein samples with abundant sulphide and gold particles were chosen for a fluid inclusion study. No unequivocally primary clustered fluid inclusions (Roedder, 1984) were identified, consistent with the reactivation and multistage development of veins in the shear zone. Abundant transgranular inclusion trails, mainly of aqueous (H$_2$O-NaCl) liquid and a carbonic (CO$_2$±CH$_4$) vapour phase (bubble), which shows relatively constant volume ratios in a single trail (0.3 to 0.4). Some of them contain minute solid phases, i.e. carbonaceous matter, probably due to accidental capture of wallrocks during the fluid trapping. Less abundant, (~2 µm) dark monophase, CO$_2$±CH$_4$ inclusions commonly coexist with the common two-phase aqueous-carbonic inclusions. Their small size did not allow for a microthermometric study. The aqueo-carbonic inclusions show polyhedral outlines or irregular shapes, with their longest dimension ranging from 4 to 15 µm. Microthermometry results are summarized in Figure 4. The microthermometric behavior of these inclusions upon cooling-heating runs includes:

- (a) nucleation of a CH$_4$ gas phase within the bubble at temperatures < -118°C and its subsequent homogenization to the liquid at ~ -82°C,
- (b) melting of solid CO$_2$ varying from -61.8 to -57.2°C, followed by homogenization of CO$_2$ to liquid, between 7.3 and 18.2°C (Fig. 4a), frequently in the presence of clathrate. The carbonic phase is, therefore, composed of variable proportions CH$_4$ and CO$_2$ (van den Kerkhof, 1990). confirmed by micro-Raman spectroscopy, which also constrained the carbonic phase as a mixture of CO$_2$ and CH$_4$ (Figs. 4b,c). Although mostly decrepitated before total homogenization, a few inclusions yielded values ranging from 199 to 358°C, with homogenization generally into the liquid state. Salinity values for the aqueous phase of these inclusions were roughly estimated between 3 and 7 wt.% NaCl eq., based on the combination of the melting temperatures of clathrate and representative CH$_4$ isochores for these inclusions (Thomas & Spooner, 1988).

5 P-T CONDITIONS

Considering that gold is closely associated with pyrite-arsenopyrite±pyrrhotite assemblage, the cationic thermometry of arsenopyrite (30.1-32.8 As at.%) coexisting with pyrite ± pyrrhotite yields a temperature range of 309-377°C. The isochores for the aqueous-carbonic inclusions indicate pressures of 1.2-2.5 kbar corresponding to the arsenopyrite temperatures, estimated for ore deposition (Fig. 4d). The close association of gold with sulphides (pyrite and arsenopyrite), combined with the estimated P-T conditions suggest that the Au(HS)$_2$ was the most likely gold bisulphide complex for
gold transport.

CONCLUSION

In view of the consistent fault and fracture controls on the deposit and considering the microstructures of the gold-bearing quartz veins, the deposit is likely formed syn-kinematically during the early stages of deformation within the host shear zones, and the master Idfu-Mersa Alam shear system. Fluid inclusions data indicate that the original fluid responsible for hydrothermal alteration and gold deposition was probably of a low salinity aqueous-carbonic solution, typical for ore-fluids of the orogenic, mesothermal lode-gold deposits (Groves et al., 2003 and reference therein), which incorporated significant concentrations of CH₄ related to hydrolysis of the carbonaceous matter during vein-fluid/wallrock interaction. Hydrolysis could have enriched the ore fluid in CO₂ and CH₄ and provided the requisite CO₂ for carbonatization. The addition of CH₄ during fluid-rock carbon interaction and carbonate precipitation may have caused a sharp decrease in fO₂ of the fluid which, as a consequence, destabilized gold-bearing sulphur complexes, liberating sulphur for the formation of Fe sulphides, and triggered gold deposition.

Figure 4. (a) Data of microthermometry of the aqueous-carbonic inclusions, (b) Raman spectra of CO₂ and CH₄ in a bubble, (c) Homogenization (Tₜ CO₂) vs. melting temperature (T_m CO₂) of H₂O-NaCl-CO₂-CH₄ fluid inclusions (data from van den Kerkhof et al. 1990; Thiéry et al. 1994). Tₜ CO₂ and T_m CO₂ are triple point and critical temperature of pure CO₂, respectively, (d) P-T field based on isochore plots for the studied fluid inclusions assuming H₂O–CO₂–NaCl–CH₄ system (Jacobs & Kerrick, 1981; Bakker, 1997).

ACKNOWLEDGEMENTS

I am grateful to Profs. G. Markl (Tübingen), H. Harraz (Tanta), M. W. U. T (Benha) for enthusiastic assistance and support in laboratory and field works.

REFERENCES


ABSTRACT: Gold occurs as isolated grains or closely associated with sulphides and gangue minerals notably carbonates, mainly in the altered banded iron-formation (BIF) in the Kalahari Goldridge deposit. Secondary ion mass spectrometry (SIMS) shows that pyrrhotite contains an average concentration 10ppm gold but pyrite is apparently gold-free. The distribution of gold in pyrrhotite is quite heterogeneous.

KEYWORDS: submicroscopic gold, Kalahari gold deposit, South Africa, SIMS

1 INTRODUCTION

The Kalahari Goldridge deposit is a typical lode-gold deposit hosted by banded iron-formation (BIF) in the Archaean Kraaipan greenstone belt in the Northwestern Province of South Africa (Fig. 1).

Mineralogical studies at the Kalahari Goldridge deposit to date (Hammond & Moore 2006; Hammond et al. 2007) revealed that despite high assay values found in host rocks particularly in pyrrhotite-rich areas, samples showed relatively minor or no visible gold grains during microscopic observations. These observations suggest that gold probably occurs at submicroscopic levels or structurally bound in lattices of the sulphides in these samples.

The presence of submicroscopic gold in sulphides has been a major contributor to refractory gold ores, which presents great difficulty in using conventional extractive metallurgy to extract the gold from these ores. At the Kalahari Goldridge mine, gold recovery currently stands at 80% or less, and tends to indicate the possible occurrence of submicroscopic gold in the ores at the deposit.

Secondary ion mass spectrometry (SIMS) was applied to pyrite and pyrrhotite ores to define the presence of gold in sulphides associated with mineralization at the Kalahari Goldridge deposit.

2 GEOLOGICAL SETTING AND MINERALOGY

2.1 Geological Setting and ore bodies

The Archaean Kraaipan greenstone belt which hosts the Kalahari Goldridge deposit stretches discontinuously in an approximately north-south orientation over a distance of 250km (Fig. 1). Four orebodies (D Zone, Watertank, A Zone, and Windmill) constitute the ore reserves at the Kalahari Goldridge deposit.
and extend for about 1.5 km along strike. Total resources comprise 43.6 million tonnes, at an average grade of 1.47 g/tonne for contained gold of approximately 2 million oz. The mineralization is associated with two sets of gently-dipping quartz-carbonate veins which dip 20-40° W and strike approximately N6° W. Mining operations by opencast method are currently based on the A and D Zones, at an average gold grade of 2.4 g/tonne with a subsequent annual production of 80,000 oz of gold.

2.2 Mineralogy

Principal mineralogy at Kalahari Goldridge includes silicates (chlorite, stilpnomelane, minnesotaite and muscovite), carbonates (siderite, ankerite-dolomite series and calcite) and opaque minerals including magnetite, pyrite, pyrrhotite and chalcopyrite. Pyrite and pyrrhotite form the dominant sulphides phases of the ore mineral assemblage.

Gold is intimately associated with pyrrhotite and pyrite and commonly occurs as inclusions in pyrite, as blebs or coarse grains along boundaries of pyrrhotite, pyrite and gangue minerals, as microcrack fillings in pyrite or as discrete grains.

3 METHODOLOGY

Microbeam techniques are increasingly applied to investigate the presence of gold in sulphides associated with many lode gold deposits (e.g. Chryssoulis et al. 1989; Cabri & McMahon 1995; Larocque & Cabri 1998). We have determined Au concentrations in pyrrhotite or pyrite grains of ore samples from the Kalahari Goldridge deposit, using a Cameca ims-1270 SIMS at the Geological Survey of Japan, AIST.

3.1 Analytical parameters

A defocused Cs⁺ primary beam was restricted to 20 µm in diameter by a circular aperture to obtain a homogeneous primary beam of about 0.2 nA. Negative secondary ions of Au were detected after being uniformly sputtered by a primary beam with total impact energy of 20 kV (a primary accelerating voltage of +10 kV and a secondary extraction voltage of −10 kV). A rectangular field aperture of 300 µm by 300 µm was introduced into the secondary ion optics, limiting the analyzed area on the sample surface to a central square measuring 3 µm by 3 µm to avoid the crater edge effect. The centering of the primary beam was ascertained each time by looking at the beam position in the field aperture of 2 mm by 2 mm.

The secondary Au− ions and matrix 34S− ions as a reference were detected without energy filtering using an electron multiplier (EM). An energy window of 50 eV was adjusted to the energy distribution curve to ensure that same energy band of Au− ions were always collected. No energy filtering was used since isobaric interference on 197Au from 133Cs32S2 was eliminated by high mass resolving power of 3300. Each 10 seconds and 3 seconds measurements for Au− and 34S−, respectively were allocated for a measurement cycle.

3.2 Standardization

Calibration of Au was conducted using external standard samples of pyrrhotite and pyrite implanted with Au at 1 MeV (The ion implantation samples were produced by the Mining and Mineral Sciences Laboratories, CANMET). After analyzing a standard for depth profiling (Fig. 2), the depth of the sputtered borehole was measured using a surface profiler to determine the relative sensitivity factor (RSF). The RSF is used to calculate the concentration in the unknown sample.

Figure 2. Typical depth profile showing distribution of Au in external pyrrhotite standard implanted with 197Au. Matrix 34S ions were also measured as a reference to calculate the RSF. Implantation dose: 1 x 1014 atoms/cm².
4 RESULTS

SIMS measurements for Au were conducted on sulphides bearing ore samples from the Kalahari Goldridge gold deposit.

Figure 3 shows a depth profile of a pyrrhotite grain. Au ions and matrix $^{34}$S ions as a reference were measured during the bombardment of the sample surface by the Cs$^+$ beam, resulting in erosion of the sample. Measurement of the depth of the resulting crater allows conversion of the time scale to a depth scale (Horizontal axis in Fig. 3) since the primary beam current stability was fairly good (fluctuation of 1-2 %) during the measurement. The depth of the crater is less than 1 $\mu$m. Figure 4 shows an enlargement of the beginning of the Au curve in Figure 3.

Figure 3. Depth profile for $^{197}$Au and $^{34}$S as a reference in a pyrrhotite grain. $^{34}$S was monitored to ensure the primary beam stability and sample homogeneity.

Figure 4. Enlargement of the beginning of the $^{197}$Au curve in Figure 3. Spatial resolution of the depth profile is very high.

Figure 5 shows a depth profile of a pyrite grain. Au intensity is very low around the detection limit.

Figure 5. Depth profile for $^{197}$Au and $^{34}$S in a pyrite grain. $1 \times 10^{-3}$ indicates signals equal to or less than that including 0 count/sec.

5 DISCUSSION

It was observed that although the Au intensity varies the intensity of the reference $^{34}$S is stable, which suggests that the Au variation is not caused by instrumental instability, but represent real values. Figure 3 show that pyrrhotite contains concentrations of gold which varies from 17 to 2 ppm with depth. The gold concentration is about 10 ppm, but changes gradually with depth (Fig. 4), which shows the heterogeneous distribution of gold in the pyrrhotite.

Pyrite, on the other hand, contains no gold (Fig. 5) with gold concentration generally less than 0.1 ppm.

The minimum sample size for the SIMS analysis is less than $1 \times 10^{-12}$ cm$^3$ and the detection limit is 0.1 ppmw. SIMS sputtering rate in this study was 0.25 nm/sec for pyrrhotite and the sputtered volume in the analysis area was about $2 \times 10^{-15}$ cm$^3$/sec. During analysis of a pyrrhotite grain containing 1 ppmw of gold, the analyzed volume contains only 30 Au atoms/sec. This constitutes the best condition to analyze a very tiny grain in the sample; however, the condition could be modified to lower the detection limit if it necessary.

Further measurements of gold as well as silver and arsenic distribution in pyrrhotite and pyrite will be conducted to define any relationship with gold. Also, SIMS data will be
discussed in conjunction with mineralogical observations to determine their relative abundance in the ores at the Kalahari Goldridge deposit.

6 CONCLUSIONS

The SIMS study revealed that pyrrhotite from the Kalahari Goldridge deposit contains an average concentration of 10 ppm of gold, while pyrite contains no gold from preliminary measurements. Also, gold distribution in pyrrhotite was quite heterogeneous.

ACKNOWLEDGEMENTS

We are indebted to J.M. Moore of Rhodes University, South Africa who initiated the Kalahari Goldridge project.

REFERENCES


The Zn-Cu deposits of the Areachap Group, Namaqualand, South Africa: Geological, Geochemical and Isotopic Characteristics

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ABSTRACT: The Areachap Group of the Northern Cape Province, South Africa is an island arc developed on the eastern margin of the polydeformed and highly metamorphosed Palaeo- to Mesoproterozoic Namaqua-Natal Belt at its contact with the Archean Kaapvaal Craton. The succession contains numerous Zn-Cu deposits of varying size and economic significance along its ~280 km exposed strike length. The deposits are dominated by Zn, with lesser Cu and minimal Pb. Protoliths of the amphibolite facies grade sequence are dominated by immature sediments or tuffaceous deposits of basic to intermediate tholeiitic to calc-alkaline composition and intercalated tholeiitic basalts. Massive Zn-Cu sulphide ore bodies are stratabound and show many similarities to VHMS, and specifically Besshi-type deposits formed in an extensional tectonic regime. These deposits likely formed in a back-arc basin to the tholeiitic to calc-alkaline volcanic arc prior to peak metamorphism at ~1150 Ma. The Areachap Belt has significant exploration potential, especially in those areas covered by a thin veneer of younger calcretes, aeolian sand or Karoo rocks.

KEYWORDS: Areachap Group, VHMS Cu-Zn deposits, amphibolite facies grade, Namaqua Province

1 INTRODUCTION

The Mesoproterozoic Areachap Group, situated along the eastern margin of the polydeformed and highly metamorphosed Namaqua Province (Figure 1) in the Northern Cape Province of South Africa, is a prominent suspracrustal sequence comprised of varying proportions of amphibolite, hornblende gneiss of intermediate composition, quartzo-feldspathic gneiss, calc-silicate and pelitic schists (Geringer et al. 1994). The sequence has been interpreted as representing the highly metamorphosed and deformed remnants of a volcanic island arc (Barton & Burger 1983; Geringer et al. 1986, 1994; Cornell et al. 1986, 1990, 1992; Jacobs et al. 1993; Thomas et al. 1994) that accreted onto the western margin of the Kaapvaal Craton at ~1.25 Ga, and was subsequently extensively metamorphosed and deformed during continental collision between the Kaapvaal Craton and the Bushmanland Terrane at ~1.15 Ga due to westward directed subduction of oceanic crust. The sequence is host to numerous base metal sulphide deposits along its ~280km strike length, from the Copperton deposit near Prieska in the south to the Areachap deposit northwest of Upington in the north, along with a number of smaller prospects throughout the belt. These deposits and prospects have been the subject of a number of studies (e.g. Theart, 1985), but their exact nature, origin and correlation with each other has been questioned. This study examines the geological, geochemical and isotopic characteristics of the Zn-Cu deposits throughout the group in order to determine their nature, origin, age and environment of formation and to assess similarities or differences between the deposits.

2 GEOLOGICAL SETTING

The Namaqua-Natal Belt of southern Africa is a region of medium- to high-grade polydeformed Palaeo- to Mesoproterozoic rocks that encircle the Archean Kaapvaal Craton to its south and west (Figure 1). The belt is comprised of a number of terranes (Bignault et al. 2002).
1983) which were amalgamated together and collided with the Kaapvaal Craton during the 1.2-1.0 GaNamaquan orogenesis (Jacobs et al. 1993; Thomas et al., 1994). At its boundary with the western margin of the Kaapvaal Craton the Namaqua-Natal belt is marked by the presence of juvenile volcanics, volcaniclastics and immature sediments of intermediate composition termed the Areachap Group. The volcanics in the northern end of the belt have Sm-Nd model ages of 2.5-1.8 Ga reflecting those in the Namaqua Province and have a significant crustal component, whereas those in the southern end of the belt have younger model ages of 1.5-1.2 Ga (Cornell et al. 1986) and represent juvenile, mantle-derived material. The Areachap Group separates the western, granitoid-dominated, high-grade granulite facies of the eastern Namaqua Province from the low-grade western margin of the Kaapvaal Craton.

Figure 1. Simplified geological map of southern Africa showing the location of the Areachap Group on the eastern margin of the Proterozoic Namaqua-Natal Belt at its contact with the western margin of the Kaapvaal Craton.

The Areachap Group massive sulphide deposits are hosted by sequences of metasedimentary rocks of immature to mature composition, with intercalated tholeiitic basalts. Gneisses and schists represent low- to medium-K tholeiitic to calc-alkaline lavas and volcanically-derived metasedimentary rocks. Shoshonitic affinities are absent. The metasedimentary rocks were derived from an intermediate (andesitic to dacitic) provenance, with a smaller felsic component. Some of the gneisses may represent tuffaceous volcanioclastic deposits.

Two varieties of amphibolite occur intercalated with the gneisses and schists and represent both sedimentary and magmatic protoliths. The hornblende-rich ortho-amphibolites have tholeiitic basaltic compositions and flat REE patterns and had a magmatic origin, whereas the para-amphibolites have more fractionated, intermediate compositions and were derived from marls.

The metadacitic footwall to the massive sulphide mineralization at the Copperton deposit has yielded a mean $^{207}$Pb/$^{206}$Pb conventional TIMS zircon age of 1285 ± 14 Ma (Cornell et al., 1990).

The Areachap Group was severely affected by high-grade regional metamorphism of upper amphibolite to lower granulite grade with temperatures generally in excess of 700°C and pressures were greater than 5.5 kbar (Cornell et al. 1992). The timing of metamorphism is poorly constrained, but Geringer et al. (1994) postulated that peak metamorphism occurred at around 1200 Ma.

3 GEOCHEMISTRY OF MASSIVE SULPHIDE ORE BODIES

The orebodies are of a massive or disseminated nature, which are dominantly pyrite-rich with minor concentrations of sphalerite and chalcopyrite. The ore bodies are tabular, stratabound and stratiform and occur in close spatial association with strongly altered lithologies represented by phlogopite-gedrite and sillimanite cordierite felses which are regarded as the metamorphosed equivalents of strongly chloritised footwall alteration rocks (Theart 1985; Theart et al. 1989).

The massive sulphide deposits are generally Zn- and Cu-dominated (Figure 2), with minor precious metal contents and minimal Pb. The largest deposit, the Copperton Mine at the southern tip of the belt, had original reserves of 47 Mt grading 1.7% Cu and 3.8% Zn (Wagener & Van Schalkwyk, 1986). The exact tonnage and grade of the smaller prospects has not been calculated due to limited amounts of drilling.

The Zn-Cu massive sulphide deposits of the Areachap Group have $\delta^{34}S$ values of between 3 $\delta^{34}S$ and 7 $\delta^{34}S$ similar to those of many VHMS and Besshi-type deposits. The larger ore bodies have higher $\delta^{34}S$ values (between 6 and 7 $\delta^{34}S$) than smaller occurrences. This suggests that a greater contribution of seawater sulphate, as opposed to a more magmatic-dominated fluid ($\sim 3 \delta^{34}S$), is more conducive to massive sulphide mineralization. A sample of barite from the
Copperton deposit, the only locality to contain significant quantities of barite, gives a δ34S value of 18.5‰, indicating a predominant seawater sulphate source.

Köppel (1980) determined a Pb-Pb age of 1305 ± 100 Ma for galena from the Copperton ore body, which, due to the proximity of the data points to the mantle growth curve, he interpreted as the age of ore formation. This model age is very similar to those of the host rock ages, as expected from VHMS deposits.

Figure 2. Base metal contents of the Areachap Group deposits. Pb-Zn-Cu ternary plot (after Franklin 1993) indicating the predominant Zn-Cu nature of the Areachap Group massive sulphide deposits.

4 METALLOGENESIS

Geochemical and geochronological constraints suggest that the highly deformed and metamorphosed Zn-Cu deposits of Areachap Group deposits formed in a volcano-sedimentary basin (likely back-arc basins). The massive Zn-Cu sulphide ore bodies are stratabound and show many similarities to VHMS, and specifically Besshi-type deposits formed in an extensional tectonic regime. Specific features that highlight a VHMS or Besshi-type origin are similar host lithology zircon and ore body Pb model ages, ore deposition in a predominantly metasedimentary succession with intercalated tholeiitic basaltic units, and a prominent altered footwall sequence (e.g. Slack, 1993; Franklin, 1993).

ACKNOWLEDGEMENTS

The financial support of the National Research Foundation (NRF) along with the Faculty of Science at the University of Johannesburg (and its fore-runner Rand Afrikaans University) for this project is gratefully acknowledged. We are grateful to the Council for Geoscience (Northern Cape Branch) in Upington who allowed us access to, and sampling of the extensive borehole core drilled through this succession.

REFERENCES


Cornell DH, Kröner A, Humphreys HC, Griffin G (1990) Age of origin of the polymetamorphosed Copperton Formation, Namaqua-Natal Province, determined by single grain zircon Pb-Pb dating. S African Jour Geol 93, 709-716


Geringer GJ, Botha BJV, Pretorius JJ, Ludick DJ (1986) Calc-alkaline volcanism along the eastern margin of the Namaqua Mobile Belt, South Africa – a possible middle Proterozoic volcanic arc. Precambr Res 33, 139-170

Geringer GJ, Humphreys HC, Scheepers DJ (1994) Lithostratigraphy, protolithology, and tectonic setting of the Areachap Group along the eastern margin of the Namaqua Mobile Belt, South Africa. S African Jour Geol 97(1), 78-100


Köppel V (1980) Lead-isotope studies of stratiform ore deposits of Namaqualand, N.W. Cape province, South Africa, and their implications on the age of the Bushmanland sequence. In: Ridge JD (Ed) 5th


Theart HFJ, Cornell DH, Schade J (1989) Geochemistry and metamorphism of the Prieska Zn-Cu deposit, South Africa. *Econ Geol* 84, 34-49


Geology and base metal-gold occurrences of Workamba area, central Tigray, northern Ethiopia.

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ABSTRACT: The Workamba area, which is part of the Arabian-Nubian Shield (ANS), is composed of mainly metasedimentary, metavolcanic rocks and granitic intrusions. These rocks are locally affected by silicification, carbonatization, sericitization and propylitic alteration. The base-metal-gold(?) mineralization in the area is hosted mainly in talc-chlorite schist within a shear zone in close proximity to the granitoid dikes. An intrusion-related mineralization is a possible scenario, however, the setting, mineralization, gangue and alteration assemblages are similar to that of shear-zone hosted (orogenic) gold. The stable isotope signatures of sulphides and associated calcite are compatible with sulphur and fluids of sedimentary or metamorphic origin, though a magmatic sulphur and fluid contribution is not excluded.

KEYWORDS: Ethiopia, Workamba, base-metals, stable isotopes

1 INTRODUCTION

Exploration has outlined a mineralized zone hosting base metal sulphides and elevated Au concentrations near the town of Workamba, northern Ethiopia (Fig. 1). The area is located 100 km northwest of Mekelle, Tigray State and lies between UTM 500 000 to 508 000 east and 1 517 000 to 1 521 800 north. This paper reports preliminary result of an ongoing study on this base-metal-gold(?) occurrence and its geological environment.

2 GEOLOGIC CONTEXT

The basement rocks of Tigrai region, northern Ethiopia, are part of the Arabian–Nubian Shield (ANS), which developed in the Neoproterozoic by rifting, arc accretion and terrane amalgamation processes during the East African Orogeny (e.g. Stern, 1994; Meert, 2003; Johnson & Woldehaimanot, 2003). These basement rocks are subdivided into the Tsaliet Group and the overlying Tambien Group (Beyth, 1972). The Tsaliet Group is mainly composed of calc-alkaline island arc rocks (Alene et al. 2000) and includes volcanic flows, well-bedded, intermediate to acidic welded tuffs, lappili tuff and agglomerates. These rocks are metamorphosed up to lower greenschist facies (Beyth, 1972; Beyth et al., 2003; Alene et
The age of the Tsaliet Group is not well constrained. Based on lithologic similarities, these rocks are correlated with the metavolcanic rocks in Eritrea (Alene et al. 2006), which were dated to \(854 \pm 3\) Ma using the Pb/Pb single-zircon evaporation method (Teklay, 1997). The Tambien Group comprises highly deformed metasediments, including slate, phyllite, graphite schist, and limestone with well preserved stromatolites, greywacke, quartzite and dolomite (Beyth, 1972; Beyth et al., 2003). The rocks were deposited in a marine environment (Alene et al. 2006). Alene et al. (2006) estimate the age of the Tambien Group to be between 800 and 735 Ma based on \(\delta^{13}C\) and \(\delta^{18}O\) and \(^{87}Sr/^{86}Sr\) characteristics. The nature of the contact between the Tsaliet and Tambien groups is controversial. Beyth (1972) recognized a unconformable contact, whereas Alene et al. (1998) describe a conformable, gradational contact.

I-type syn- and post-tectonic granitoids intruded both the Tsaliet and Tambien groups (Tadesse et al. 2000; Alene et al., 2000, 2006; Asrat, 2002). The deformation of the syn-tectonic granitoids is manifested by mylonitic fabrics. The ages of the syn-tectonic granitoids range from 800 to 750 Ma, whereas post-tectonic plutons were emplaced around 550 Ma (e.g. Tadesse et al., 2000, Asrat et al., 2001 and references therein).

Two deformation phases (D1, D2) are recognized in the rocks of the Tsaliet and Tambien groups (Alene et al., 2006). They were caused by N-S or E-W compressional stress, respectively (Alene et al., 2006). D1 resulted in tight folds, lineation and pervasive foliations, while D2 formed long wave length, upright, open parallel folds. The ages of syn- and post-tectonic granitoids constrain the ages of these deformation phases to a range between 800 and 550 Ma.

### 2.1 Prospect Geology

In the study area rocks of both, the Tsaliet and Tambien groups are exposed (Fig. 1). Vast outcrops of lower metavolcanic rocks of the Tsaliet Group occupy the north western part of the study area (Fig. 1). Strong epidotization or propylitic alteration is observed towards the contact with silicified rocks, which form the upper portion of the Tsaliet sequence. The silicified rocks are exposed as an northeast trending belt in the central part of the area. Outcrops of the overlying Tambien Group cover the southeastern part of the study area. The Tambien Group consists mainly of talc-chlorite schist, slate, phyllite, and graphite-bearing schist. These rocks are locally hydrothermally altered showing silicification, sericitization, carbonatization, and/or chloritization. The rocks of the Tsaliet and Tambien groups exhibit D1 foliation with an average strike of N40°E and dip of 60° NW. An up to 100 m thick monzogranite dike intruded the Tambien Group in its lower part. Dike emplacement occurred along the strike of foliation but the dike also locally cuts the foliation. Aplitic dikes are observed within both, the Tsaliet and Tambien groups. The aplites are affected locally by propylitic alteration.

Two generations of quartz veins were recognized. Early veins occur as 1 to 5 cm parasitic folds in the hinges of D1 folds. Veins of the second generation are 0.5 to 1 m thick, and undeformed. They are parallel to and/or cut foliation at angles roughly between 30° and 60°.
They also cut D1 folds. Ductile to brittle shear deformation in these rocks increases towards the monzogranite dike, which is expressed in increasing density of foliation planes, intense crenulation cleavage, abundant tension gashes, closely spaced fractures cutting foliation, and closely spaced second-generation quartz veins. The monzogranite dike is, however, undeformed and can therefore be correlated with the 550 Ma post-tectonic granites.

3 MINERALIZATION

Mineralization observed within Tsaliet and Tambien group rocks includes copper oxide (mainly malachite) on cleavage planes in particular at two locations in the northern part of the study area. Following stream sampling targeted on gold, a geophysical survey, and trenching, drilling penetrated a zone with basemetal sulphides in the rocks of the Tambien Group. The down-hole geology, shown in Fig. 2, corresponds to an up-sequence stratigraphic succession.

Base-metal sulphides occur locally in the metamorphic, sheared and hydrothermally altered stratified rocks, whereas intrusive rocks are barren. Pyrite, sphalerite, galena and chalcocpyrite are the main sulphide phases. Pyrrhotite and neodigenite are minor components. The sulphides occur dispersed or in discontinuous veinlets together with calcite and quartz gangue, post-dating shear deformation. Assaying identified potentially economic Au concentrations in the highly sheared talc-chlorite and carbonate-quartz-chlorite schists (National Mining Corporation). Aplites locally have elevated Au contents (up to 122 ppb in a chip sample), whereas monzogranites are barren.

 Sulphur isotope ratios of pyrite and/or chalcocpyrite, sphalerite and galena range from 1.8 to 9.1 ‰ with an average value of 5.2 ‰. No significant variations in the δ34S values or systematic changes in these values among the different analyzed sulphide species with regard to the host rock type are recognized.

 Hydrothermal calcite yield δ18O (VPDB) values between −19.1 and −15.5 ‰ and δ13C (VPDB) values between −5.6 and +1.8 ‰. Tiny two-phase, liquid-rich vapor-bearing fluid inclusions exist in calcite intergrown with sulphides. The vapor bubble occupies about 30% of the inclusion volume.

4 DISCUSSION

The volcanic rocks of the Tsaliet Group (~854 Ma) are thought to have formed from orogenic magmatism related to island arc accretion (Alene et al. 2000). The overlying metasediments of the Tambien Group (~800 to 735 Ma) were deposited in marine environment (Alene et al. 2006). Both rock units were metamorphosed and deformed before granitoid dike intrusion and base-metal mineralization took place. We assume that the monzogranite and aplite dikes in the study area are part of the widespread Neoproterozoic I-type arc magmatism of which the 608 Ma Negash pluton (143Nd/144Nd (initial) 0.512031 - 0.5121314 and 87Sr/86Sr(initial) = 0.70256 - 0.70346) exposed north of Mekelle is an example (Asrat 2002). The rocks in the target area are affected by intense silicification, carbonatization, sericitization and propylitic alteration. The base metal mineralization is associated with calcite and quartz gangue and hosted mainly in talc-chlorite schist within a shear zone in close proximity to the granitoid dikes. An intrusion-related mineralization is a possible scenario. Copper oxide showings north of the drilled area could indicate a porphyry-type Cu mineralization at depth and the base-metals in the target area may represent distal facies of this mineralization. However, the setting, mineralization, gangue and alteration assemblages are similar to that of shear-zone hosted (orogenic) gold. Elevated Sb, Hg and As concentrations with arsenopyrite are typically associated with orogenic gold mineralization. We have not identified arsenopyrite, though whole rock geochemistry on core samples suggest a general enrichment in As (up to 433 ppm) and in Sb (commonly around 2 ppm locally with 12-14 ppm) in the mineralized zone. Preliminary studies on fluid inclusion in calcite intergrown with sulphides suggest that fluids were not hypersaline, although an estimation of the salinity has still not be achieved.

The δ34S values of sulphides from 1.8 to 9.1 ‰ overlap with those found in shear-zone hosted gold deposits (e.g. Klein et al. 2005). The sulphur may be derived from the metasedimentary host rocks or from a magmatic source, although the δ34S values exceed the range commonly accepted for sulphur of magmatic origin. However, the sulphur isotope signature may result from direct reduction of magmatic SO2 by the carbon-bearing metasediments (e.g. Ohmoto & Rye 1979), with or without a sulphur contribution from the host.
rocks. The stable isotope signature of hydrothermal calcite differs from that of nearby Proterozoic limestones ($\delta^{18}O_{(VPDB)} = -4.7$ to $-13.9\%o$ and $\delta^{13}C_{(VPDB)} = -4.5$ to $+6.0\%o$; Alene et al. 2006) in $\delta^{18}O$ but lies within their range of $\delta^{13}C$ values. The calculated stable isotope composition of a fluid in equilibrium with the hydrothermal calcite at an average temperature of 300 °C, as obtained from fluid inclusion microthermometry, would have $\delta^{18}O_{(VPDB)}$ values between $-25.7$ and $-21.1\%o$ and $\delta^{13}C_{(VPDB)}$ values between $-3.6$ and $+3.8\%o$ (fractionation factors for calcite-H$_2$O of Friedman & O'Neil 1977; for Calcite-CO$_2$ of Ohmoto & Rye 1979). This estimated oxygen isotope signature is compatible with both a magmatic and metamorphic fluid source. The carbon most likely is derived from metasedimentary sources. From these isotopic data, the role of the dikes or related plutonic bodies at depth for the base-metal occurrence in the target area remains still unclear. They may be unrelated to the mineralization or provided heat to drive hydrothermal cells or contributed fluids, metals and sulphur.

5 CONCLUSION

The base-metal-gold(?) occurrence in the Workamba area shows similarities in sulphide and alteration mineralogy, and trace element characteristics with shear-zone hosted (orogenic) gold mineralization elsewhere. The stable isotope signatures of sulphides and associated calcite are compatible with sulphur and fluids of sedimentary or metamorphic origin, with or without a magmatic sulphur and fluid contribution. The role of the dikes or related plutonic bodies at depth is still uncertain.

ACKNOWLEDGMENT

Solomon Gebresilassie acknowledges funding by the German Academic Exchange Service (DAAD). The Department of Applied Geology, Mekelle University, and National Mining Corporation are thanked for logistic support during the fieldwork.

REFERENCES


SEA-FLOOR SYSTEMS (IGCP 502)

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Plagioclase-phyric basalts of Menez Gwen and Lucky Strike (Mid-Atlantic Ridge): pre-eruptive history from melt inclusion studies

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ABSTRACT: The Menez Gwen and Lucky Strike are basalt-hosted, modern seafloor hydrothermal systems located in the Mid-Atlantic Ridge. In order to address the potential magmatic contribution of ore metals into these systems, we have studied fresh porphyritic basalts sampled around the active vent areas. Basalts from both sites have E-MORB type signatures and plagioclase is the dominant phenocryst phase, although olivine and clinopyroxene also occur in places. Plagioclase phenocrysts contain abundant melt inclusions that were thoroughly studied with image analysis software to determine several parameters (e.g., area, equivalent diameter, roundness). SEM/EDS analyses of exposed melt inclusions indicate the presence of Fe, Cu and Ni metal precipitates.

KEYWORDS: basalt, Mid-Atlantic Ridge, Menez Gwen, Lucky Strike, melt inclusions

1 INTRODUCTION

Magmatic fluids are now thought to be major sources of ore metals in modern seafloor hydrothermal systems and their ancient analogues. This becomes more evident for large accumulations of volcanogenic massive sulphides (e.g. Stanton 1994; Yang & Scott 2002; 2006). The study of melt inclusions trapped in host crystals has revealed important clues about the behavior of metals and volatiles in the pre-erupted magma and their degassing into seafloor hydrothermal systems, (Yang & Scott 1996; 2002; 2005). The Menez Gwen and Lucky Strike sites on the Mid-Atlantic Ridge are vigorous seafloor hydrothermal systems venting high-temperature fluids. In order to access the possible magmatic contribution of metals and volatiles into these systems, we have studied melt inclusions hosted in plagioclase phenocrysts from fresh, unaltered porphyritic basalts.

2 GEOLOGICAL BACKGROUND

The Menez Gwen (37°50’N) and Lucky Strike (37°17’N) seafloor hydrothermal systems on the Mid-Atlantic ridge occur on axial sea-mounts in the middle of their second-order segments with relatively high magmatic budgets exhibiting fresh lavas and lava lakes (Fouquet et al. 1994; 1995). At Menez Gwen, the hydrothermal activity is recent, with anhydrite-rich chimneys growing on top of fresh pillow basalts, whereas Lucky Strike contains sulphide chimneys venting high temperature fluids that produce flanges rich in barite and in Fe and Zn sulphides (Fouquet et al. 1994). High-temperature fluids issuing from both sites have higher pH (3.4-5), low Cl and low transition metal contents suggesting phase separation in the subsurface (Fouquet et al. 1994; Charlou et al. 2000; Douville et al. 2002).

The recently discovered crustal magma chamber 3km below the Lucky Strike volcano and vent field, with axial bounding faults that penetrate the magma chamber (Singh et al. 2006), strongly suggests the preponderance of magmatic-hydrothermal processes within these systems. It also explains the reported release of volatiles (e.g. CO2, H2S, CH4 and He) through magmatic and volcanic activity (Charlou 2000).
3 METHODS

Basalts were sampled from the Menez Gwen and Lucky Strike hydrothermal fields between 1994 and 2002 during the DIVA, FLORES and SEAHMA cruises. Thirteen representative rock samples were selected for whole-rock geochemical analysis. Standard, doubly-polished thin sections (30µm to 150µm thick) from twenty-seven representative samples were selected for petrographic studies, SEM/EDS and microanalysis (EPMA).

Plagioclase, olivine, clinopyroxene, and volcanic glass were analyzed using a CAMECA SX 50 electron microprobe with three wavelength dispersive spectrometers and an accelerating voltage of 15 kV.

Modal abundances were determined in thin polished sections (30µm) from 15 representative samples with a minimum of 1500 counts per section. Mineral phases suspended in quenched glass, i.e., phenocrysts and microphenocrysts within groundmass, represent solid phases and liquid phases, respectively.

Digital analysis software (LEICA – QWin) was used to capture images and measure several parameters of both the devitrified opaque melt inclusions and glassy melt inclusions as well as their contained bubbles (e.g. area, length, breadth, roundness, equivalent diameter). Measurements were calibrated with a microscale under the same magnification. Features with a roundness index (rd) equal to the unity have a circular shape and the equivalent diameter represents the diameter of a circle having the same area as the feature. In melt inclusions that approximate the circular form, the volume of the melt inclusion (V MI) and enclosed bubbles (V b) can be calculated by the formula (4/3)πr³ where r is the radius (1/2 of equivalent diameter).

4 PETROGRAPHY AND GEOCHEMISTRY

Most basalt samples are porphyritic although some are moderately phric to aphyric with plagioclase being the dominant phenocryst phase. The larger megacrysts of plagioclase reach up to 2cm, whereas most plagioclase, clinopyroxene and olivine phenocrysts are between 2.5 and 3mm and rounded exhibiting marginal corrosion and slight compositional zoning.

Plagioclase phenocrysts are texturally complex with growth zoning, commonly exhibiting impressive amounts of aligned melt inclusions, resorbed margins and skeletal shapes. This complexity is not reflected in the mineral chemistry since plagioclase is nearly homogeneous (An89; n=153). Groundmass varies from glassy to microcrystalline and vesicles vary in size and frequency representing 0.6 to 45% of the total area.

The bulk-rock compositions of the basalts from Menez Gwen and Lucky Strike are very similar and are enriched in incompatible elements and LREE, consistent with an E-MORB signature. Only two samples from Menez Gwen deviate from these compositions, and these are less enriched in incompatible elements and LREE (closer to T-MORB signature) and less vesicular (0.6 to 3.8% of total area).

5 IMAGE ANALYSIS

Devitrified opaque melt inclusions are the most common type observed in the samples. Glassy melt inclusions, where present, are in close association with devitrified melt inclusions (Fig. 1) and may contain one or more bubbles and, rarely, mineral precipitates.

Figure 1. a) Coexisting devitrified opaque melt inclusions and glassy melt inclusions with bubbles in plagioclase phenocryst; b) detail of a).

Overall, glassy melt inclusions tend to be larger than devitrified melt inclusions. The areas of inclusions vary widely, both in devitrified melt inclusions (8.8 µm² - 1426.5 µm²; average 152.86 µm²) and glassy melt inclusions with bubbles (27.15 µm² - 2379.8 µm²; average 220.41 µm²). Since the average roundness index is close to one in glassy melt inclusions (1.14; n=182) and included bubbles (1.09; n=199), volumes could be calculated;
V_{MI}=3216.1 \mu m^3 and V_b=150 \mu m^3. V_b/V_{MI} ratios are around 6.2 vol % but vary significantly from 0.7 to 16.3. The same occurs with clinopyroxene (average 10.0 vol%) and olivine (5.3 vol%).

6 SEM/EDS

Melt inclusions that were exposed during the polishing process were subjected to SEM-EDS analysis. Preliminary results indicate that the interior of vapor bubbles contained precipitates with S, Si, Fe, Cu and Ni (Fig. 2).

Figure 2. Scanning electron microscope photographs illustrating exposed melt inclusions in thin polished sections; a) secondary electrons (SE) images and b) back-scattered electrons images (BE) are from the same melt inclusion and c) is the EDS spectra of the white circle in (a) and (b); d) overview of three exposed melt inclusions.

7 DISCUSSION

The similarities in geological setting and geochemical compositions between the two sites suggest that like Lucky Strike, Menez Gwen likely has an underlying magma chamber that provides heat to the hydrothermal system. Melt inclusion evidence indicates that the ore metals in the magmatic system may have a magmatic source. The varying V_b/V_{MI} ratios are indicative of heterogeneous melt entrapment of coexisting immiscible phases during crystal growth. Furthermore, the precipitates in the bubbles inside the melt inclusions are themselves indicative of an immiscible metal-rich fluid in the pre-erupted magma of the Menez Gwen and Lucky Strike systems. These preliminary data indicate that metal-rich magmatic fluids are strong contributors to the seafloor hydrothermal system at Menez Gwen and Lucky Strike.

ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada, the CREMINER/LA-POSC 101 and the POCTI U.I. 518 co-financed by FEDER. The authors wish to thank CREMINER (SEAHMA POCTI/MAR/15281/1999) and IFREMER for the samples given. George Kretschmann and Álvaro Pinto are gratefully acknowledged for the help with the SEM and LEICA QWin system, respectively.

REFERENCES


Yang KH, Scott SD (2005) Vigorous Exsolution of Volatiles in the Magma Chamber Beneath a Hydrothermal System on the Modern Sea Floor of the Eastern Manus Back-Arc Basin, Western Pacific:
Evidence From Melt Inclusions. *Econ. Geol.* 100: 1085-1096

Epidotes of the Troodos Ophiolite: A direct link between alteration of dykes and release of base metals into ore-forming hydrothermal systems?

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ABSTRACT: The role of source rocks in the formation of Cyprus-type Volcanogenic Massive Sulphide (VMS) deposits is not fully understood. In this paper we suggest that the formation of epidosites – episode + quartz ± chlorite ± titanite rocks commonly found at the base of ophiolitic sheeted dyke complexes – has the potential to release cobalt and zinc into active hydrothermal ore forming systems. New geochemical and mineralogical data from the sheeted dyke complex of the Troodos ophiolite indicates that progressive alteration of greenschist facies altered metabasalts to end-member epidosites results in decreasing base metal concentrations (Zn, Co) in individual dyke units. We believe this relationship provides the clearest evidence that epidosites act as source rocks for VMS deposits, and, moreover, the process of epidositisation provides a method of mobilizing metals such as Co and Ni that are considered generally immobile under typical greenschist grade alteration.

KEYWORDS: VMS, basalt, hydrothermal alteration, ophiolite, Troodos

1 INTRODUCTION

Understanding the source-deposit relationship for Volcanogenic Massive Sulphide (VMS) deposits is fundamental both for future mineral exploration and to increase our understanding of ocean floor hydrothermal processes and ocean-crust fluxes. Although it has long been known that metals are stripped from the oceanic crust by high-temperature fluids and redeposited in ore-bodies as the fluids cool, the details of this process are poorly understood. For example, it has been proposed that metal depleted “epidosites” (dykes altered to an assemblage of epidote + quartz ± chlorite ± titanite) are the source of metals in Cyprus-type VMS deposits (e.g. Richardson et al. 1987). However, the movement of base metals within sub-seafloor hydrothermal systems and into ore deposits has not been directly linked with the formation of these potential source rocks. The movement of metals traditionally considered immobile during sub-seafloor alteration, such as Co and Ni, but also found in ore deposits (e.g. Skouriotissa, ~6 Mt, with 2.5% Cu, 1% Zn, 0.35% Co and 0.1% Ni) also has not satisfactorily been addressed.

2 THE ROLE OF EPIDOSITES IN ORE FORMATION?

Epidotes are found in the sheeted dyke complex of many supra-subduction zone ophiolites (e.g. Troodos (this study), Samail (Nehlig et al. 1994), Josephine (Harper et al. 1995)) in distinct zones up to 1km or more across dyke strike. Epidote zones are commonly spatially...
related to plutonic rocks and comprise a mixture of distinct epidosite and metabasalt units. The percentage of individual epidosite units present varies from around 40% to as high as 80%, but is generally around 60% (this study). 100% epidosite unit areas are very rare within lower sheeted dyke unit systems, and the majority of epidosite appears to have selectively replaced entire dyke bodies. However, other distinct types of epidosite (e.g. haloes around quartz veins or intercalating with irregular contacts to metabasalt units) are often seen within epidosite zones.

Previous workers used the generally depleted nature of these units in some base metals (using Cu and Zn as evidence) when compared to protolith analyses to suggest that epidosites play a fundamental role as source rocks for Cyprus-type mineral deposits (e.g. Richardson et al. 1989). Oxygen isotopic evidence from the Marathasa and Solea valley areas of the Troodos ophiolite (Schiffman et al. 1990) also suggests that these epidosites were altered at much higher water-rock ratios than the background alteration represented by actinolite-albite-chlorite greenschist facies metabasalts.

Nevertheless, the formation and the role played by epidosites in ore forming systems is still a poorly understood process. This is further complicated by work undertaken by Bickle & co-workers (1998) who suggest, using strontium isotope analysis of samples from the Troodos ophiolite, that fluid fluxes which formed the epidosites were similar, if not identical, to the fluid flux present in the background metabasalt. Also, although some metals are depleted (primarily Cu) in epidosite zones, other important metals such as Co, which grades up to 0.35% in some Troodos ore deposits, do not seem to be depleted. In contrast Cu appears to be generally depleted throughout the entire sheeted dyke complex.

This conflicting evidence has cast doubt on the role of epidosites as source rocks in VMS systems. However, it is generally agreed that epidosite zones are thought to develop from intermediately altered chlorite-quartz-epidote units and, through further interaction with hydrothermal fluids, progress towards an epidote-quartz end-member (Figure 1). This is supported by petrological investigations conducted during this study. However, quantifying the release of base metals into hydrothermal systems during progressive alteration of these units has not previously been investigated.

3 METHODOLOGY

Mapping and sampling of metabasalts and
epidosite units from epidosite zones within the Troodos ophiolite was undertaken during 3 separate field seasons. Sampling was on a variety of scales from centimeter scale across individual epidosite and metabasalt units to km long transects over entire epidosite zones, sampling at 30-50m intervals. A number of samples from background altered metabasalt and fresh rocks were also taken for comparison to epidosite unit samples.

In order to quantify chemical and mineralogical changes represented by epidosite facies alteration geochemical analysis was undertaken on samples obtained during these field seasons. Whole rock samples were analysed by XRF for major and trace elements at the University of Leicester and by solution ICP-MS for a selection of trace elements at the British Geological Survey. Mineralogical analysis at the University of Leicester was carried out using a combination of thin section description and semi-quantitative XRD analysis using crushed whole rock powders and XRF analytical data.

4 RESULTS

Whole rock geochemical analyses of epidosite samples are shown in Figure 2. These plots represent the progressive alteration of epidosite units from transitional chlorite dominated samples ("Least Altered") to epidosite end-member (epidote-quartz) compositions ("Most Altered").

5 DISCUSSION

The new geochemical data presented in this paper indicate a direct relationship between the progressive alteration towards epidosites and the release of Zn and Co into the ore forming hydrothermal fluids (Figure 2). The decrease in modal proportion of chlorite correlates strongly with decreasing Zn and Co – two important metals in Cyprus-type ore deposits. These data are in direct contrast to data from fresh glass protolith analyses which, for example, show increasing Zn with decreasing MgO, an inversion of the epidosite relationship.

A simple interpretation of these data is that Zn and Co are contained mainly in chlorite within these altered rocks. Alternatively, these elements may be distributed between epidote and chlorite with the correlation being due to progressive leaching of metal and a progressive decrease in modal chlorite, both of which could be attributed to increased fluid flux. These data are in direct contrast to the background green-schist facies alteration, where typical igneous incompatible–compatible relationships are preserved within the sheeted dyke complex. Figure 3 shows a transect across a single dyke in the background green-schist altered sheeted dyke complex. The preservation of igneous relationships for metals such as nickel, cobalt and, somewhat surprisingly, zinc, suggests that they are generally immobile under typical sub-seafloor green-schist facies alteration – as seen in previous work undertaken on this style of alteration (e.g. Baragar et al. 1990). This would suggest that another form of alteration is needed to mobilize these metals, epidosite formation being our favored method.

In contrast to these metals, copper concentrations do not correlate with mineralogy. Instead, Cu is generally depleted to very low levels (<4 ppm) in most epidosite zone dykes compared to metabasalt dyke levels (average ~80 ppm, e.g. Baragar et al. 1990). However, both metabasaltic dykes and epidosites are locally enriched in Cu (epidosites generally up to ~50-100 ppm, background up to 2500 ppm - e.g. Baragar et al. 1990). This rare enrichment to protolith levels, and occasionally above, is...
interpreted to indicate that Cu was initially mobilized during the early stages of hydrothermal alteration but was locally re-deposited. The localized deposition of copper – unlike cobalt or zinc – may also indicate that copper was mobilised but not removed from the sheeted dyke complex during initial intrusion and intrusion-related hydrothermal metamorphism. Subsequent re-mobilisation and removal of copper from the sheeted dyke system via incorporation into the hydrothermal system could then take place during the formation of epidote units.

6 CONCLUSIONS

Epidote formation plays a key role in the formation of Cyprus-type VMS deposits. The mobilisation of cobalt and zinc by the formation of epidotes is a process that enables the movement of these metals. This process does not occur within typical greenschist facies alteration encountered in ophiolitic sheeted dyke complexes. This suggests that the only way to form Co- and Zn-bearing Cyprus-type VMS deposits is via the epidote facies alteration at depth within the sheeted dyke complex. The presence of copper anomalies throughout the sheeted dyke complex also suggests that copper was locally mobile during the background greenschist alteration event and in many cases the copper did not leave the sheeted dyke complex. During epidote formation any background facies dykes with copper anomalies would also undergo epidote alteration. This, whilst releasing zinc and cobalt into the hydrothermal system, would also release the copper contained by the anomalous dyke units.

This documentation of a direct link between progressive alteration and the release of base metals confirms the importance of epidote formation in forming Zn and Co-rich VMS deposits, whilst also indicating a certain amount of ‘independence’ for Cu within these ore forming hydrothermal systems. These data also allow us to explain the presence of Co in significant amounts within larger Cyprus-type VMS deposits, and suggests Co and associated elements may have uses in the exploration and testing of VMS prospects and targets.

ACKNOWLEDGEMENTS

SMJ acknowledges funding and support for PhD research from the British Geological Survey University Collaboration Scheme (BUCS) and from the University of Leicester. Fieldwork was funded by a Society of Economic Geologists Student Research Grant, and by the Edgar Pam Fellowship of the Institute of Materials, Minerals and Mining (IoM3), both to SMJ. EMED Mining and the Geological Survey of Cyprus helped with logistics during fieldwork. JN & SRNC publish with the permission of the Executive Director, British Geological Survey (NERC)

REFERENCES


Sulphur-isotope variations in seafloor and sub-floor, Cyprus-type VMS deposits of the Northern Apennine ophiolites (Italy): preliminary results.

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ABSTRACT: Sulphur isotope analyses of sulphide minerals have been carried out for the first time on VMS deposits in Tethyan ophiolites of the Northern Apennines. The overall range of δ³⁴S is between -2.9‰ and 11.4‰. The average δ³⁴S is 2.6‰ in seafloor stratiform deposits, 5.9‰ in stratabound ores within basalt, 9.6‰, 8.9‰ and 5.8‰ in stockwork veins crosscutting basalt, gabbro and serpentinite, respectively. Inorganic, thermochemical reduction of seawater sulphate is assumed to be the dominant source of sulphur in the deposits. However, the lower, negative δ³⁴S values recorded in stratiform ores indicate involvement of sulphate-reducing bacteria in the exhalative vent processes. In contrast, the lower δ³⁴S values observed in serpentinite-hosted veins may indicate incorporation of mantle-derived sulphur in the hydrothermal fluids.

KEYWORDS: Sulphur isotopes, VMS deposits, Northern Apennines, ophiolite, Italy

1 INTRODUCTION

Volcanic-Massive-Sulphide (VMS) deposits associated with ophiolites are the fossil analogues of modern black smokers. Deposits formed by precipitation of sulphides from hydrothermal solutions, on the ancient seafloor or within the rocky substrate, not far below the seawater-sediment interface. Among the various mineralogical and geochemical studies that have contributed to the better understanding of these deposits, sulphur isotope geochemistry has been critical in determining the source of sulphur which forms the major, non-metallic constituent of the ore. Cursory examination of the literature indicates, however, a relative scarcity of data concerning sulphur-isotope investigation of VMS deposits in Tethyan ophiolites (Huston 1999). This paper reports the preliminary results of the first study of sulphur isotopes for VMS deposits associated with Tethyan ophiolites of the Northern Apennines of Italy.

2 GEOLOGICAL BACKGROUND

The Mesozoic ophiolites of the Northern Apennines (Figure 1) represent the oceanic lithosphere underlying a marginal basin of the western Tethys. They are distinguished from
coeval ophiolites exposed in the Western Alps and to the west of the Sestri-Voltaggio line, because of the lack of the high-P, low-T, Alpine-age metamorphism. Several sulphide deposits are known in the Apennine area since the Bronze Age, some of which were exploited for copper extraction until the early seventies. Despite their economic importance over times, the VMS nature of the ore deposits was recognized only recently (Ferrario & Garuti 1980, Garuti & Zaccarini 2005). The deposits are characterized by a Cyprus-type, Fe-Cu-Zn sulphide assemblage and occur at different stratigraphic positions in the ophiolitic pile, suggesting distinct hydrothermal convective cells at various stages during the slow spreading of the oceanic basin (Figure 2).

Field relations indicate that the stratiform ores were deposited on the ocean-floor by hydrothermal vents, and suffered long-lasting exposition to seawater and submarine weathering, prior to burying under pillow basalt or pelagic sediments.

Garuti and Zaccarini (2005) have described abundant sulphide textures reflecting replacement of biogenic material (Figure 3). Stratabound deposits consist of an upper zone of massive sulphide, usually underlain by networked and fissure filling sulphide (stringer ore) intergrown with chloritized pillow basalt. The deposit formed during the lava outflow, just below the basalt-seawater interface, and underwent only limited submarine weathering. The stockworks occur as discordant veins within basalt, gabbro or serpentinite, below the ancient ocean floor. Sulphide textures consistent with crystallization and grain coarsening under hydrothermal conditions are preserved (Figure 4).

3 SAMPLES AND METHODS

A total of 26 samples from 11 mining localities representative of ore deposits in stratiform, stratabound and stockwork-vein settings were selected for this preliminary investigation (Figure 1). Sulphur isotopes analyses were performed on single sulphide minerals picked up from polished section under the reflected-light microscope: pyrite (17 samples), chalcopyrite (15 samples) sphalerite (3 samples) and pyrrhotite (two samples). The analyses were carried...
out at the Serveis Científic-Tècnics (University of Barcelona, Spain), using a combustion apparatus equipped with Delta C Finnigan MAT, continuous flow, isotope-ratio mass spectrometer, and TC-EA elemental analyzer, following the method of Giesemann et al. (1974). The results are given as $\delta^{34}\text{S}_{\%o}$ values relative to the Cañon del Diablo (CDT) standard. The analytical precision ($2\sigma$) is within ±0.2‰.

Figure 4. Idiomorphic recrystallized pyrite in quartz with chlorite spots, from stockwork veins. Scale bar = 250 µm.

4 RESULTS

The whole set of calculated $\delta^{34}\text{S}_{\%o}$ ranges between -2.9 and 11.4 (av. = 6.0‰), if one anomalous value of 22.8 is discarded (Figure 5). Only minor variations are observed among sulphide minerals, chalcopyrite having slightly higher values than coexisting pyrite and sphalerite, in stockwork and stratabound deposits. Slightly higher $\delta^{34}\text{S}$ are found in stratabound stringers (av. = 8.0‰) with respect to the overlying massive ore (av. = 5.0‰), and in stratiform massive sphalerite (av. = 5.1‰) compared with adjacent Fe-Cu ore (av. = -0.2‰). In general, there is a significant decrease in $\delta^{34}\text{S}$ from stockworks (av. = 8.1‰), to stratabound (av. = 5.9‰) and stratiform ores (av. = 2.6‰), these latter showing negative values, down to -2.9‰ in some cases. Furthermore, the stockwork veins display variation of $\delta^{34}\text{S}$ as a function of host-rock lithology, with a decrease in the average value from 9.6‰ and 8.9‰, in the veins hosted in basalt and gabbro, to 5.8‰ in those hosted in serpentinite.

5 PRELIMINARY CONCLUSIONS

It is commonly held that sulphur in VMS deposits is predominantly derived from the inorganic, thermochemical reduction of seawater sulphates, with the possible contribution of sulphur from leaching of sulphides in the host volcanic rocks, or extracted from a juvenile magmatic fluid (Ohmoto 1986, Huston 1999). The data presented for the Northern Apennine sulphide deposits are in broad agreement with this interpretation, with some important exception, however.
depositional reworking) of the sulphide with the involvement of reducing-bacteria that would be consistent with the abundant biogenic textures reported from these deposits (Garuti & Zaccarini 2005). Field evidence indicates that the stockwork deposits formed in a sub-seafloor environment, isolated from cold seawater. Their average δ³⁴S (= 8.1‰) is consistent with the assumed inorganic-reduction of seawater sulphates. However, the relatively low value reported from veins hosted in serpentinite may indicate incorporation of minor amounts of sulphur derived from leaching of sulphides with δ³⁴S close to the mantle ratio.

The case of the Northern Apennines, Cyprus-type deposits provides evidence for fractionation of sulphur isotopes in response to variation of the depositional environment (sea-floor vs. sub-seafloor) and host rock association (basalt vs. serpentinite), in a VMS forming system within the Jurassic Tethys.

ACKNOWLEDGEMENTS

E. Aracil is thanked for his assistance in the sulphur isotope analyses. F.Z. thanks the “Juan de la Cierva” grant.

REFERENCES


ABSTRACT: Peralkaline metarhyolites that host volcanogenic massive sulphide (VMS) deposits in the Bonnifield district, Alaska, have elevated high-field-strength-element (HFSE) and rare-earth-element (REE) contents. Herein we identify the accessory minerals that contain these trace elements and use textural relationships to propose that magmatically-derived hydrothermal deposition of HFSE and REE minerals (Nb-rutile, yttrobetafite, bastnäsite-(Ce), xenotime) overlapped with precipitation of submarine-hydrothermal Fe-Zn-Pb sulphides. Fluorite may have precipitated contemporaneously with the HFSE- and REE-rich minerals. Magmatic-hydrothermal fluids with abundant F and Cl (± CO₂ ± S), mixed with non-magmatic Fe-, Zn-, Pb-, and S-rich fluids in the shallow subsurface, during seafloor VMS mineralization. Magmatic-hydrothermal fluids may have transported and deposited some of the base metals and sulfur in the Bonnifield VMS deposits.

KEYWORDS: Bonnifield district, peralkaline rhyolite, VMS deposits, yttrobetafite, bastnäsite

1 INTRODUCTION

The Bonnifield volcanogenic massive sulphide (VMS) deposits, located on the northern flank of the Alaska Range in east-central Alaska, occur within a belt of Devonian-Mississippian volcano-plutonic complexes and associated siliciclastic and carbonaceous sedimentary rocks along the ancient Pacific margin of North America. Both VMS and sedimentary-exhalative (SEDEX) deposits occur within the belt. Bonnifield is unusual, however, because its major deposits are hosted in peralkaline metarhyolite (Dusel-Bacon et al. 2006, and references therein).

This paper focuses on the tectonic, magmatic, and hydrothermal conditions that accompanied bimodal magmatism in an extensional, back-arc submarine setting. We report here the results of microbeam analyses of accessory mineral phases that account for the elevated HFSE and REE contents in the metarhyolites. Textural relationships among these accessory minerals and the sulphides provide insights into the magmatic to hydrothermal transition in peralkaline-related VMS systems.
its. Carbonaceous phyllite is found within all members of the Totatlanika Schist. The Wood River assemblage consists of metavolcanic and metasedimentary rocks on the south flank of the anticline.

3 BONNIFIELD DISTRICT GEOLOGY

Mineralization occurs near the contact between phyllitic felsic metavolcanic and subordinate carbonaceous rocks of the Mystic Creek Member and overlying, predominantly metasedimentary, rocks of the Sheep Creek Member. Diamond drilling just north of Red Mountain, named for its distinctive 1,800m-thick zone of quartz-sericite-pyrite footwall alteration, revealed the DC North massive sulphide deposit (Smit 1999). Two styles of mineralization are evident in the DC North horizon: (1) "Discovery-style," which consists of massive to semi-massive Zn-Pb-Ag mineralization within, and at the base of, an aphanitic, intensely altered siliceous metahyolite, and overlying stringers and disseminations of chalcopyrite and pyrite. (2) "Fosters Creek-style," hosted by pyritic metamudstone in the hanging wall of, and along strike from, the aphanitic siliceous metahyolite, consists of disseminations and laminae of sulphides, and zones of semi-massive to massive pyrite, sphalerite, galena, and chalcopyrite. Host rocks of the "Fosters Creek-style" mineralization are interpreted to have been deposited in a synvolcanic sedimentary basin (Smit 1999). A possible synvolcanic quartz porphyry intrusion is cut by multiple veins of quartz, fluorite, pyrite, and sphalerite in the central footwall area where the Discovery and Fosters Creek zones overlap (Grayd Resources Corporation 1999). The stockwork fluorite veins are cut by veins and lenses of fine-grained yellow sphalerite and minor pyrite, suggesting that these sulphides formed in the shallow subsurface and not as exhalative precipitates on the sea floor.

The WTF deposit occurs ~3km northeast of Red Mountain. Whole-rock trace-element geochemistry and mineralogy of the WTF and the DC deposits are similar and support the interpretation of Smit (1999) that places the WTF and the DC deposits on the northern and southern limbs, respectively, of a syncline.

The Anderson Mountain VMS prospect, located 32km southwest of the Mystic Creek deposits occurs within felsic to mafic metavolcanic rocks and associated carbonaceous metasedimentary rocks of the Wood River assemblage.

4 TRACE ELEMENT GEOCHEMISTRY

Bonnifield igneous rocks have experienced low-grade metamorphism in the Mesozoic and earlier seafloor-hydrothermal alteration; therefore, we used immobile elements (e.g., Nb, Ta, Y, Yb, Ti, Zr, Hf) to identify their original geochemical characteristics. Metahyolites of the Mystic Creek Member and the metabasalts from other members contain elevated HFSE, REE, Y, and Ga contents (Dusel-Bacon et al. 2006). Dark grey shales intercalated with Mystic Creek metahyolite also show HFSE and LREE enrichments, suggesting a significant peralkaline rhyolitic tuff component in the seafloor sediments. On Nb/Y vs Zr/TiO₂ and Yb vs Ta discrimination diagrams, Mystic Creek metahyolites plot as comendite having within-plate tectonic affinities; associated metabasalts are alkali basalt with ocean-island basalt affinities. Metahyolites from the other members of the Totatlanika Schist have rhyolitic to dacitic compositions and volcanic-arc affinities. Wood River assemblage metavolcanic rocks are mostly sub-alkaline and span a broader compositional range that includes andesite. Metahyolites have volcanic arc and transitional within-plate affinities and metabasalts have calc-alkaline arc and E-MORB affinities.

5 HFSE- AND REE-RICH ACCESSORY MINERALS

We used scanning electron microscopy (SEM) with linked energy-dispersive spectrometry, and quantitative electron microprobe analysis, to identify the mineral phases that contain the elevated HFSE and REE in three Mystic Creek Member metahyolite samples associated with the WTF and DC VMS deposits.

5.1 Sample 04ADb11A (WTF deposit area)

This strongly foliated metahyolite is cut by an intensely deformed, pytgmatic veinlet consisting of grain aggregates of major yttrioxide-fite, minor Nb-rutile and xenotime, and sparse monazite (Fig. 1A). Muscovite prisms surrounding the veinlet are aligned in the axes of the folds, but the minerals in the veinlet are not. Yttrioxide-fite (Y,Fe(REE)₂(Ti,Nb,Si,Ta)₃O₈OH, a member of the pyrochlore group, occurs as
zoned 1-10 µm grains in which the zoning is defined largely by Si variations. In parts of the veinlet, Nb-rutile forms aggregates of skeletal grains with inclusions or intergrowths of xenotime. Monazite occurs as anhedral grains <5 µm in diameter, isolated along the margins of the veinlet or in contact with grains of xenotime. The lack of tectonic alignment of the yttrobetafite, Nb-rutile, and xenotime grains in the veinlet may reflect recrystallization of these minerals during regional metamorphism, or preservation of magmatically-derived hydrothermal minerals that were unaffected by the penetrative deformation that produced the pytgmatic folds and aligned muscovite grains.

5.2 Sample 97ADb60G (near DC deposit)

This unfoliated altered metarhyolite contains large (1-3 mm) clots of secondary iron oxides, possibly after magnetite. Fe-Mg carbonate is abundant locally. The matrix (quartz+albite+muscovite) contains discontinuous, 5-20 µm-wide veinlets composed mainly of anhedral zircon with minor yttrobetafite and sparse bastnäsite-(Ce) [(Ce,La,Nd,Pr)(CO₃)F] and pyrite. The veinlets are irregular, not planar, and in places wrap partly around quartz phenocrysts. The clots of iron oxide contain inclusions of bastnäsite-(Ce). Bastnäsite-(Ce) and Nb-rutile also occur as disseminated grains throughout the matrix of the metarhyolite (Fig. 1B); one grain of bastnäsite-(Ce) is in contact with euhedral pyrite. Several other clusters of euhedral pyrite in the section contain spatially associated grains of bastnäsite-(Ce). Some quartz phenocrysts and rounded to elliptical quartz+K-feldspar intergrowths ~100-200 µm in diameter are completely surrounded by thin (5-10 µm) rims composed of anhedral Nb-rutile, together with sparse 1 µm grains of yttrobetafite, bastnäsite-(Ce), and cassiterite.

5.3 Sample DC96-3A-273 (Discovery Zone)

This drill core sample is a weakly foliated, pyritic metarhyolite. It contains 15 vol % disseminated euhedral pyrite with small (5 µm diameter) inclusions of galena. Minor sphalerite occurs as isolated disseminated grains and inclusions in pyrite. Most quartz phenocrysts (±albite±muscovite) are surrounded by thin (to 20 µm) rims of euhedral pyrite and sparse grains of anhedral bastnäsite-(Ce). A few euhedral grains of pyrite are in contact with anhedral grains of bastnäsite-(Ce) (Fig. 1C). Euhedral prisms of Nb-rutile 30-50 µm in length are locally surrounded by thin (<5 µm) rims of disseminated pyrite and are variably replaced along cleavage planes by quartz and fine-grained (1 µm) pyrite.

![Figure 1. SEM Backscattered Electron (BSE) images showing HFSE- and REE-rich accessory minerals in peralkaline metarhyolite of the Mystic Creek Member. A, pytgmatic veinlet composed of yttrobetafite (ytb) with minor Nb-rutile (ru) and xenotime (xen) and sparse monazite (mz) from the WTF deposit (sample 04ADb11A). B, disseminated bastnäsite-(Ce) (bas) from the DC deposit area (sample 97ADb60G). C, bastnäsite-(Ce) intergrown with pyrite (py) from the DC deposit (sample DC96-3A-273). Other mineral abbreviations: ab, albite; mu, muscovite; qtz, quartz.](image-url)
PHYSICAL CONDITIONS OF BONNIFIELD MINERALIZATION

Geologic, geochemical, and isotopic evidence suggests that the Mystic Creek Member metarhyolite erupted in an extensional, back-arc basin associated with a continental-margin volcanic arc that included rocks of the Wood River assemblage (Dusel-Bacon et al. 2006).

Sillitoe (1982) recognized that VMS deposits commonly form in bimodal volcanic sequences that are typically associated with extensional environments. Therefore, it is not surprising that the peralkaline within-plate metarhyolite of the Mystic Creek Member hosts the largest VMS deposits of the Bonnifield district. The rarity of inherited zircon cores and the paucity of zircon, in general, in Mystic Creek peralkaline metarhyolites, suggest that some of the pre-existing zircons dissolved due to the peralkaline magma composition or to relatively high magmatic temperatures. The Mystic Creek rhyolitic magmas likely erupted at temperatures where they had only begun to crystallize zircon or, in some cases, were above the temperature of zircon saturation (Watson & Harrison, 1983). Peralkaline rhyolites typically are chlorine-rich, which may contribute to their capacity for carrying metals and evolving chlorine-rich fluids.

Although the geochemistry of peralkaline rhyolites is well established in the literature, few workers have described the mineralogical hosts of HFSE and REE in such rocks. To our knowledge, this is the first study to investigate the HFSE and REE mineralogy of peralkaline rhyolites associated with VMS deposits.

Textural relationships in the metarhyolites support a model in which late-magmatic and magmatic-hydrothermal deposition of HFSE and REE minerals overlapped with precipitation of hydrothermal Fe-Zn-Pb sulphides. We hypothesize that one or more magmatically-derived vapor ± fluid phases formed early Nb-rutile, yttrobetafite, bastnäsite-(Ce), and casseriterite that surround quartz grains and quartz-K-feldspar intergrowths of volcanic origin. Coeval or later magmatic-hydrothermal fluids deposited yttro-betafite, minor xenotime, and Nb-rutile in fractures in rhyolite lava (or tuff), after eruption onto the sea floor; fluorite may have precipitated contemporaneously. Within cooling peralkaline rhyolite, deposition of pyrite, galena, and sphalerite from seawater-dominated subsurface hydrothermal fluids was coeval with deposition of bastnäsite-(Ce) and Nb-rutile by magmatically-derived fluids. This interpretation implies that F- and Cl-rich (and possibly CO₂- and S-rich) magmatic-hydrothermal fluids mixed with non-magmatic, volcanogenic Fe-, Zn-, Pb-, and S-rich fluids in the shallow subsurface during seafloor VMS mineralization. Our model raises the possibility that magmatic-hydrothermal fluids in peralkaline magma of the Bonnifield district transported and deposited some of the base-metals and sulphur in the VMS deposits, in addition to HFSE and REE.

ACKNOWLEDGEMENTS

We thank R.L. Oscarson for some of the SEM images for our study, and J.B. Lowenstern and R.A. Koski for helpful comments on the manuscript. Pacific Alaska Resources and Grayd Resource Corporation provided access to drill core and company reports on the VMS prospects.

REFERENCES


Recognition of high-T rhyolite melts in the Rosh Pinah – Skorpion Zn-Pb district, Southern Namibia

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ABSTRACT: The base metal mining district of Rosh Pinah and Skorpion in Southern Namibia with its Zn-Pb(-Ag-Ba) and Zn-only deposits, has been interpreted mainly in terms of sediment-hosted metallogenesis. However, the presence of bimodal volcanic and subvolcanic rocks within the Late Proterozoic sequence has been increasingly acknowledged over the last few years. The succession includes dykes and sills, volcanic domes and flows, as well as hyaloclastic, pyroclastic and volcanioclastic rocks. The determination of zircon saturation temperatures for most of the metarhyolites from the vicinity of both deposits reveal anomalously high melt temperatures, ranging between 850°C and 1000°C. Such high-T rhyolite melts reflect anomalously high advective heat transfer into the volcano-sedimentary basin fill. This high heat flow likely caused the development of long-lasting and highly efficient convection cells which resulted in the leaching of a mixed volcano-sedimentary source rocks and the formation of base metal sulphide deposits.

KEYWORDS: zirconium saturation temperature, Gariep Belt, base-metal sulphide deposits

1 GEOLOGICAL INTRODUCTION

The Gariep Belt is part of the late Proterozoic/Early Palaeozoic Pan-African system of orogenic belts and forms the southern coastal branch of the Damara Orogen. It consists of the para-autochthonous Port Nolloth Zone (PNZ) in the east and the allochthonous Marmora Terrane (MT) in the west, separated by the Schakalsberg thrust (Frimmel & Frank, 1998). The volcano-sedimentary lithostratigraphy comprises, on the sedimentary side, siliciclastic and carbonate rocks from high-energy debris flows, conglomerates and turbidites to shallow-water pyritic black shales and stromatolitic limestones. In contrast, the bimodal volcanic component consists of metabasaltic dykes, sills and extensive thin flows which locally display preserved basaltic pillows (Fig. 1) and rhyolitic domes, thick highly viscous flows (Fig. 2), breccias (Fig. 3) and hyalo-/ pyroclastic deposits (Fig. 4).

Figure 1. Metabasalt with pillows structures, 6 km W of Rosh Pinah Mine.

Figure 2. Thick metarhyolite flow with columnar jointing, 5 km N of Rosh Pinah Mine.
Individual zircons from one metarhyolite (Fig. 5) have been dated at 752 ± 5.5 Ma (Borg et al. 2003) and another metarhyolite has been dated at 741 ± 6 Ma (Frimmel et al. 1996b). Both are interpreted to belong to the Rosh Pina Formation, which is regarded as a marginal initial rift-fill sequence (Frimmel et al. 1996a). This sequence hosts the Rosh Pina Zn-Pb-Ag massive sulphide deposit and the Skorpion non-sulphide Zn deposit. The later has formed by supergene oxidation and metal fractionation of a pre-existing Zn(-Pb-Cu) massive sulphide deposit, of which a stockwork remnant is still preserved at depth (Borg et al. 2003). Geochemically, the metarhyolites are of calc-alkaline affinity, locally with very high potassium contents.

2 ZIRCON SATURATION TEMPERATURES

The original magmatic melt temperatures of the metarhyolites have been determined by application of the method developed by Watson & Harrison (1983). This method determines the zircon saturation temperature (T_Zr) and is based on the increasing zirconium content of the melt with increasing temperature. In this method, T_Zr is calculated according to the equation:

\[ T_{Zr} = \frac{12,900}{2.95 + 0.85M + \ln(496,000/Zr_{melt})} \]

Here, \( T \) is the absolute temperature in degrees Kelvin and \( M \) is the cation ratio (Na + K + 2Ca)/(Al x Si). \( Zr_{melt} \) is the concentration of zirconium in the melt with respect to that in zircon (~496,000 ppm). All temperatures within this study are reported in °C.

With the help of the \( T_{Zr} \), rhyolites can also be classified with regard to their VMS fertility (Barrie, 1995). High-T rhyolites have been metallogenetically related to some Cu-Zn and Cu-Pb-Zn VMS deposits in the Abitibi Subprovince, Canada, where these melts were the heat source for the metallogenically fertile hydrothermal systems.

Barrie (1995) established four groups of rhyolites depending on their SiO_2 and Eu contents as well as their ratios of Zr/Y, La_8/Yb_8 and Rb/Sr. Group one and two have been classified as high-silica rhyolites with \( T_{Zr} \) between 840-940° C and high Zr contents of about 500 ppm. These groups are associated with more than 90% of the VMS deposits in the Abitibi

Figure 3. Altered stockwork breccia in massive porphyritic metarhyolite with chlorite alteration and barite veinlets (Farm Spitzkop). The metarhyolite is part of the main volcanic centre, proximal to the intersection between the main basin margin fault and a transform fault.

Figure 4. Photomicrograph of accretionary lapilli in marble, Farm Spitzkop, 6km SE of Skorpion Mine. (thin section, ppl).

Figure 5. Magmatic zoned zircons from a metarhyolite some 3 km N of Skorpion.
Subprovince. Thus, Barrie (1995) concluded that rhyolites with high $T_{Zr}$ and high SiO$_2$ contents, can be used as a tool for base metal exploration.

In our study, we have calculated $T_{Zr}$ for eleven rhyolite samples (Table 1), which can be assigned to Barrie’s’ groups according to temperature (Fig. 6). It is important to note that “group three rhyolites” (800-870° C), which are characterised by some of the lowest melt temperatures, are not represented.

Table 1. $T_{Zr}$ and Zr content of Gariep rhyolites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zr [ppm]</th>
<th>$T_{Zr}$ [°C]</th>
</tr>
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<tbody>
<tr>
<td>06014</td>
<td>656</td>
<td>939</td>
</tr>
<tr>
<td>06021</td>
<td>1066</td>
<td>954</td>
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<tr>
<td>C-3-1116</td>
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</tr>
<tr>
<td>FELSC-02</td>
<td>114</td>
<td>759</td>
</tr>
</tbody>
</table>

To test if the rhyolites of the Rosh Pinah Formation can be assigned to the groups of Barrie (1995), the samples are shown on a Zr/Y vs. emplacement temperature ($T_{Zr}$) (Fig. 7).

Six samples can be assigned to groups one and two by temperature (black colours). Samples in white belong to group four by temperature but plot outside the field of group four. The reason for this is their lower Zr/Y and high Ca contents, which influence the calculation of $T_{Zr}$.

Applying the model of Barrie (1995), the “hot rhyolites”, plotting in the fields of groups one and two, and at higher temperatures, are likely to have served as a heat source for the hydrothermal systems that formed the Skorpion and Rosh Pinah massive base-metal sulphide deposits.

2.1 Heat flow and base metal fertility

According to Barrie (1995), group one high-silica rhyolites are analogous to high-temperature silicic volcanic rocks found in provinces containing hot spots related to mantle plumes. This could also apply to the initial continental rift stage in the development of the Gariep Rift and might reflect a mantle plume or local hot spot. The felsic volcanic domes and associated thick rhyolitic flows are spatially related to a prominent intersection between the first-order basin margin fault and a transform fault, the Zebrafontain Fault. This fault intersection appears to control the location of the bi-modal magmatism with its metallogenically fertile volcanic rocks. This cluster is presently the only one known within the Port Nolloth Zone.
3 CONCLUSIONS

For years, the base-metal sulphide deposits of Rosh Pinah and Skorpion, were generally interpreted to be SEDEX-style mineralization. Zircon saturation temperature determinations of the metarhyolites which are intercalated with the metasedimentary host rocks (Fig. 8), give anomalously high melt temperatures.

Figure 8. Thin rhyolitic sill with devitrified margins in meta-arkose at Skorpion (borehole SKGT 12).

These hot rhyolite sills and volcanic rocks have transferred heat efficiently into the basin sediments. Here, the heat flow was likely the main driving force for the hydrothermal convection cells which leached sedimentary and mafic and felsic volcanic rocks and formed the massive sulphide deposits. Fundamental controls on ore deposit location within the basin are thus major fault intersections, high crustal heat flow, and volcanic centres with high-T rhyolites in a thick siliciclastic/volcaniclastic package.

ACKNOWLEDGEMENTS

Support by both, Anglo American Corporation and Kumba Resources is gratefully acknowledged. We particularly thank Jan Peter and Dan Layton Mathews who first suspected the rhyolites to be “hot stuff” during an IGCP-502 field workshop.

REFERENCES

Frimmel HE, Hartnady CJH, Koller F (1996a) Geochemistry and tectonic setting of magmatic units in the Pan-African Gariep Belt, Namibia. Chemical Geology 130: 101-121
The relationship between shale and giant massive sulphide deposits: More than a spatial coincidence?

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ABSTRACT: Numerical modeling based on the geology and geochemistry of the massive sulphide deposits of the Iberian Pyrite Belt and their underlying siliciclastic sediments shows that moderately oxidized shale can be the source of metal-rich but sulphide-poor hydrothermal brines. These fluids can migrate long distances through large faults until they find a suitable geochemical trap. Reaction with fluids and rocks rich in H₂S promotes sulphide saturation and the precipitation of large sulphide masses. Thus, the giant massive sulphide deposits of the IPB may have formed by the circulation of normal basinal brines without needing to invoke metal-rich magmatic fluid source.

KEYWORDS: Geochemistry, massive sulphides, Iberia, numerical modeling

1 INTRODUCTION

Genetic models for volcanic and sediment-hosted base metal massive sulphide deposits have been hampered by the problem of finding the source of metals and reduced sulphur. Numerical calculations in these low temperature hydrothermal systems show that reduced sulphur and metals cannot be transported by the same fluid unless unrealistically large amounts of hydrothermal fluids have been involved in the system (Anderson 1975; Sverjensky 1989). Alternative models include: (a) transport of metals by sulphide-poor fluids with later in situ addition of reduced sulphur via fluid mixing or reaction with host rocks, and, (b) transport of metals and sulfate by oxidized fluids, with the sulfate being later reduced synchronously with metal deposition (Sverjensky 1989; Cooke et al. 2000). However, the major problem of the first alternative is where and how such H₂S-depleted fluids are formed. In fact, average reservoirs/metal sources are usually sulphur-rich. This is especially significant in shale-related deposits, where the presumed metal source may have had significant (authigenic?) pyrite.

However, numerical modelling shows that, paradoxically, fluids equilibrated with shale can be quite metal-rich but sulphur poor. We have tested such a model in the Iberian Pyrite Belt (IPB), where there is a direct spatial, genetic and chronological relationship between shale and giant massive sulphide deposits.

2 GEOLOGIC AND METALLOGENIC SETTING

The IPB includes a thick volcaniclastic (is this the PQ plus VS groups or only the VS – not clear) sequence deposited in pull apart structures during the oblique collision between an exotic terrane, nowadays represented by the South Portuguese Zone, and the Iberian Autochthonous Terrane (Silva et al. 1990) during late Devonian to early Carboniferous. The sequence is rather monotonous and includes several thousand m of siliciclastic sediments (PQ Group) overlain a complex unit with felsic and mafic volcanic rocks interbedded with volcaniclastic rocks, shale and chemical sediments (VS Complex).

The VS Complex hosts a large number of massive sulphide bodies, forming perhaps the largest concentration of sulphides on the earth’s crust. The massive sulphides are either interbedded with late Devonian shale as in the southern IPB or as massive to tabular bodies replacing felsic volcanic rocks as in the northern IPB (Tornos 2006). Both styles of mineralization have an underlying stockwork that only locally penetrates into the PQ Group, suggesting that the hydrothermal fluids have equili-
brated (or failed to interact?) with the underlying sediments.

Isotope geochemistry shows that ore forming fluids equilibrated with rocks with a large crustal residence time, very likely the shale and sandstone of the PQ Group. Fluids are characterized by high $\delta^{18}$O but variable $\delta D$ signatures, 0-8‰ and -45 to 5‰, respectively, and have radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7073-0.7203), $^{207}\text{Pb}/^{206}\text{Pb}$ and $\gamma$Os values. These values are consistent with the derivation of metals and fluids from highly evolved crustal sources. Fluid inclusion data show that hydrothermal fluids were CO$_2$-poor brines having salinities up to 24 wt% NaCl eq., but usually ranging between 3 and 12 wt% NaCl eq. (see Relvas et al. 2001, Munhá et al. 2005, Tornos 2006 and references therein). Sulphur isotope values of sulphides are very variable, between -34 and +21‰, and consistent with a dual derivation of the sulphur, from the biogenic reduction of seawater sulfate and from the leaching of the underlying sedimentary sequence (Velasco et al. 1998).

Some stockworks below the massive sulphide deposits have an assemblage enriched in sulphur-poor minerals, such as pyrrhotite, tellurides and magnetite, while these minerals are minor or absent in the overlying deposits. This suggests that deep fluids were sulphur-depleted and only mixing with external sulphur can produce large deposits.

Different studies have claimed a derivation of metals and fluids from magmatic sources. The main arguments for such a model are the presence of deep plutonism contemporaneous with massive sulphide formation, the isotopic signatures coupled with the fluid inclusion data (Solomon & Quesada 2003) and the high efficiency of magmatic fluids in the formation of massive sulphides (Yang & Scott 1996). However, the absence of large hydrothermal systems with typical magmatic alteration (e.g., Corbett 2001) suggest that magmatic fluids were minor, if not absent, in the IPB hydrothermal systems.

Barrie & Hannington (1999) have shown that there is a close correlation between the metal ratios in the source rocks and the related massive sulphide deposits. The Cu:Zn:Pb ratio of massive sulphides and of rocks belonging to the PQ Group is very variable but the average, recalculated to total tonnage of the orebodies, is strikingly similar. The ratio in the PQ Group is 28:53:19 while that of the massive sulphides is 25:52:23. This close agreement strongly supports the isotopic and geological results and confirms that the major source of metals in the IPB is the PQ Group.

3 NUMERICAL MODEL

A numerical model has been constructed assuming the equilibrium of fluids with the PQ Group using the SOLVEQ/CHILLER code (Reed & Spycher 1988) with a modified SOLTHERM database including recent data on the solubility of base metals. The composition of a fluid equilibrated with the PQ Group has been based assuming equilibration of shale with a fluid having a total salinity of 9%NaCl equiv. The shales of the PQ Group are made up of phengite, quartz chlorite and minor amounts of both plagioclase and K feldspar. Pyrite is a fairly common accessory mineral and locally it is accompanied by traces of magnetite and pyrrhotite. Systematic geochemical sampling has shown that most of the PQ shale has been deposited in an oxic to sub-oxic environment (Tornos et al. in press).

This assemblage indicates that fluids were pH buffered by a quartz-feldspar-white mica assemblage - a feature consistent with the absence of large hydrothermal zones below the massive sulphides.

Calculations at different temperatures, pH and redox conditions show that the solubility of the metals is strongly dependant on the fO$_2$ of the system (Figs. 1 and 2). For example, at 300°C and a pH of 5.0, highly reducing systems (log fO$_2$ 3.5 units below NNO, near C-CO$_2$...
(equilibrium) can transport more reduced sulphur (1885 ppm) than combined Cu (1 ppm), Zn (283 ppm), Pb (8 ppm) and Fe (28 ppm). However, at intermediate redox conditions (between the NNO and HM buffers), the solubility of metals increases dramatically to 7 ppm Cu, >10000 ppm Zn, 1000 Pb and 8300 ppm Fe while the solubility of sulphur drops to only 36 ppm.

Reaction of such a fluid with seawater that has 90% of its sulphate reduced to H$_2$S leads to the precipitation of massive sulphides with an average base metal content similar to that of many deposits of the IPB. These calculations show that inflow of the hydrothermal fluid in an anoxic bottom with high degree of biogenic reduction of seawater sulphate can produce giant massive sulphide deposits.

Mass balance calculations show that only a small depletion in metals of about 5 ppm of each is needed for forming all the massive sulphides in the IPB. Thus, metal leaching will not have a major geochemical effect on the source rocks.

4 DISCUSSION AND CONCLUSIONS

The numerical results show that fluids equilibrated with weakly oxidized (magnetite-rich but carbon poor) siliciclastic sediments are moderately base metal and iron-rich but sulphur deficient brines. These fluids can travel long distances within sedimentary basins without changing their chemical composition nor leaving a halo of hydrothermal alteration. Only when approaching the seafloor, where major chemical and thermal changes take place, fluids react with the host rocks and mix with seawater producing the stockwork zone. On the seafloor fluid mixing dominates and deposition of massive sulphides takes place.

The formation of giant massive sulphide deposits in the IPB is probably due to the combination of several key factors including the presence of a thick immature siliciclastic sequence that was quickly followed by rifting and related high heat flow. This promoted quick dewatering and channeling of fluids along restricted extensional structures in an overall transpressional regime, promoting high fluid flow. Fluid flow modeling of Conde et al (2005) shows that during the onset of convective hydrothermal circulation during the late Devonian, first batches of fluids vented to the seafloor included most of the basinal water generated by sediment maturation. Venting of these fluids into anoxic bottoms rich in biogenic sulphur lead to the formation of the ore deposits.

This simple model can perhaps be also applied to the genesis of other styles of mineralization such as volcanic-hosted massive sulphides, sedimentary-exhalative ores, Irish-type deposits or even Mississippi Valley ones (e.g., Goodfellow et al 1993; Plumlee et al 1994; Wilkinson et al 2005). Many of these deposits are underlain by a thick (meta-) siliciclastic sequence and some show evidence for the circulation of sulphur-depleted fluids.

ACKNOWLEDGEMENTS

The study has been funded by the DGI-FEDER project BTE2003-290 and the IGME. We thank C. Conde, M. Solomon and F. Velasco their comments on different aspects of this work.

REFERENCES


Evidence supporting an exhalative magmatic origin for the Lombador orebody, Neves Corvo, Iberian Pyrite Belt, Portugal

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ABSTRACT: Meso- and micro-scale textures in the Lombador massive sulphide orebody (Neves Corvo) suggest that sulphide deposition occurred on the sea floor, probably in previously recognized topographic lows. Except for two negative values of likely biogenic origin (-6.3, -6.6 ‰) the sulphide sulphur isotopic data (-1.0 to 3.7 ‰) are characteristic of Sn±Cu ores elsewhere and support the thesis that the ore-forming fluids at Neves Corvo contained a major component derived from an underlying granitic complex. Such a source might explain the low Zn and Pb ore grades both at Neves Corvo and elsewhere in the Iberian pyrite belt.

KEYWORDS: Lombador; Neves Corvo; exhalative magmatic

1 INTRODUCTION

Carvalho & Ferreira (1994) recognised that the massive sulphide lenses at Neves Corvo mostly lie in depressions separated by topographic highs covered in places by thin lateral extensions of the massive sulphide lenses (their “ore bridges”). Relvas et al. (2006a,b) concluded from evidence in the companion paper and from stable isotope values that the seawater-dominated fluids included a significant magmatic component. The Sn- and Cu-rich ores were formed by venting of ore-forming fluids onto the sea floor, and footwall veining and shallow, subsurface replacement (Hennigh & Hutchinson 1997; Relvas 2006a). The Lombador orebody is one of five massive sulphide lenses within the Neves Corvo deposit. (Fig. 1) and has not been mined, information coming solely from drilling.

Fig. 1. The distribution of the individual orebodies of the Neves Corvo deposit (from Somincor internal report, 2000). Location of studied six drill-holes in Lombador.
2 LOMBADOR MASSIVE SULPHIDE BODY

The Neves Corvo deposit lies in the Volcano-Sedimentary Complex (VS) which overlies shales and quartzites of the PQ Group (Oliveira et al. 2004; Tornos 2006; Fig. 2). The Lombador orebody is a single, stratiform lens and the immediate host rocks are jasper-siderite-(Fe-dolomite), late Strunian grey shales and volcaniclastic and coherent, dominantly acidic volcanic rocks (Oliveira et al. 2004; Rosa et al. 2005).

Fig. 2. Section 20 of the Lombador orebody. The grey-wackes belong to the Mertola Formation which overlies the Volcano-Sedimentary Complex (VS), above the PQ Group rocks (modified from Somincor internal report, 2000). MZ: Zn-rich, MC: Cu-rich, ME: low grade, FZ, FC, FE: stockwork (fissural) ore.

Stockwork-type veins lie beneath in chloritised volcanic rock, shale or the PQ Group (Fig. 2). The Cu-Zn orebody includes repetitions as a result of shallow thrusting. The massive copper ore averages 3.40% Cu, 0.36% Zn, 0.31% Pb, and 900 ppm Sn. Individual intersections or units within the massive lens are up to 18 m thick and separated generally by shales or shear zones. Cu is only locally richer at the base of these units (2 out of 9 intersections), most not varying systematically in content; similar observations have been made about many of the orebodies in the Iberian pyrite belt (Solomon et al. 2004). The stockworks are locally enriched in Cu or Zn (fissural ore; Fig. 2). For Sn, individual 1 m lengths of core and average values of individual intersections or units range from about 1400 ppm to several hundred ppm Sn.

Parts of the massive sulphide are fragmental, with clasts or nodules of siliceous material and/or pyrite, and parts are clearly banded; others consist of bands of massive pyrite, shale and fragmental material, most of which appear to be primary. Significant lengths of core have a fine grained, fragmental texture. The examples of Figure 3 display show alternation of variably pyritic shale and fragmental pyritic bands, graded bedding, and possible small load casts.

Pyrite is the dominant mineral in the massive sulphide (ca. 85% according to Gaspar 1996), and is accompanied by Fe-poor sphalerite, chalcopyrite (replaced by stannite) and minor arsenopyrite. The pyrite occurs as variably recrystallised aggregates, with grain diameter ranging from sub-micron to 1-2 cm, without or with only a weak tectonic fabric (Fig. 4). Etching reveals swirls, concentrically banded crusts, banded circular textures and framboids.

Fig. 3. Three cores from the Lombador ore, right way up. The core width is approximately 2.2cm.

3 DEPOSITION OF THE LOMBADOR SULPHIDES

The meso-scale shale/sulphide layering and the sedimentary textures suggest open-cast deposition of sulphide and mud, or at least substantial reworking of pre-existing sulphide material and mud. The micro-scale textures are typical of those resulting from quenching of sol
-utions strongly supersaturated in Fe monosulphides, followed by rapid crystal growth.

Given the earlier identification of basins separated by topographic highs, a likely depositional scenario could involve exhalation of ore-forming fluids sourced from below, and settling of quenched, metastable, Fe-S minerals to the basin floor, deposition of muds occurring during pauses in exhalation. These features point to deposition in brine pools that once stabilised, effectually exclude seawater from entering the massive sulphide.

4  SULPHUR ISOTOPES AND THE ORIGIN OF THE ORE METALS

$\delta^{34}\text{S}$ values determined on pyrite ore and individual pyrite grains range from -6.6 to 3.7 ‰ (Fig. 5), not markedly different from those of Yamamoto et al. (1993) gathered from other Neves Corvo orebodies (-5.0 to 6.0 ‰) and our own studies. The two most negative values (-6.6, -6.3 ‰) are from very near the tops of two of the lenses, and may indicate a contribution of sulphur by biogenic reduction of seawater sulphate, a feature of many pyrite belt deposits. The mantle-like signature of the remainder (-1.0 to 3.7 ‰) is identical to that in many Sn and Sn-Cu ores of eastern Australia, most of which have been shown to be hosted by, or sourced from, granites with near-mantle $\varepsilon^{141}$Nd signatures (the tin granites of Solomon & Groves 1994). Such an origin has already been proposed for the Corvo and Graça ores (Relvas et al. 2006a, b) and is supported by the presence of highly saline inclusions in quartz of the massive sulphide ore (Moura 2005).
Tin granites yield reduced, saline fluids with at least several hundred ppm each of Cu, Pb and Zn, with Zn>Pb>Cu but low S (e.g. Heinrich & Ryan 1992). Zn and Pb sulphide veins distant from proximal Sn and Sn-Cu ores in eastern Australia generally owe their existence to acquisition of local reduced sulphur (op. cit.; Solomon & Groves 1994). The lack of evidence in the Lombador orebody of an exotic S contribution (e.g. from PQ sedimentary rocks), and only a modest biogenic contribution, may explain the relatively low Zn and Pb grades. The major modified seawater component of the ore-forming fluids identified by Relvas et al. (2006b) does not appear to have contributed significant S.

5 CONCLUSIONS

Meso-scale interlayering of shale and fragmental pyrite, and microscopic textures indicative of strong super-saturation and rapid crystallization, combined with previously identified topographic basins, supports deposition of the Lombador massive sulphide body in a brine pool. Sulphide sulphur isotope data, except for two values indicating a small biogenic contribution, are identical to mantle-like values seen in Sn±Cu ores in eastern Australia and support previous propositions that a major component of the ore-forming fluids was derived from a granite pluton. The relatively low Zn and Pb grades of the orebody may reflect the low S content of such fluids.

REFERENCES


Felsic volcanic rocks from Azinhalinho, Beja, Portugal: relationship with Iberian Pyrite Belt magmatism.

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ABSTRACT: The Azinhalinho volcanic rocks are hosted in the Frasnian Gafo Formation and display very similar geochemical signatures to some volcanic rocks from the Iberian Pyrite Belt (IPB), namely anomalously low HFSE concentrations, possibly caused by low temperature crustal melting, which translate into classification problems. Considering the lack of radiometric dates and clear field relationships, the similarity between the geochemistry of Azinhalinho volcanic rocks and IPB volcanic rocks can be explained in two possible ways. The Azinhalinho volcanic rocks can be considered the product of a volcanism that preceded the volcanism that occurred in the IPB, which is widely interpreted as being of late Famennian to Middle Visean age. In this case, the volcanism of Azinhalinho would have happened synchronously with the Late Devonian Phyllite-Quartzite Group sedimentation in the IPB basin, but already in a very similar setting to the one in which IPB volcanism would develop later. Alternatively or complementary, both volcanisms could have been approximately contemporaneous, in which case the volcanism of Azinhalinho would represent conduits or feeders to the volcanism of the IPB.

KEYWORDS: Iberian Pyrite Belt, volcanism, felsic

1 GEOLOGICAL SETTING

A series of small outcrops of felsic volcanic rocks occurs near the village of Azinhalinho, approximately 20km south of Beja, Portugal. This area is in the transition between the Pulo do Lobo Antiform and the Iberian Pyrite Belt (IPB), which are both part of the South Portuguese Zone. Traditionally, the volcanic rocks from Azinhalinho have been interpreted as being within turbiditic shales and graywackes of the Frasnian Gafo Formation of the Chança Group (Pulo do Lobo Antiform), which was thrust over younger formations of the IPB, occurring immediately to the South (Oliveira et al, 1988, Oliveira et al, 2006).

In fact, the volcanic rocks from Azinhalinho occur immediately to the SW of the quartzite-rich Pulo do Lobo Formation and associated Atalaia Formation. The volcanic rocks occur within siliceous shales and quartzwackes, which are interpreted to belong to the Gafo Formation of Frasnian age. Two apparently continuous bands of volcanic rocks run NW-SE, the north-eastermost containing intensely chloritized granular felsic to intermediate rock and the south-westernmost containing granular felsic rock. Outcrops along these bands are poorly preserved and contacts with enclosing rocks are hard to observe, despite some continuous exposure along the Terges creek and the IP2 road. Additionally, small discontinuous tabular bodies of coarse quartz-feldspar-phyric porphyry occur throughout the area.

2 PETROGRAPHY

The chloritized granular felsic to intermediate rock is a medium-grained holocrystalline equigranular rock. Its texture is intergranular, with anhedral quartz, plagioclase and K-feldspar grains. Some samples contain hornblende, which is commonly chloritized. The granular felsic rock is also a medium-grained holocrystalline equigranular rock. However, hornblende is absent and alteration chlorite is
therefore scarce. In addition, quartz and feldspar grains occasionally display granophytic intergrowths. The quartz-feldspar-phyric porphyry contains large (<4mm) quartz and, in smaller amounts, feldspar and plagioclase phenocrysts in a microfelsitic groundmass. These quartz phenocrysts are occasionally euhedral, but frequently display resorption embayments and reaction rims.

Regarding the opaque mineralogy, all rock types contain accessory amounts of goethite pseudomorphs after pyrite.

3 GEOCHEMISTRY

Twenty-four samples were collected and subject to multi-element analysis. On immobile elemental plots, using Al, Zr and Ti, for example, the three different rock types clearly plot along distinct alteration lines that converge towards the origin, reflecting elemental covariation, despite some possible fractionation effects. The chloritized granular felsic to intermediate rock has Al$_2$O$_3$/TiO$_2$≈15 and Zr/TiO$_2$≈150, while the granular felsic rock has Al$_2$O$_3$/TiO$_2$≈30 and Zr/TiO$_2$≈400 and the quartz-feldspar-phyric porphyry has Al$_2$O$_3$/TiO$_2$≈40 and Zr/TiO$_2$≈600.

On the TAS diagram of Le Maitre et al (1989), the granular felsic rock samples plot on the rhyolite field, but towards the dacite field (Fig. 1). The quartz-felspar-phyric porphyry samples plot clearly within the rhyolite field. However, considering the mobile nature of the elements used on this diagram, these results should be treated with caution. To avoid the mobility of major elements, a diagram using immobile elements can be used. When plotted on the Winchester & Floyd (1977) diagram, the porphyry and the granular felsic samples plot in the rhyodacite/dacite fields (Fig. 2). Within this field, the samples plot towards the rhyolite field, suggesting that they are towards the more felsic side and both rock types should therefore be classified as rhyodacite. In this case, the classification of these rocks on the TAS diagram, discussed above, likely reflects silicification processes previously described in IPB rocks (Rosa et al, 2004).

Regarding the chloritized granular felsic to intermediate rock, their samples plot on the dacite field of the TAS diagram (Fig. 1), compatible with petrographic description, namely the presence of hornblende. However, on the Winchester & Floyd (1977) diagram, these rocks plot between the andesite and andesite/basalt fields (Fig. 2). This is in stark contrast with the petrography and can therefore be interpreted to result from anomalously high Ti concentrations, coupled with anomalously low Zr concentrations caused by the low-temperature crustal fusion that generated the magma that yielded this rock type. Rosa et al (2004) report on similar classification problems with felsic rocks from Albernoa, located less than 5km to the South of Azinhainhinho, but already within the IPB.
renders these diagrams not appropriate, as can also happen to the Winchester & Floyd (1977) diagram, as seen above. In fact, if HFSE concentrations were higher, as would happen under crustal fusion at higher temperatures, the Azinhalinho rocks would plot in the within-plate field. This is similar to what happens with IPB rocks (Rosa et al., 2004; Rosa et al., 2006), for which a strike-slip tectonic model is proposed by Silva et al. (1990) and Quesada (1991), compatible with a within-plate geochemical signature.

It is apparent, from the geochemistry data, that the Azinhalinho rocks can be compared to felsic rocks from the IPB. The granular rhyodacite and the rhyodacite porphyry can be compared with felsic rocks from Serra Branca (Rosa et al., 2006). These rocks have HFSE concentrations that provide consistent results in the Winchester & Floyd (1977) diagram, but the temperature of crustal fusion may have not been enough to cause complete melting of the refractory phases in which HFSE reside and therefore they do not provide proper results on the tectonic discrimination diagrams of Pearce et al. (1984). The Azinhalinho granular dacite corresponds to a less evolved equivalent of the rhyodacites present in Albernoa (Rosa et al., 2004), just a few kilometres South, with both rock types displaying characteristic anomalously low Zr and other HFSE concentrations, which affect not only their classification on the Pearce et al. (1984) diagrams, but also on the diagram of Winchester & Floyd (1977).

While there are no radiometric dates or any clear field evidence on whether the Azinhalinho volcanic rocks are intrusive or extrusive, these rocks can be interpreted as corresponding to feeders that cut across older rocks to generate the IPB volcanism stratigraphically above, or as extrusive domes or flows corresponding to an older volcanism but whose setting must have already been similar to the setting present during the IPB volcanism, as indicated by their similar geochemical signatures. Considering the lack of associated volcanogenic sedimentation and the geochemical similarities between the Azinhalinho granular dacite and the nearby Albernoa rhyodacites, it is possible that the dacitic volcanism, at least, was approximately contemporaneous with IPB volcanism and, in this case, could correspond to feeders to the extrusive rhyodacites from Albernoa.

4 CONCLUSIONS

Based on the similar geochemical signatures of the volcanic rocks from Azinhalinho and the volcanic rocks from the IPB, we consider that the Azinhalinho volcanism was formed in a setting similar to that of the IPB volcanism, i.e., within-plate volcanism resulting from oblique collision. However, radiometric dates are needed to clarify whether the Azinhalinho volcanism preceded or was broadly contemporaneous with IPB volcanism. In case the Azinhalinho volcanism was earlier than the IPB volcanism, it could have been contemporaneous with Gafo Formation sedimentation and of extrusive nature. Alternatively, if the two volcanisms were broadly contemporaneous, the Azinhalinho volcanism must have had an intrusive nature, likely corresponding to feeders to IPB volcanic rocks.

ACKNOWLEDGEMENTS

This work was sponsored by a grant from the POCTI program of the Fundação para a Ciência e Tecnologia (Portugal). The authors would like to acknowledge Carlos Rosa for his helpful comments.

REFERENCES


Rosa D, Inverno C, Oliveira, V, Rosa C, (2004) Geochemistry of volcanic rocks, Albernoa area, Ibe-


Remobilization: a key for Neves Corvo richness?

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ABSTRACT: A fluid inclusion study on quartz and cassiterite from the Neves Corvo Cu and Sn ores and also from the metavolcanic and metasedimentary lithologies above the ores was performed in order to characterize the fluids participating in the ore genesis. Except for the massive sulphide ores, all the samples have shown evidences of being affected by metamorphism. The strongest evidence is the ubiquitous aqueous carbonic inclusions that have high fluid pressures, attaining 300 MPa at the homogenization temperature. This precludes their formation on or near the seafloor. It is suggested that, at least in part, the Neves Corvo richness is a consequence of intense remobilization acting during the orogenic metamorphism.

KEYWORDS: Neves Corvo, fluid inclusions, copper, tin.

1 INTRODUCTION

The Neves Corvo mine located in the Iberian Pyrite Belt (IPB-Fig. 1) is the richest Cu and Sn deposit ever found in the Belt. Between 1988 and 2005 the mine has produced copper and tin concentrates. From 2006 onwards the mine produces copper and zinc.

Neves Corvo is a concealed deposit with five orebodies (Corvo, Graça, Neves, Lombardor and Zambujal) with a total amount of 300 million tonnes (Mt) of massive sulphides and stockworks, including 45 Mt @ 6% Cu plus 4.5 Mt @ 12% Cu and 2.2% Sn.

The two main characteristics of this huge deposit that distinguish it from all other IPB orebodies are: (1) the existence of high grade ores (average 8% Cu with large volumes with more then 20% Cu, mainly as chalcopyrite but also as tennantite-tetrahedrite) and, (2) the abundance and grades of the tin ores, locally with metric blocks of almost pure cassiterite (up to 65% Sn). In terms of metal content Neves Corvo is a World Class Deposit for copper and tin (Laznicka, 2006).

Although the deposit has been extensively studied in the last ten years (see for instances Relvas et al., 2002), many questions remain unclear. In order to enlighten some issues related with metallogeny and particularly with the genesis of some unusual ore types (rubané ores) and high-grade stockwork areas in the deposit it was undertaken a fluid inclusion study on the entire stratigraphic section. This contribution is a presentation of the main results and interpretations.

2. REGIONAL GEOLOGY

The IPB is an arcuate belt located in south Portugal and Spain with around 250 x 50km. It is composed of three main lithologies: 1 (the older)- is the Phyllite-Quartzite Formation (PQ), which was the former sandy-shale substrate; 2- the Volcano-Sedimentary Complex (VS) ranging in age from late Famennian to late Viscean, and 3- the Mértola Formation a Flysch succession dated as late Viscean to early Serpukhovian (Oliveira et al, 2004).

The VS comprises a lower and an upper suite. In the Neves Corvo area it is possible to recognize several units within the VS, viz.: one basic volcanic unit, three dolerite sills, four felsic volcanic units, and a mineralised horizon of massive sulphide ores. Using palynomorphs Oliveira et al., (2004) dated the ores as 354.8 – 354.0 Ma.

Around twenty million years after the massive sulphide formation the IPB was affected by orogenic metamorphism and tectonics. In
consequence there are in the Neves Corvo many vertical inversions due to overthrusts.

3. NEVES CORVO MAIN ORE TYPES

There are three different types of mineralization: 1-massive sulphide (M), 2- fissural (F) or stockwork, and 3- rubané (R). The massive mineralization is the most important. The fissural is on the footwall of the massive sulphide bodies and is characterized as a stringer like veinlets of sulphides on the volcanics or shale lithologies. The rubané is a banded mineralization always on top of the massive sulphide deposits.

Several ore types are considered according to the metal involved (identified by the letters C, T, and Z, respectively for copper, tin and zinc). This research was done on MC, FC, RC, RT ore types, and ME (massive sulphide with less then 2 % Cu).

4. METHODS

Microthermometric studies were conducted on more than one thousand fluid inclusions on quartz from all the stratigraphic levels (metavolcanic and metasedimentary lithologies) above the ores, and from all the copper and tin ore types. Also all the five orebodies were sampled.

Micro spectrographic Raman analysis was also done on more than forty selected fluid inclusions in order to quantify their gas content.

Vitrinite reflectance, and illite crystallinity measurements were performed in selected sample, in order to constrain the fluid composition and geological temperatures during orogenesis.

5. RESULTS

The study was carried out on the following stratigraphic levels, from top to bottom:

Figure 1. Simplified geological map of the Iberian Pyrite Belt (adapted from Oliveira, 2004).
Mertola Formation (6), Volcano Sedimentary Complex (7); Jasper & Carbonate Unit (3); Main thrust (5), RT ore (3), RC ore (4), MC ore (4) and FC ore (22). With the exception of the MC ore, all the analysed quartz was of metamorphic origin. The numbers given refer to the number of samples. In this quartz two different fluid types were observed:

1- An aqueous carbonic fluid (H$_2$O-CO$_2$-CH$_4$-NaCl) often with liquid CO$_2$ at room temperature;

2- An aqueous fluid with low salinity. The aqueous carbonic fluid is considered to have resulted from the liberation of water during metamorphism. The organic (gas) component must have been acquired when the fluid percolated organic-rich metasediments (black shales), which are very common at the footwall of the massive sulphides.

The water gas-free low salinity fluid seems to correspond to the final hydrothermal fluid that percolated the rocks during uplift. This fluid occurs as transgranular arrays of inclusions.

The homogenization temperatures (n=531) reveal that 95% of the H$_2$O-CO$_2$-CH$_4$-NaCl fluid inclusions are within the range 210º-330ºC. However for the water low-salinity inclusions the homogenization temperatures presents a peak at 170º-180 ºC.

Isochores were traced showing that the likely fluid path was: 1- the aqueous carbonic fluid attained a maximum pressure around 320 MPa at a temperature of 300º ± 10ºC. At this point, an oscillatory pressure gradient acted, probably derived by movements in the near by A-type subduction located few kilometres on the north (present coordinates). The maximum temperature of 350ºC occurred at this stage when the pressure reached a value been between lithostatic and hydrostatic gradients. At the end of the hydrothermal cycle, the fluids where trapped at temperatures lower then 200ºC in a hydrostatic regime.

The vitrinite reflectance and the illite crystallinity measurements (Moura et al., 2001; Moura & Rocha, 2003) gave temperatures very consistent with those resulted from the fluid inclusions study.

6. MAIN CONCLUSIONS

Strong remobilization and reconcentration of copper and tin (and possibly zinc) affecting the ores above and below the massive sulphides is suggested by:

1- the fact that thrust tectonics are important in the region being responsible for at least three tectonic repetition on the Neves Corvo area

2- the interpretation that some of the thickest massive sulphide bodies are probably of tectonic origin (Gaspar, 1996).

3- the observation that the ratio chalcopyrite / pyrite veinlets in the hangingwall and footwall are higher then the same ratio on the massive sulphide bodies

4- the abundance of dense aqueous carbonic fluid inclusion from metamorphic origin inside the hangingwall and footwall ore minerals.

5- the complete absence of dense aqueous carbonic fluids in the massive ores, due possibly to the rheology of these rocks that facilitates strain accommodation in the contacts

6- the fact that the Cu grade at Neves Corvo hanging wall ores are much higher than average, concerning the other IPB deposit.

This last evidence, and the fact that fluids from all other IPB deposits (with the exception of La Zarza and Tharsis) are CO$_2$ deficient, support the hypothesis that the remobilization at Neves Corvo was promoted by H$_2$O-CO$_2$ rich fluids and attained a better degree of efficiency then at other places in the belt (Toscano et al., 1997; Almodóvar et al. 1998; Nehlig et al. 1998, Sanchez-Espana et al., 2003; Marignac et al., 2003; Moura, 2003).

It was not an intention of this study to determine whether the remobilization inside the massive sulphide bodies was important or not. However it seems likely that at least locally the remobilization must had affected the sulphide bodies as well.

REFERENCES


Evidence of Mn-oxide biomineralization, Vani Mn deposit, Milos, Greece

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ABSTRACT: We present evidence that precipitation of primary Mn-oxide minerals in the Vani volcanic hosted hybrid epithermal-VMS-type Mn-oxide and barite deposit was in part biogenically mediated. Manganese-oxides pseudo morphically replace small (1–5 µm) spherical cell-like structures, and branching filamentous constructions (< 60 µm long) probably representing manganese oxidizing bacteria. In addition, silicified consortia of spherical (5–10 µm), filamentous, sheathed, septate and spiral (~50–200 µm) fossilized bacteria, proposed to represent photosynthetic thermophilic cyanobacteria, were found in quartz paragenetically related to the Mn ore. Fluid inclusions indicate formation temperatures around 100°C. XRD and EMP analyses suggest X-ray-amorphous hollandite-group like Mn-oxide phases, and poorly crystalline todorokite and vernadite. These findings suggest a biological link between bacterial and mineralization processes.

KEYWORDS: biogenic Mn-oxides, todorokite, Milos, fossil bacteria

1 INTRODUCTION

Bacteria, as well as fungi, play a dominant role in the oxidation of dissolved Mn$^{2+}$ in natural aqueous systems leading to Mn$^{4+}$ oxide mineral precipitation (Tebo et al. 2004). In addition, manganese bio-oxides have been experimentally synthesized using Mn(II)-oxidising bacteria to catalyse Mn(II) oxidation (see Tebo et al. 2004 and references therein). Biogenic Mn-oxide mineral deposition has been reported in relation to modern submarine hydrothermal mineralization from the Lau Basin (Juniper & Tebo 1995), Juan de Fuca Ridge (Buatier et al. 2004). However, there has been little evidence so far of biogenically precipitated Mn-minerals associated with manganese deposits (Tebo et al. 2004). The Vani Mn-oxide deposit, Milos, offers an unique opportunity to study Mn-biomineralization because its sunlit shallow-marine seafloor venting paleo-hydrothermal system (Plimer 2000; this study) is ideal environment supporting biological processes (e.g. Reysenbach & Cady 2001). Vani has been considered by previous workers as a stratabound Mn deposit formed by subsea-floor replacement of porous volcaniclastic rocks (Glasby et al. 2005; Liakopoulos et al. 2001; Hein et al. 2000), diageneric processes (Skarpelis & Koutles 2004) and submarine hot spring-type processes (Plimer 2000).

This paper reports, for the first time, geological, mineralogical and fossil-bacteria evidence for Mn biomineralization in the volcanic-hosted transitional epithermal and shallow-marine exhalative system of Vani.

2 GEOLOGICAL EVIDENCE

The Vani Mn deposit occurs on the island of Milos, which is located on the active south Aegean Volcanic arc. Milos comprises U. Pliocene–Pleistocene calc-alkaline, volcanic and sedimentary successions that document the transition from the shallow submarine to subaerial volcanic environments (Stewart & McPhie 2006). Milos hosts the first documented example of hybrid VMS-epithermal Au–Ag (+base metals) deposits (Naden et al. 2005; Kilias et al. 2001).

The Vani Mn-ores are spatially associated with U. Pliocene–L. Pleistocene (2.5–1.5 Ma) submarine to subaerial dacitic volcanic complexes; mineralization is hosted in medial to distal fossiliferous (Haustator biblicatus sp.-Skarpelis & Koutles 2004; P. Koskeridou, pers. Comm.) synvolcanic sandstone, and within underlying dacitic hyaloclastite (Stewart &
Manganese mineralization in Vani exhibits a range of ore deposit styles:

- **Sub-seafloor replacements, infillings and imprecipitations;**—these occur as stratiform to stratabound Mn-oxide sheets and lenses at at least three different levels within the hosting volcaniclastic succession.

- **Mound- and/or sheet-style shallow-water seafloor exhalative mineralization**—this occurs in the form of Mn-oxide rich chaotic melange of collapsed, toppled, eroded, and brecciated, and/or in situ white smoker chimneys and chimney rubble, debris and fragments (Fig. 1A). This ore type is buried in hydrothermally altered (adularia, sericite, chlorite, kaolinite, montmorillonite and silica; Likaopoulos et al. 2001) bioturbated sandstone. The morphology of this ore type is very similar to U. Pliocene to Pleistocene hydrothermal Mn chimneys from Central Pacific pelagic sediments (Usui et al. 1997). Chimney textures and zonations are similar to those observed in modern ocean floor black smoker hydrothermal vents (i.e. Herzig & Hannington 1995; Fouquet et al. 1993), and the Palaeochori bay active hydrothermal field in southern Milos (Valsami-Jones et al. 2005).

- **Mn-oxide hydrothermal crusts (geyserite, exhalite)** occurring as cauliflower structures (Fig. 1C) and plates; these are identical to those found in the Hine-Hina field of the Lau Basin (Fouquet et al. 1993).

- **Structurally controlled stringer networks** that occur in the stratigraphic footwall of dacitic hyaloclastite, through the stratabound Mn-oxide ore and also in the volcaniclastic sandstone in the hanging wall. This network is enveloped by adularia-sericite-chlorite+pyrite alteration. The stockworks share the same textural and fluid characteristics with the Profitis Ilias transitional VMS-epithermal Au–Ag deposit south of Vani (Kilias et al. 2001; Naden et al. 2005), and modern epithermal systems (Hedenquist et al. 2000).

- **Subaerial Mn-rich mud pools**—these are rare in occurrence and exhibit preserved concentric rings that are interpreted to be bubble collapse structures (Fig. 1D) and may indicate localised subaerial exposure of the hydrothermal system.

3 MINERALOGICAL EVIDENCE

X-ray Diffraction and Electron Microprobe analyses suggest that Mn-oxides consist of X-ray-amorphous hollandite-group-like minerals (BaO: 2–14 wt %, PbO 1–11 wt %), romanechite-like and MnO2-like phases; in addition XRD studies reveal the presence of poorly-crystalline todorokite and vernadite which are known as biogenic minerals (Tebo et al. 2004).

4 FLUID INCLUSION EVIDENCE

Aqueous two-phase fluid inclusions (L>V) in barite and quartz from stringer networks, chimneys and sheet-like ore show first melting temperatures (Tc) from –41.5 to –35 °C that cluster around –35 °C, hydrohalite melting (T_hyd) from –25.2 to –19 °C and T_m-ice between –12.4 and 0.2 °C. Low temperature microthermometric data are comparable to those of seawater and may be modelled by the H2O–NaCl–MgCl2 system (Dubois & Marignac 1997). Liquid homogenization temperatures (T_h) range from 95 to 297 °C. Salinities show a wide range from 0.1 to 17 wt % NaCl + MgCl2 eq. T_h–salinity relationships are best explained by extreme boiling and vaporization of seawater and seafloor exhalative hydrothermal activity around 100 °C (minimum T_h), and, mixing of seawater either with condensed boiled-off vapour or heated meteoric water. Pressure estimates suggest seawater depths of 40 to 50m and hydrostatic depths of at least 100-150m for the stockwork/feeder zone. Combined with geological evidence this data indicate that Vani constituted a sunlit white smoker-type palaeo-
hydrothermal system. The Vani palaeo-fluids are similar to the Palaeochori bay active seafloor exhalations (Valsami-Jones et al. 2005) in terms of salinity, temperature and phase.

5 FOSSIL BACTERIA EVIDENCE

SEM imaging and polarised light microscopy of samples from exhalative and hydrothermal edifices reveal manganese-mineralized and silicified textures resembling fossil biofilms and microbialites. These consist of small (1–5µm) spherical cell-like structures, and branching filamentous constructions (< 60 µm long). In addition, silicified consortia of spherical (5–10µm), filamentous, sheathed, septate and spiral (~50–200µm) structures were found in quartz veins related to manganese mineralization. We interpret many of these structures as fossil bacteria, or phenomena associated with bacteria. This is based on the identification criteria of Westall & Folk (2003):

- **Geological plausibility:** Sunlit seafloor venting hydrothermal systems like Vani are ideal environments for growth of bacteria under extreme conditions (Reysenbach & Cady 2001)
- **Size:** Most of the Mn mineralized, and silicified, structures in Vani (Fig. 2) fall within the size range of modern bacteria and cyanobacteria, respectively (Westall & Folk 2003).
- **Shape and Cell wall morphology:** The spherical structures, and the branching filamentous constructions in Vani Mn-ore have the morphological characteristics of modern Fe–Mn oxidising bacteria (Reysenbach & Cady 2001; Juniper & Tebo 1995); whereas the silicified spherical, filamentous, sheathed, septate and spiral (~50–200µm) structures are identical to living cyanobacteria (Fig. 2).
- **Cell division and reproduction textures:** Associations of two or more round shaped structures and branching is interpreted to represent bacterial cell division and vegetative reproduction respectively (Fig. 2B).
- **Colony formation and species consortia:** The great number of discrete clusters that resemble bacterial-like structures are interpreted as bacteria colony formation (Fig. 2B), while the consortia of many different species of round, oval, spiral and filamentous bacteriomorphs is consistent with modern bacterial occurrence.
- **Pseudomorphosis** (Southam & Saunders 2005): Hollandite-group-like minerals in Vani have pseudomorphs after bacteria (Fig. 2).

6 CONCLUSIONS

Vani may represent the only example to date of a Quaternary shallow-marine (0–50m), emergent, hybrid epithermal-VMS-type Mn-oxide deposit, preserved on land. This geological setting combined with the identification of Mn-oxide and associated silica textures as fossil bacteria, the presence of todorokite and vernadite, and poorly-crystalline Mn-oxide phases, may support a bacterial origin for Vani Mn-ores. We envisage that photosynthetic cyanobacteria, and other manganese-oxidizing bacteria, have contributed to the formation of Vani by promoting chemical oxidation of Mn$^{2+}$ and precipitation of Mn-oxides through the photosynthetic release of molecular oxygen and/or enzymatic chemical catalysis.

ACKNOWLEDGEMENTS

Financial support from the University of Athens (ELKE) to S. P. Kilias (KA 70/4/3373, 70/4/6425) and the SEG Hugh Exton McKinstry fund (2006 and 2005) to K. Detsi is gratefully acknowledged.

REFERENCES

Juan the Fuca Ridge. *American Mineralogist* 89:1807-1815


Naden J, Kilias SP, Darbyshire DBF (2005) Active geothermal systems with entrained seawater as analogues for transitional continental magmatic-hydrothermal and volcanic-hosted massive sulfide mineralization-the example of Milos island, Greece. *Geology* 33:541-544


Geology of the Salt River volcanogenic massive sulphide (VMS) deposit, South Africa

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ABSTRACT: The Salt River Zn-Cu-Pb ± Ag-Au deposit is hosted by the Mesoproterozoic volcanogenic sedimentary rocks of the Geelvloer Sequence of the Northern Cape Province, South Africa. The stratigraphy of the Geelvloer Sequence consists of a basal package of volcanic rocks that are gradationally overlain by a thick package of volcanic, volcaniclastic, volcanogenic and calc-silicate-rich rocks collectively deformed during the ~1000-1200 Ma Namaquan Orogeny. Economic base-metal sulphide minerals are restricted to three zones, they consist of a capping semi-massive to massive, very fine- to fine-grained, durchbewegung-textured pyritic horizon (Upper Sulphide Zone) with localized stringer mineralization in Mg-rich altered rocks that become less conspicuous downwards (Middle to Lower Sulphide Zones). Geologic and mineralogic evaluations suggest that volcanism, sedimentation and base-metal sulphide mineralization occurred contemporaneously in a back-arc basin environment. Textural evaluations of the various sulphide horizons indicate that the Upper Sulphide Zone represents sulphide exhalation onto the seafloor, while the Middle Sulphide and Lower Sulphide Zones represent footwall stringer mineralization in Mg-rich altered footwall rocks. In conclusion, geologic, textural and mineralogic investigations of the Salt River deposit indicate that it represents a volcanogenic massive sulphide (VMS) or Kuroko-type base-metal mineralization.

KEYWORDS: VMS, Namaqualand, Mesoproterozoic, Copper-Zinc-Lead, South Africa

1 INTRODUCTION

In 1974, investigations of an aeromagnetic anomaly on the farm Adjoining Geelvloer 197 by Phelps Dodge Corp. lead to the discovery of an unassociated suboutcropping gossan. Subsequent geologic, geophysical and geochemical surveys resulted in the definition of a sub-economic orebody with an inferred resource of 7.2 Mt grading 2.31% Zn, 0.86% Cu, 0.51% Pb, 24 g/t Ag and 0.64 g/t Au. In spite of this, due to the low-grade and tonnage of the resource, the property was repeatedly dropped, picked-up and explored by various exploration companies until 1997 when the mineral rights were purchased from the farmer by Thabex Exploration Ltd.

In conjunction with the increase in metal prices, extensive diamond drilling and geologic work has resulted in upgrading of the orebody to an indicated resource of 42.5 Mt at 1.47% Zn, 0.65% Cu, 0.28% Pb, 12.3 g/t Ag and 0.18 g/t Au.

Figure 1: Map showing the South African extent of the Namaqua Province, location of the Salt River deposit and other important base-metal deposits/districts, as well as the tectonic subprovinces of the Namaqua Province.
g/t Au with a high-grade zone measuring 4.6 Mt at 3.35% Zn, 0.56% Cu, 0.54% Pb, 11.6 g/t Ag and 0.09 g/t Au. However, it should be noted that the deposit remains open down plunge to at least 3000m or roughly 1300m below surface.

2 REGIONAL GEOLOGY

The Salt River deposit occurs at the southeastern outcrop limit of the Bushmanland Subprovince of the Namaqua Province (Fig. 1). The Namaqua Province represents a crescent-shaped belt of Palaeo- to Mesoproterozoic volcano-sedimentary rocks deformed and metamorphosed during the Namaquan Orogeny (1000-1200 Ma) and that crops out throughout southwestern Africa.

2.1 Stratigraphy

The supracrustal rocks of the Salt River deposit belong to the informally termed Geelvloer Sequence of the Bushmanland Group (McClung 2007). Schematically summarized in Figure 2, the stratigraphy of the Geelvloer Sequence consists of a basal pink-brown augen gneiss with numerous similarities to the intrusive granites of the Namaquan Orogeny (~1000-1200 Ma) and that crops out throughout southwestern Africa.

2.2 Structure and Metamorphism

Based on the structural and metamorphic investigation conducted by Macalaren (1988), the Geelvloer Sequence appears to have undergone similar styles of deformation and degrees of metamorphism as the remainder of Bushmanland Subprovince (Joubert 1986; Colliston & Schoch 2002; McClung 2007). In short, the rocks of the Bushmanland Subprovince underwent three phases of deformation and metamorphosed during the Namaquan Orogeny (~1000-1200 Ma). The first phase of deformation [D2] consists of tight, isoclinal folding [F1-F2] associated with prograde to anatectic amphibolite-facies metamorphism [M1-M2] synchronous with the emplacement of numerous granitic intrusives that were rapidly followed by southward directed thrusting. The second phase of deformation [D3] can be further subdivided into an early [D3a] event characterized by large-scale open, asymmetrical folds [F3] and amphibolite- to granulite-facies metamorphism [M3], while the latter [D3b] event consists of north-northeast trending monoclinal folds with eastward dipping limbs [F4], late retrograde metamorphism [M4] and oblique shearing.

3 MINERALIZATION

3.1 Mineralogy

Petrographic, XRD and SEM investigations reveal that pyrite is the most abundant sulphide,
followed by sphalerite, chalcopyrite and galena with accessory concentrations of digenite/covellite and an unidentified highly reflective mineral (sulphosalt?). In thin-section, pyrite is observed to be fringed, cross-cut by and intergrown with sphalerite, chalcopyrite and galena. Furthermore, some crystals of sphalerite display intense chalcopyrite disease, while digenite/covellite forms an alteration halo on crystals of chalcopyrite. Due to the apparent absence of precious metal-bearing minerals, interelement correlations have been used and suggest that Ag is associated with Pb, possibly as argentiferous galena, and Au is associated with Cu, possibly as auriferous chalcopyrite.

3.2 Styles of mineralization

Base-metal sulphide mineralization of the Salt River deposit is largely restricted to the Massive Sulphide Horizon and Footwall Greywacke Unit of the Lower Biotite Gneiss; however, minor amounts of base-metal sulphide mineralization are locally observed in the Lower Hangingwall Greywacke Unit and rarely in the Middle Calc-silicate Unit (see Fig. 2). Four distinct styles of mineralization have been identified, they are: 1) semi-massive to massive, 2) mineralized biotite-chlorite schist, 3) stringer mineralization in Mg-rich altered rocks and 4) mineralized calc-silicate rocks. The semi-massive to massive style of mineralization is characterized by a very fine- to fine-grained, semi-massive to massive, durchbewegung-textured pyritic horizon. In contrast, mineralized biotite-chlorite schist is characterized by disseminations to stringers of semi-massive pyrite and chalcopyrite with lesser amounts of sphalerite and galena in foliated and contorted biotite-chlorite schist interbedded with Mg-rich altered rocks. Analogous to the latter, stringer mineralization in Mg-rich altered rocks consists of disseminations to stringers of semi-massive pyrite and chalcopyrite with lesser amounts of sphalerite and galena in a foliated quartz, cordierite, phlogopite and amphibolite-rich rock unit; this type of alteration is aerially restricted to the higher-grade portion of the deposit. Although restricted to a few intersections, mineralized calc-silicate rocks consist of silicified and/or brecciated calc-silicate rocks of the Middle Calc-silicate Unit cross-cut by veins of pyrite, chalcopyrite and sphalerite.

3.3 Sulphide horizons

As alluded to above, sulphide mineralization is largely restricted to three sulphide horizons, termed Upper, Middle and Lower Sulphide Zones (Fig. 3). The Upper Sulphide Zone (USZ) is characterized by a capping of semi-massive to massive sulphide with stringer mineralization in Mg-rich altered rocks becoming less conspicuous downwards. In contrast, the Lower Sulphide Zone (LSZ) comprises semi-massive to stringers of sulphide in biotite-chlorite schist and Mg-rich altered rocks with unmineralized Mg-rich altered rocks directly overlying the mineralized schist. In the higher-grade portion of the deposit, a third zone is developed between the USZ and LSZ. Termed the Middle Sulphide Zone (MSZ), it consists of sulphide stringers in Mg-rich altered rocks.

4 DISCUSSION

Detailed local and regional-scale geologic and stratigraphic evaluations of the Salt River deposit suggest that the Geelvloer Sequence was deposited in a tectonically active east-

![Figure 3: Schematic cross-section through the Salt River VMS deposit during deposition of the sulfide minerals, modified from Hutchinson et al. (1971).](image-url)
northeast trending trough or half-graben. The presence of intraformational conglomerates in the Lower Biotite Gneiss and Upper Calc-silicate Gneiss are interpreted as evidence for deposition in an actively subsiding depositional environment. Analogously, the presence of thick laterally extensive calc-silicate rocks to the west-northwest and mixed shallow subaqueous volcanic rocks and calc-silicate rocks to the east-southeast (Fig. 3) further support deposition in structurally-controlled secondary or tertiary basins. The ubiquitous presence of bimodal volcanic, volcaniclastic and volcanogenic rocks throughout the Geelvloer Sequence, close spatial association with the granodiorite-tonalite intrusives of the T’Oubep Suite to the northeast and similar U-Pb zircon ages (i.e. ~1200 Ma) for the Geelvloer Sequence (McClung 2007) and T’Oubep Suite (Joubert 1986) indicate that volcanism and sedimentation occurred contemporaneously in a back-arc basin.

In addition to the above stated, the close spatial association between sulphides, volcanic rocks and Mg-rich footwall alteration, as well as the widespread occurrence of chalcopyrite disease in sphalerite, suggest that the Salt River deposit was formed in association with submarine volcanic activity, i.e. as a volcanogenic massive sulphide (VMS) or Kuroko-type deposit. Furthermore, the fine grain size of individual sulphide minerals, semi-massive to massive and laterally extensive nature of the Massive Sulphide Horizon (i.e. USZ) indicates that it may have formed through exhalation onto the seafloor. In contrast, the Cu-rich stringer mineralization and abundance of Mg-rich altered rocks in the MSZ and LSZ, suggest that they represent footwall stringer mineralization as described by Sangster (1972).

5 SUMMARY

In conclusion, geologic and mineralogic studies of the Salt River deposit indicate that contemporaneous volcanism, sedimentation and base-metal sulphide mineralization occurred in a back-arc basin roughly dated at 1200 Ma. Likewise, textural evaluations of the various sulphide horizons indicate that the USZ represents sulphide exhalation onto the seafloor, while the MSZ and LSZ represent footwall stringer mineralization in the footwall alteration zone. Geologic, textural and mineralogic investigations of the Salt River deposit indicate that it represents another example of volcanogenic massive sulphide (VMS) or Kuroko-type base-metal mineralization in South Africa.

ACKNOWLEDGEMENTS

The authors would like to thank the Thabex board members for allowing us to present these results. We would also like to thank Mr. D.M. Le Roux and M.E. de Villiers for many insightful discussions, as well as Dr. F.J. Kruger, Mr. S.J. Theron and G.J. Martin for conducting petrographical and mineralogical investigations.

REFERENCES


Maclaren AH (1988) The geology of the area east of Pofadder with emphasis on shearing associated with the Pofadder Lineament, northwestern Cape; PRU Bulletin, Univ. of Cape Town, 35: 135.


Os isotope variations within the ultramafic-hosted Ashadze hydrothermal field (13°N MAR)

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ABSTRACT: Osmium isotope composition in the studied sulphides from the Ashadze hydrothermal field varies in a wide range of values $^{187}\text{Os}/^{188}\text{Os}$ from 0.2261 to 1.9709 and is higher than the known isotope estimations for the similar modern oceanic fields. Isotope composition of the host peridotites and gabbro-norites - 0.1234-0.2325 and 0.3062-0.5664, and can be compared with the data for the Logatchev and Rainbow hydrothermal fields, also developed over ultramafic basement. There is no correlation between the types of hydrothermal sulphides and osmium composition, which evidences to a more complicated character of hydrothermal process than ordinary mixing of fluid with oceanic water.

KEYWORDS: Re-Os isotope system, sulphide hydrothermal system, MAR

1 INTRODUCTION

Great potential of Re-Os isotope system as a tool for hydrothermal sulphide ore study and searching of the metal sources has already been demonstrated (Ravizza et al., 1996; Brügmann et al., 1998; Sharma et al., 2000; Cave et al., 2003). It was shown that the main sources for Os and Re in submarine hydrothermal systems are seawater, rocks of hosted oceanic crust (sediments, basalts, ultramafics), hydrothermal fluid and extraterrestrial dust. But, the data about pristine plume component with prominent mantle-like signatures are very limited (Cave et al., 2003; Sharma et al., 2000) and lacks further investigation in order to find out the true significance of this source in the process of oceanic ore formation. The main goal of the present investigation was to study behavior of Re-Os isotope system in the process of modern hydrothermal sulphide formation and to determine the role and share of mantle substance in this process. To solve these problems we choose modern Ashadze hydrothermal field developed over ultramafic basement and represented by different types of sulphide formations – from massive sulphides and smokers to secondary Fe-Mn and hydrogenic crusts.

2 GEOLOGICAL SETTINGS

The Ashadze hydrothermal field located at 13°N, 44°50′W (Fig.1) was discovered in 2003 and later in 2005 extended during the cruises of r/v Professor Logatchev (Beltenev et al., 2005). The Ashadze hydrothermal field as a whole is located on the western slope of the MAR rift valley. It differs from all previously discovered MAR fields which are localized on the eastern rift slopes or in the axial part of the rift valley. The Ashadze field consists of a cluster of three or more hydrothermal sites, both active and inactive, hosted in ultramafic rocks. Being related to one tectonic step the Ashadze-1 and Ashadze-3 sites are situated approximately at the same water depth 4000-4200m (deepener than all other MAR fields) and at the same distance from the rift valley (2km). There is tectonic control of Ashadze sites: they are related to the intersection of a deep along-axis marginal fault and a transverse sub-latitudinal tectonic dislocation. The host rocks for the deposits are gabbroids and serpentinitized peridotites which are very common in the rift valley slopes at this segment of the MAR.
The dimension of the Ashadze-1 site was estimated as 450x350m (Fig.1). It includes two main mounds and adjacent metalliferous sediments highly enriched in Fe, Cu and Zn. Sulphide deposits are mainly represented by chimneys’ fragments. The most abundant are Fe-Cu-Zn (pyrrhotite-isocubanite-sphalerite) chimneys; chimneys of Fe-Cu and Cu specialization are less represented. Different samples of massive sulphides are enriched in Zn, Cu, Au, Co and some other elements. The Cu enrichment correlates with the age of deposits: Ashadze-2 sulphides have the age 21-22 kyr while Ashadze-1 is much younger 2-7 kyr.

2.1 Mineralogical characteristics of sulphides

Sampling of hydrothermal sulphides for the present investigation was done by TV-grab at 4 station within the Ashadze-1 hydrothermal field located at the east (1319, 1087) and west (1008, 1036) of the field (Fig.1). The material is represented by chimneys and massive sulphides. The chimneys can be divided into three types. But high-temperature chalcopyrite and pyrrhotite-isocubanite chimneys are rare while the high- and middle-temperature ones composed mainly by sphalerite are the most common. 1 type: chalcopyrite chimneys with tube diameter up to 12cm are made up by chalcopyrite of radial texture. They have characteristic circular rhythmical layered structure. In some samples there are about 12 rhythms, their thickness increases from 1 mm on the outside to 2cm in the centre. Besides chalcopyrite in the central layers there is isocubanite and in the outer layers – bornite and secondary Cu sulphides. Constantly there occur rare grains of Co-pentlandite. Sometimes there are found millerite and native copper. These chimneys are enriched in Cu (29.8 %), Co (0.314%), Ni (1230 ppm), Se (1200 ppm) in comparison with the other sulphides of the field. Gold content is not high – 1.98 ppm. 2 type: pyrrhotite-isocubanite (±sphalerite) chimneys with tube diameter up to 20cm are not layered (Fig.2a). They are made up by massive pyrrhotite–isocubanite aggregates with fine pores and channels. The same minerals (±sphalerite) are observed along these channels but here they are larger in size and idiomorphic. All the main minerals show high Co content (up to 1.7 %). These chimneys are enriched in Co (0.54%), Bi (5.7 ppm), Au (6.4 ppm). Ni content is very low in comparison with first type. 3 type: chimneys with sphalerite predominance are clearly zoned (Fig.2b). The outer part is made up by sphalerite, the centre – by pyrrhotite and isocubanite with variable sphalerite content. In this chimney type there

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Figure 1. Geological map of Ashadze-1 (13°N) hydrothermal field (compiled after Beltenev, 2006).
1 - Pleistocene - Holocene carbonate (50%<CaCO3<75%) coccolite-foraminiferal silt, 2 - ultramafics and gabbro bedrocks, 3 - ultramafics and gabbro partly covered by sediments, 4 - geological boundaries (TV profiling data), 5 - supposed hydrothermal field boundary, 6 - main sulphide bodies, 7 - sulphide-bearing sediments (Cu+Zn>0.25%), 8 - metalliferous sediments (Fe>10%), 9 - tube complexes, 10 - mineralized peridotite covered by limonite and manganese crusts.
are found rare Ag minerals (argentite, argentopyrite), Pb (galena), and native gold with Pt inclusions. This type of chimneys is enriched in Zn and Cd, Ag, Sb, Sn, but Au content is - 1.2 ppm.

Massive sulphides are rare. They are heterogeneous with very different structures and minerals ratio. a) Pyrrhotite-isocubanite varieties make up the basement of the pyrrhotite-isocubanite chimneys or represent massive-layered zone of conduits within the host rocks. In some samples pyrrhotite and isocubanite are present almost in equal portions, also, there is found troilite. b) Massive sulphides with sphalerite predominance are the most typical for basal parts of sphalerite tubes. They have typical spotty texture. All massive sulphides are enriched in Au (8.8-12 ppm).

2.2 Analytical methods

Re and Os concentration and Os isotope composition of 15 hydrothermal sulphide samples and 14 host rocks were determined by negative thermal ionization mass spectrometry using a Finnigan MAT-262 and TRITON (for Os measurements) and high resolution ICP mass spectrometry using Neptune machine (for Re measurements) at the IPGP. The chemical separation procedure has been described elsewhere (Birck et al., 1997).

3 RESULTS AND DISCUSSION

Re and Os content in the studied sulphides varies from 600 to 6000 ppt and from 4.7 to 157 ppt, correspondingly, Re/Os ratio is in the limits from 15 to 460. There is no distinct correlation between Re and Os content and osmium isotope composition and the type and mineralogical composition of sulphides (Fig.3). Thus, for massive sulphides of pyrrhotite-isocubanite composition which made up the zone of supplying channel, there are determined the lowest (600 and 4.7 ppt) and the highest (3800 and 157 ppt) Re and Os content. At this Re and Os variations in sulphides from zonal chimneys are also considerable – from 800 to 4700 ppt for Re and 4.7-34.6 ppt for Os (Re/Os=24-461). Host gabbro-norite and peridotites are characterized by more constant compositions which are within limits of typical composition for the mantle rocks of oceanic crust (Escrig et al., 2005): Re in the unaltered peridotites varies within 30-800, gabbro-norites – 100-2400 ppt, osmium – 600-1500 (Re/Os = 0.02-1.3) and 3.2-5.7 ppt (Re/Os=24-730), correspondingly. While the altered, serpetinized by hydrothermal process, gabbro-peridotites by content and Re/Os ratio are comparable with the studied sulphides (Re-600-1500, Os-10-60 ppt, Re/Os=12-140).

Osmium isotope variations in the sulphides from the Ashadze hydrothermal field (Fig.3) $^{187}$Os/$^{188}$Os – 0.2261-1.9709 is higher than the known evaluations for sulphide fields of the Atlantic and Pacific oceans (Ravizza et al., 1996; Brügmann et al., 1998; Sharma et al., 2000). As it can be seen on Fig.3 these variations cannot be explained only by mixing of oceanic water with hydrothermal fluid in the sulphide forming process. Osmium composition in the studied massive sulphides and zonal chimneys is higher by its absolute value not only than average isotope composition of oceanic water ($^{187}$Os/$^{188}$Os 1.04-1.06) but the average composition of rive- rine outflow (1.4-1.5) as well and supposes the participation of old substance in the formation of hydrothermal fluid. This substance could be
Figure 3. $^{187}$Os/$^{188}$Os vs. $1/\text{[Os]}$ (ppt) diagram. Dotted fields: 1, 2, 3 – peridotites, gabbro-norites, sulphides Logatchev field (Kuhn et al., 2005); 4 – Rainbow deposits (Cave et al., 2003), 5 – TAG sulphides (Ravizza et al., 1996; Brügmann et al., 1998); ROC – recycled old oceanic crust (Escrig et al., 2005); asterisk – seawater (Sharma et al., 2000).

represents modern continental sediments, but their absence in the zone of the hydrothermal discharging (axial zone of the mid-oceanic ridge) does not allow to use them as a potential contaminant. Participation of subcontinental mantle substance in the formation of hydrothermal sources also cannot support the necessary osmium composition in the sulphides. Accumulation of radiogenic osmium by sulphides in situ due to Re decay is problematic too because of rather low Re/Os ratio in the studied sulphides and very short live-time of hydrotherms (not more than 7 kyr). The main possible explanation is heterogeneity of mantle sources for modern oceanic hydrotherm and participation of substance from subducted old oceanic crust in their formation (Escrig et al., 2005). It is necessary to mark that similar variations of osmium isotope composition, but not so radiogenic, have been obtained for sulphides from the Logatchev field (Kuhn et al., 2005) (Fig.3) which is also developed over ultramafic basement and is located at the similar depth (about 3000m).

4 CONCLUSIONS

At present time it is not possible to explain for certain the reasons of presence of so radiogenic osmium isotope compositions in modern hydrothermal sulphides, because there are no such important data as the composition of hydrothermal fluids. The studied hydrothermal field is the only known one with such deep location and, perhaps, this fact determines the abnormal Os compositions. It is possible, that at such depth, the fluid enriched in juvenile substance reaches the ocean bottom practically unchanged. In case there was some kind of phase separation it could be accompanied by formation of high mineralized brine and low salinity phase with higher content of gas compound. Geochemical behavior of osmium and rhenium under such conditions is obscured and requires additional experimental investigations.

ACKNOWLEDGEMENTS

The study is partly founded by grant RFFBR 05-05-64628 and INTAS young scientist fellowship program 05-109-4465.

REFERENCES


ABSTRACT: The Arroyo Rojo Zn-Cu-Fe prospect is a massive sulphide body hosted by a submarine volcano-sedimentary sequence. Sulphides are comprised of pyrite, occurring as porphyroblasts, in a layered matrix of sphalerite with minor chalcopyrite and galena. A hanging wall sulphide assemblage is marked by the presence of pyrite disseminated in shale matrix with minor sphalerite and rare chalcopyrite and galena in volcanic matrix. Types of hydrothermal alteration identified in the deposit include sericite, chlorite-epidote, and silica. Ore petrography has revealed primary and secondary textures product of deformation and remobilization during low-grade regional metamorphism. The available data allow us to suggest that the deposit is result of stratabound replacement of rhyolites and black shales.

KEYWORDS: VMS, Tierra del Fuego, styles, textures, stratabound replacement

1 FOREWORD

Arroyo Rojo is the principal VHMS prospect within a submarine volcano-sedimentary complex that belongs to the so-called Complejo Deformado of the Andes of the Tierra del Fuego (Quartino et al., 1989). The prospect was explored in the 1970s. For the last decade the investigations have been aimed on the regional definition of the explored prospects (Acevedo et al., 2005) and older mining works (Ametrano et al., 1999).

In this contribution, the investigation of the geology, mineralogy and mineral chemistry of Arroyo Rojo prospect was undertaken to (1) define mineralization styles, (2) characterize the mineralogical association, and (3) identify primary textures and their post-ore modifications.

2 REGIONAL GEOLOGY

The geological history of the area is related to tectonism during Gondwana supracontinental fragmentation in Mesozoic times in the southernmost portion of South America. The succession of extensive to compressive and transcurrent tectonic regimes led to a complex geological record in a back-arc basin.

Locally, two formations can be recognized: Lemaire Fm. (late Jurassic) belongs to a submarine volcano-sedimentary complex (Kranck, 1932), consisting of epiclastic rocks (turbidites, conglomerates, chert and black radiolarian, and carbonaceous mudstone), volcanic and volcaniclastic rocks of rhyolitic composition, subvolcanic quartz porphyries and basaltic esplilites, and the Yahgan Fm. (late Jurassic - early Cretaceous), which consists of breccias and conglomerates, sandstone, sandy and silty turbidites, black tuffaceous mudstones and tuffs, intruded by tholeiitic to calc-alkaline and spilitic basaltic rocks (Olivero & Martinioni, 1996). The contact between these formations is dominantly tectonic, except in less deformed areas where the contact with the lower Cretaceous sequence is unconformable.

The above formations underwent low-grade regional metamorphism and are strongly deformed with a highly penetrative cleavage which has completely obliterated the original stratification in the fine-grained facies.

3 SAMPLES AND METHODS

A suite of over 120 samples was mostly collected in 4 drill cores (AR2, AR3, AR4 and AR6) of the Arroyo Rojo orebody, representing the various lithological units and ores and the
different alteration assemblage recognized in
the deposit. Three representative samples were
taken from each drill hole to identify any min-
eralogical, textural or compositional trend in
depth. The geological characterization of the
samples was performed by means of optical and
scanning electron microscopy (SEM) at the
University of Zaragoza and electron probe mi-
cro-analysis (EPMA) in the University of Bar-
celona. Specimens were etched with HNO₃
(60%) to enhance definition of any textures
present.

4 MINERALIZATION STYLES

Three different styles of mineralization can be
distinguished:

• A massive sulphide body varies from 0.3 to at
  least 10 m thick, and has a strike length of
  120 m. In general the massive sulphides occur
  immediately below a feldspar-phyric, locally
  amygadaloidal, rhyolite unit. Most of the min-
eralization occurs in tabular, homogeneous
  massive sulphide lenses composed of pyrite
  and sphalerite with lesser amounts of galena
  and chalcopyrite. Locally, the massive sul-
  phides are bands of sphalerite and galena with
  fine-grained pyrite.
• Sulphide lenses hosted by black shales. Sul-
  phide minerals are generally fine grained and,
  millimeter- to centimeter-scale layering, par-
  allel to stratification and/or regional foliation,
  is common. Layering as well as the presence
  of pyrite framboids, strongly supports sedi-
  mentary deposition.
• Quartz–sulphide millimetre- to centimetre-
  scale stockwork is hosted by both rhyolites
  and shales and is characterized by the lack
  significant alteration envelopes. All these
  veins are concordant or crosscut the regional
  foliation.

The alteration types, in order of decreasing
abundance, are (1) sericite, (2) chlorite-epidote,
and (3) silica (quartz). It should be noted that it
is difficult, in places, to distinguish hydrother-
mal sericite alteration from that which formed
in the felsic rocks in response to both seafloor
alteration (keratophyres) and regional meta-
orphism and deformation. Alteration has not
been fully recognized in the massive sulphide-
hosted by shales, possibly because it is obliter-
ated by regional metamorphism.

5 MINERALOGY AND PETROGRAPHY

Mineralization consists of irregular coarse-
grained (mm) porphyroblasts of pyrite in a lay-
ered fine-grained matrix of sphalerite with mi-
nor chalcopyrite and galena, hosted by rhyolites
or black shales. Locally, tetrahedrite along with
rare bouronite can be observed. Nevertheless,
AR6 drill hole intersects an ore body hosted by
rhyolite marked by a distinct ore assemblage
consisting of semi-massive to massive pyrite.
The hanging wall of the volcanic-hosted ore
bodies is marked by the presence of pyrite, with
rare sphalerite, chalcopyrite and galena. Pyrite occurs as euhedral to subhedral and frambooidal isolated grains distributed in two size populations (60-80µm and 15µ), and as irregular to frambooidal aggregates (100-1000µm) disseminated in a volcanic matrix. In contrast, only pyrite is recognized in the hanging wall of the shale-hosted ore bodies. Pyrite occurs as euhedral to anhedral fractured crystals 300 to 1000µm in size, preferred elongated crystal of 20µm and tiny euhedral-subhedral to framboidal disseminated crystal of 5 to 40µm. Atoll structures and coarsely aggregates (300-800 µm) of irregular, frambooidal or radiating group of pyrite crystals are disseminated in the slaty matrix.

Ore petrographic observations led us to identify primary depositional textures and secondary textures as a result of remobilization and/or deformation.

5.1 Primary textures.

Pyrite frambooids are the only primary sulphide depositional textures identified. Although etching of aggregates and isolated crystals revealed numerous pyritic overgrowths with frambooidal, colloformal and euhedral relicts cores that indicate primary depositional textures (Fig. 1.A). Some euhedral grains show growing zoning delineated by a concentric pattern of inclusions (Fig. 1.B). Likewise, etching revealed that most of the frambooidal aggregates are polyframboidal or aggregates of radiating group of pyrite crystals.

Sphalerite, chalcopyrite and galena are less competent than pyrite and consequently growth microstructures are usually obliterated. Nevertheless, a few laminar and low density growth twins are preserved in coarser sphalerite grains along with weakly grain boundaries and also some broad parallel-side growth twins in chalcopyrite in the sense of Frater (1985) and (Cox & Etheridge, 1984), respectively (Fig. 1.C).

5.2 Secondary textures.

Cracks and microfractures pyrite porphyroblasts are filled with more ductile phases (gangue, sphalerite, chalcopyrite and galena) by plastic injection (Fig. 1.D). In areas of intense brittle deformation, there was significant grain-size reduction, like zones of brittle shearing typical cataclastic texture, in which isolated grains of pyrite of about 20 µm can be distinguished. The rigidity of pyrite porphyroclasts is also manifested by pressure shadows of quartz, chlorite and muscovite (Fig 1. E). Pyrite elongation parallel to foliation has been observed in a mylonitized shale-hosted specimen. According to Cook et al. (1993), this texture is due to a pressure solution mechanism, which is most common in predominant chlorite and biotite bandings. Pressure solution is also an important mechanism in the metamorphic deformation of pyrite, as evidence the presence of indentation and sutured grain boundaries. This mechanism is possibly responsible for the delicate overgrowths on relict cores of the aforementioned primary textures (Brown & McClay, 1993). Finally, pyrite also shows evidences of ductility as support dislocations lattice represented by alignment of etch pits forming subgrains walls that indicate the onset of polygonization.

Along with the development of subgrains, twinning and dislocation lattices provide evidence of deformation in sphalerite, chalcopyrite and galena. Galena exhibits the most ductile behaviour, even though its softness displays in a few cases abundant lattice dislocations indicating an incipient granoblastic recrystallization (Fig. 1.F). Sphalerite displays narrow and wedge-shaped deformation twins. Well-developed sphalerite grains display preferred oriented lattice dislocations forming a low-density grid, in which lacking of subgrains is basically a constant (Fig. 1.G) Array of etching pits, showing lattice dislocations, are almost absent in sphalerite with chalcopyrite inclusions. On the other hand, chalcopyrite displays boundary grains and subgrains, showing elongate shapes with a slight orientation of some deformation lamellar twins.

Recrystallization and annealing textures are present in sphalerite and minor galena and pyrite mass. According to Brown and McClay (1993) pyrite shows, despite its nature, a tendency to recrystallize at low-grade metamorphic conditions. In effect, pyrite displays heterometric granoblastic mosaics of fine-grained recrystallized grains with triples junctions of approaching 120°. Galena also shows triple junctions in polygonal grains of granoblastic textures. Sphalerite etching revealed a broadly well-developed polygonal recrystallization to finer grain size with triple-grain junctions. Within these grains numerous parallel-sided twins can be interpreted as annealing twins that reduce the free surface energy at triples unions grain margins (Frater, 1985). Occasionally, new recrystallized grains surround coarse grains with deformational twins or lattice dislocations.
with abundant annealing twinning as those described by Brill (1989) (Fig. 1.H). Following these authors the above microfabrics are the consequence of the dislocation creep flow as a mechanism of deformation.

6 CONCLUSIONS

The Arroyo Rojo massive sulphide deposit hosts different styles of mineralization, perhaps reflecting contrasting geological settings. Most of the massive sulphides are hosted by a felsic volcanic sequence and share some features including the presence of a pervasive hydrothermal alteration, the systematic lack of hydro thermal edifices above the stockworks and the existence of replacive fronts on felsic volcanic rocks. On the other hand, the shale-hosted sulphides are marked by the presence of sedimentary structures in both the footwall and hanging wall, the absence of major hydrothermal alteration in the hanging wall, the dominance of homogeneous fine-grained pyrite, the lack of sulphates and the presence of biogenically derived sulphur. Moreover, ore petrography indicates that low-grade metamorphism and deformation did not obliterate primary textures.

The above criteria lead us to propose that the deposit formed by stratabound replacement processes (Solomon et al., 2004).

ACKNOWLEDGEMENTS

This research has been supported by Proyecto CGL2004-05055/BTE of the DGES and by the Programa de Reconocimiento y Ayudas a Grupos de Investigación del Gobierno de Aragón 2005-07 (Mineral Resources Group). CB is an applicant of the Programa F.P.U. (AP2005-0244).

REFERENCES


Geology and geological setting of Devonian Besshi-type Cu-Zn sulphide deposits at Ashele, Xinjiang, northwest China

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ABSTRACT: The Ashele Cu-Zn deposit is the most economically important and typical volcanic hosted massive sulphide deposit in the Chinese Altay, northwest China. It is hosted within a suite of bimodal submarine volcanic rocks of the early to Middle Devonian Ashele formation. The massive sulphide orebody is underlain by a stockwork zone and a hydrothermal alteration pipe that consists of strongly sericitized and chloritized rocks. The host rocks of the Ashele deposit are of calc-alkaline affinity. Both the mafic and felsic volcanic rocks are magnesium-rich, and are similar to boninites. Based on the geological characteristic of the deposit and the geochemical characteristics of the host bimodal volcanic rocks, the Ashele Cu-Zn deposit can be classified as a Besshi-type VMS deposit that formed in a fore-arc basin.

KEYWORDS: Ashele, Besshi-type, Cu-Zn deposit, Fore-arc basin, Xinjiang

1. INTRODUCTION

The Chinese Altay is the southern part of the Altaids orogenic collage, and it occupies the Northern corner of Xinjiang, China (Windley et al., 2002). The region is currently the most important producer of base and noble metal resources in China, and hosts such VMS deposits as Ashele (Cu-Zn), Keketale (Pb-Zn), Mengku (Fe-Cu), and the Duolanasayi orogenic Au deposits. The Ashele Cu-Zn deposit was the largest producer, with Cu+Zn metal reserves that totaled more than 1 million tonnes; it was discovered in 1989 and mined out in 2004. Although it has been studied for nearly 20 years, there is ongoing debate about the tectonic setting in which it formed. Some authors believe the deposit formed in an intra-continental rift setting because the host volcanic rocks are bimodal (Wang et al., 1998). In this paper, we will pay attention to the geochemical characteristics of the host rocks of the deposit, and suggest another possible tectonic setting.

2. REGIONAL GEOLOGY

The Ashele deposit is located in Habah county, northwest Xinjiang. It is located on the southern edge of Altai Mountain and belonging to the southern part of the Altaid orogen (Sengör et al., 1993). The deposit area is comprised of the Qi’ye and Ashele Formations. The predominant Ashele Formation is early to middle Devonian in age, and consists of a suite of bimodal submarine volcanic rocks that host the deposit. The Qi’ye formation is a suite of late Devonian volcanic rocks. The faults in the area all strike NNW-SSE or N-E. Intrusive rocks are

Fig. 1 The Geological map of Ashele Cu-Zn deposit (after No.4 Geological party of Xinjiang Bureau of Geological and Mineral Resources)
not widespread in the Ashele mine district. The intrusions are concentrated in the eastern part of the area. The rocks underwent greenschist to lower amphibolite facies regional metamorphism, and were folded into synclinal basins during associated Hercynian deformation.

3. DEPOSIT GEOLOGY

Ashele was the largest (Fig.1), economically most important producer of Cu and Zn in the Chinese Altay. It consisted of 10 mineralized zones, and total Cu+Zn reserves are more than 1 million tonnes at an average grade of 2.43% Cu, 2.7% and Zn. The deposit also had total reserves 21.9 tonnes of Au, 1,286 tonnes of Ag, 1,807 tonnes of Ga, 2,789 tonnes of Gd, and 1,807 tonnes of Se.

The deposit underwent several phases of folding, with axial planes dipping east and striking N-S. The No. 1 orebody is the largest one of the orebodies, and had Cu+Zn reserves of more than 1 million tonnes. This orebody is located near the hinge of an overturned syncline. The lenticular or banded orebody shows stratabound characteristics and occurs at the contact between basaltic footwall rocks and dacitic tuff of the hanging wall.

The most common sulphide minerals are pyrite, chalcopyrite, sphalerite, and galena. Barite, sericite, chlorite and calcite are the main gangue minerals. The No.1 orebody is mineralogically and compositionally zoned. Black banded ores which consist of layers of pyrite, and sphalerite, occur near the top of the main orebody, and massive yellow ores enriched in pyrite and chalcopyrite occur in the middle and lower part. From the bottom upward, the No.1 orebody can be subdivided into 6 layers. The first (lowermost) layer is disseminated pyrite. The third layer is banded mainly pyrite + chalcopyrite. The fourth layer is massive fine- to medium-grained pyrite. The fifth layer is massive pyrite + chalcopyrite. The sixth (uppermost) layer is massive sphalerite + chalcopyrite + pyrite. The Cu/Zn ratio within these layers decreases upwards. The No.1 orebody is underlain by a hydrothermal alteration pipe. Hydrothermal alteration styles include sericitization, silicification, chloritization, pyritization, and carbonation.

4. RESULTS AND DISCUSSION

Major and trace element and isotopic analyses were carried out at the Institute of Geology and Geophysics, Chinese Academy of Sciences. The samples fall in the basalt and dacite region in the total alkalis-silica (TAS) diagram (Fig. 2A). All samples plot in the calc-alkaline field on an AFM diagram (Fig. 2B). Based on the major element data, the host rocks of the Ashele deposit are a suite of calc-alkaline bimodal submarine volcanic rocks (Wang et al., 1998). In general, rocks of calc-alkaline affinity are a product of island arc magmatism. All samples show negative Nb and Ta anomalies and positive Sr anomalies with high field strength element depletions on a primitive mantle normalized spider diagram (Fig. 3). Therefore, the volcanic rocks in Ashele mine district are typical island arc volcanic rocks. The bimodal assemblage of the volcanic rocks means that the island arc magmatism was an extensional event (Wang et al., 2000). The average value of ($^{87}$Sr/$^{86}$Sr) and εNd(t) for host rock is 0.7056 and 4.2 respectively, calculated at an age of 380 Ma (Li et al. 2004), indicating that the volcanic rocks originated from an island arc source. Boninites were recognized some years ago in the Ashele mine district (Niu et al., 1999), and they are typically thought to form in a fore-arc basin setting (e.g., Hickey et al., 1982). On this basis, we propose that the Ashele deposit and its volcanic host rocks formed in a fore-arc basin setting. The ore geological characteristics of the Ashele deposit are similar to the Besshi-type VMS deposits on the southern Japanese island of Shikoku (Watanabe et al., 1993).
et al., 1998). Some Besshi-type deposits are thought to have formed in a fore-arc basin setting (e.g., Geringer et al., 1987), and based on the geochemical characteristics of the volcanic rocks and the ore geology, we propose that the Ashele Cu-Zn deposit formed in a fore-arc basin setting.

5. CONCLUSIONS

The Ashele Cu-Zn deposit is a typical volcanic host massive deposit in Xinjiang, northwest China. The host rock of the deposit is a suite of bimodal submarine volcanic rocks. Based on the major, trace and isotope element of the volcanic rocks, we conclude that the volcanic rocks formed in a fore-arc basic setting. We believe the Ashele Cu-Zn deposit is similar to the so-called Besshi-type deposits in Shikoku, Japan, based on the ore features and the petrotectonic setting. Therefore, the Ashele Cu-Zn deposit is a late Palaeozoic Besshi type deposit formed in a fore-arc basin setting.

ACKNOWLEDGEMENTS

This study was financed by the Ministry of Science and Technology of China (2001CB409801), and the Chinese Academy of Sciences (KZCX3-SW-137). Zhenlin Guo, Gang Wang, offered help during sampling in the field. The authors appreciate the editorial assistance of Jan Peter.

REFERENCES


Mineralogy and sulphur isotopes of the San Fernando VMS deposit, central Cuba

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ABSTRACT: The San Fernando deposit, central Cuba, is a volcanic-hosted massive sulphide deposit in the Cretaceous Los Pasos Formation. Here, we present results of a petrographic and isotopic study to characterize the deposit. The Los Pasos Formation is characterized by bimodal volcanism with tholeiitic basalts formed in an island-arc environment. The deposit is zoned, with a pyritic stockwork beneath the massive sulphides. Stratabound and stratiform zones have a pyritic base, a chalcopyrite-rich central part, and an upper Zn-Pb-rich part. Replacement depositional processes likely were important in all these zones. Isotopic data suggest that sulphide sulphur came from a mixture of thermochemically reduced seawater sulphate and magmatic sulphur or sulphur leached from the volcanic host rocks. The deposit was affected by contact metamorphism during emplacement of a Cretaceous granitic intrusion. The data indicate San Fernando is a Kuroko-type VMS deposit.

KEYWORDS: Textures, sulphur isotopes, VMS deposits, central Cuba

1 INTRODUCTION

Significant amounts of Cu, Zn, Ag, Cd, Pb and Au occur in the central Cuba mining district. Several VMS deposits occur in the volcanic and volcanosedimentary rocks of the Cretaceous Los Pasos formation, central Cuba. The most economically significant are the San Fernando, Antonio, Los Cerros and Júcaro Cu-Zn-Pb-Ag deposits. Many of these deposits were mined until 1960.

The San Fernando deposit was discovered in 1827. The estimated resources are 4.4 Mt grading 3.2% Cu, 5.8% Zn and 126 g/t Ag (Krasno 1999). Despite its economic importance, little has been published on the central Cuba VMS mining district.

The present work reports the geology and a petrographic and mineralogical study and preliminary data of the sulphur isotope composition to characterize the San Fernando deposit.

2 GEOLOGICAL BACKGROUND

2.1 Regional Geology

The Los Pasos Formation outcrops over a 35-40km long by 4-6km wide area. It is comprised of Lower Cretaceous bimodal volcanic rocks that are mainly rhyolitic to rhyodacitic and basaltic in composition, and these are in-
interpreted to have been emplaced in the initial stages of development of a tholeiitic island arc. The basaltic rocks commonly occur in the lower part of the formation. Rhyolitic rocks are dominant in the middle, and the uppermost part is comprised of explosive, subvolcanic porphyritic rhyolites and lesser pillow lavas. These extrusive rocks are crosscut by dykes which represent the feeder zones of this volcanism.

The Los Pasos Formation was hydrothermally altered during formation of the sulphide deposits. The most common alteration styles are silicification, haematitization, kaolinitization and chloritization. In addition, they have been affected by pre-Eocene deformation. As a result, E-W folds dipping 20-60º N, and several fault systems trending N040º and N130º were developed.

The rocks of the Los Pasos formation have been intruded by the Manicaragua felsic intrusive stock comprised of plagiogranite and diorite. This intrusive body caused contact metamorphism and strong recrystallization of the volcanic rocks in the surrounding area (Díaz de Villalvilla & Dilla 1985).

In spite of the tectonic complexity of the area, with abundant lateral facies changes, a stratigraphic section could be constructed: a) a basal rhyolitic unit, formed by porphyritic lavas with interbedded breccias b) mafic lavas, followed by intermediate to basic tuffs, c) a rhyolitic unit, and laterally rhyolitic tuffs d) more than 400m of mafic tuffs and e) basaltic lavas flows. The Upper Cretaceous calcalkaline rocks of the Matagua Formation overlie these rocks.

2.2 Structure of the deposit

The massive sulphide orebodies of the San Fernando deposit lie in the lower part of the Los Pasos Formation, at the contact between the basal rhyolitic unit and the mafic lava flows. These rocks are located in the north flank of an anticline trending 110º and dipping 45-75º N. A conjugate set of fractures trending NW-SE and NE-SW cut the deposit.

Stratiform-, stratabound- and stockwork-type mineralization are recognized (Fig. 1). The stratiform massive sulphides, up to 30m thick, are located at the contact between the basal rhyolites and the rhyodacitic breccias. Three subunits are recognized: a lower body, with pyrite as the main sulphide and minor sphalerite and chalcopyrite; a middle body, composed of pyrite and chalcopyrite and tetrahedrite-tennantite and high gold and silver contents; an upper body where sphalerite is the dominant sulphide, with lesser pyrite and galena, and minor chalcopyrite. The Cu-Zn stratabound mineralization is interbedded with rhyolite.

The stockwork zone, comprised of quartz-sulphide (mainly pyrite with minor chalcopyrite and sphalerite) veins 10µm- to several cm-wide, lies at the base of the deposit under the massive sulphide body. A wide zone of hydrothermally altered rock occurs around the veins.

In addition to the sulphides, chert and barite beds also occur within the volcanic sequence.
TEXTURES AND PARAGENETIC SEQUENCE

Mineralization at San Fernando exhibits complex textures. In addition to those produced by hydrothermal replacement processes, contact metamorphism resulted in recrystallization and overprinted most of the primary textures. Mineral textures were reequilibrated and remobilized during this process. Nevertheless, five stages in the formation of the deposit can be recognized from the ore textures (Fig. 2).

The first stage prior to the sulphide mineralization is the deposition of the host volcanic rocks. During the second stage, sulphide mineralization formed by replacement of the primary mineralization and produced massive or semimassive sulphides, mainly sphalerite, chalcopyrite, pyrite, tennantite and arsenopyrite. These minerals exhibit recrystallisation textures due to the contact metamorphism. Barite replaced by sulphides or by Ba-phylllosilicates can also be present.

The third stage is defined by a lower temperature mineral assemblage characterized by the absence of chalcopyrite. In addition to pyrite in this stage, sphalerite and arsenopyrite, Ag-rich tetrahedrite (freibergite) accompanied by electrum and galena are developed in veins which cut the early formed sphalerite.

The fourth stage is characterized by late replacement processes. The minerals formed during this stage exhibit metamorphic reequilibration textures of previously formed minerals. Consequently, there is an increase in the grain size, development of granoblastic textures, triple points and curved borders in minerals. Locally, poikiloblastic growths, mainly in pyrite and sphalerite, can occur. During this stage in the middle massive stratiform ore several Ag-rich minerals are formed, mainly hessite, matildite, pyrargirite, stromeyerite and acanthite. These minerals and löllingite replace tetrahedrite.

During the fifth stage there was minor remobilization in narrow veins. The development of zinalsite and armenite is important in the stratabound mineralization. These minerals have not been affected by the contact metamorphism. In this stage arsenopyrite replaces löllingite

SULPHUR ISOTOPES

For sulphur isotopic analyses, single grains of sulphide minerals, pyrite, chalcopyrite and sphalerite were hand picked. Sulphides were analyzed using a Delta C Finnigan MAT continuous flow isotope-ratio mass spectrometer with an elemental analyzer, a TC-EA according to the method of Giesemann et al., (1974). Analyses were carried out at the Serveis Científic-Tècnics (University of Barcelona, Spain).

δ³⁴S values of sulphide minerals range between -0.5 ‰ and 7 ‰ (Fig. 3), (av. = 2.7‰). δ³⁴S values of pyrite cover the entire range, whereas δ³⁴S of chalcopyrite ranges from 0.3 ‰ to 3.1 ‰. In profile 22 (Fig. 1), δ³⁴S values of chalcopyrite and sphalerite (19 samples) range from 0.4 ‰ to 2.7 ‰, where the highest and silver contents occur.

DISCUSSION AND CONCLUSIONS

The Los Pasos Formation contains two rhyolitic units, including explosive pyroclastic rocks. The San Fernando deposit occurs at the top of the lower rhyolitic unit. The ore deposit and volcanic host rocks have been intruded by the Manicagua granodioritic pluton and its associated hydrothermal vein complex. This process produced a strong metamorphic recrystallization in the San Fernando deposit, with the development of granoblastic textures and most of the primary textures were obliterated, sulphides were remobilized at the local scale and Bi and Te were introduced from the vein fluids.

Textural observations indicate that most of the mineralization in the San Fernando deposit formed by the replacement of previously deposited minerals. The paragenetic sequence indicates that relatively low-temperature sulphides such as sphalerite are partly replaced by higher
temperature chalcopyrite. This “zone refining” process occurred in other deposits and is attributed to the continuous circulation of hotter fluid through parts of the deposit previously formed at lower temperatures (Large 1992; Ohmoto 1996).

Ohmoto (1996) indicates that gold is deposited preferentially in association with chalcopyrite replacing sphalerite in the “black ores”. Nevertheless, in the San Fernando deposit gold mineralization and tetrahedrite with the highest Ag contents are associated with sphalerite and have been located in fissural stages of replacement in the lower stratiform zone.

Sulphur isotope data indicate that sulphide sulphur originated by the thermochemical reduction of marine sulphate, and from a magmatic source, or was leached from volcanic rocks. This last contribution of sulphur probably increased during the formation of the higher temperature mineralization, characterized by chalcopyrite, sphalerite and tennantite. Isotope reequilibration has not been reached during metamorphism.

Based on the geodynamic environment, type of associated volcanism, structure of the ore mineralization and sulphur isotope data, the San Fernando deposit can be classified as a Kuroko-type deposit.

ACKNOWLEDGMENTS

This research was sponsored by projects from the AECI (Programas de Colaboración con Iberoamérica), from the Spanish project BTE2001-3308, and from the research grant 2005-SGR-00589 of the Catalanian Government. The company Central Geological Mining Enterprise provided samples and maps. E. Aracil is thanked for her assistance with the sulphur isotope analyses. Comments by J. Peter are highly appreciated.

REFERENCES


Lava-cryptodome-pumice cone volcanoes: the principal type of felsic volcanic centre in the Iberian Pyrite Belt

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ABSTRACT: The Volcanic-Sedimentary Complex of the Iberian Pyrite Belt (IPB) comprises an Upper Devonian to Lower Carboniferous submarine succession with a wide variety of felsic volcanic facies. The architecture of the felsic volcanic centres include lavas/domes, pyroclastic units and intrusions that define lava-cryptodome-pumice cone volcanoes. The diversity of volcanic facies recognized in different areas of the IPB mainly reflects variations in proximity to these volcanoes. The studied volcanoes range in diameter from 2 km to >5 km and their thickest sections vary from ~400m to >800m. The intrusions are cryptodomes and partly-extrusive cryptodomes up to 2 km long and up 200m thick. At the Neves Corvo deposit the mineralization relates to rhyolitic lavas that overlie a ~1Ma older, relatively thick fiamme-rich volcaniclastic unit. In several other locations of the belt, however, the pyroclastic units include sulphide clasts that may have been derived from coeval massive sulphide accumulations on the sea floor, which widens the exploration potential of volcanic facies analysis in this province.

KEYWORDS: Iberian Pyrite Belt, felsic volcanic centre, volcanic facies, VHMS deposits

1 GEOLOGIC SETTING

The Iberian Pyrite Belt (IPB), in the south of Portugal and Spain, hosts more than 85 giant massive sulphide deposits amounting to more than 1700 million tonnes of sulphide ore. The ore deposits are hosted by a submarine volcanic succession dominated by felsic units, and mudstones that constitute the Upper Devonian to Lower Carboniferous Volcanic-Sedimentary Complex (VSC).

2 VOLCANIC CENTRES

Detailed logging and mapping of volcanic facies in several volcanic settings of the IPB, which include three areas in Portugal (Neves Corvo, Albernoa and Serra Branca) and five road and river sections in Spain (Paymogo quarry, Odiel River, Cerro de Andévalo, El Almendro-Villanueva de Castilejos and La Aulaga) were used to characterize the principal type of felsic volcanoes of the IPB.

The most common felsic volcanic facies identified in the VSC of the Iberian Pyrite Belt are coherent facies, monomictic breccia, fiamme-rich breccia and sandstone and crystal-rich sandstone. These volcanic facies are interbedded with volumetrically dominant, non-volcanic sedimentary facies, consisting mainly of mudstone, which comprises approximately 75% of the VSC (Tornos, 2006). Different combinations and proportions of these facies shaped the architecture of the studied felsic volcanic centres.

Felsic coherent and monomictic breccia facies constitute lavas, domes and intrusions, whereas fiamme-bearing facies represent pyroclastic facies, most likely sourced from intra-basinal vents.

The effusive units (lavas/domes) comprise relatively thin (3-10m) coherent cores that are surrounded by thick intervals (up to 200m) of felsic monomictic autoclastic breccia (jigsaw-
fit breccia facies and clast-rotated breccia facies). These monomictic breccia intervals include both hyaloclastite and autobreccia, although hyaloclastite is much more abundant than autobreccia. Laterally, the lavas/domes grade to aprons of resedimented autoclastic breccia and sandstone. The lavas/domes have a distinctive sediment-matrix igneous breccia at their top contacts that has been interpreted as peperite in many locations of the Belt (Boulter, 1993; Boulter et al., 2001; Allen, 2001; D'Onaire et al., 2002). In the study areas, detailed analysis of the sediment-matrix igneous breccias and their relationships with the surrounding units indicate that these breccias were formed by infiltration of fine sedimentary particles in the hyaloclastic carapace of the lavas/domes.

Relatively small aphyric to quartz-feldsparphyric units intrude and disrupt the stratigraphy at different levels. These units are dominated by coherent facies, comprising relatively thin margins of autoclastic breccia. Some of these units are clearly intrusive showing peperite at the upper contact and represent cryptodomes. Other units grade laterally to thick and unstructured, small-volume aprons of resedimented autoclastic debris. These units define partially-extrusive cryptodomes.

The pyroclastic units comprise fiamme-rich facies, and were produced by felsic explosive eruptions, probably at submarine intrabasinal vents. These facies are widespread in the IPB, being interpreted as deposited from syn-eruptive, water-supported, gravity currents.

The fiamme-rich facies define two types of units: thick graded fiamme breccia and sandstone, and bedded fiamme breccia and sandstone. Units of thick graded fiamme breccia are relatively abundant throughout the IPB. The thickest units can be up to 60m thick and have relatively small extents (up to 5 km at Serra Branca). They have irregular, discordant and erosive basal contacts. These units comprise a thick, massive, poorly sorted lower zone made of fiamme, irregular and angular clasts of black mudstone, dense rhylite clasts, and crystal fragments. The lower zone grades upwards to a massive intermediate zone (up to 15m thick) that is mainly composed of fiamme and crystal fragments. The top zone (up to 7m) is typically massive or diffusely laminated, comprising siliceous mudstone with fiamme up to 6-10cm across. These thick graded fiamme breccia and sandstone units are interpreted to consist mainly of pyroclasts (fiamme that was formerly pumice and quartz and feldspar crystal fragments) and contain accessory or accidental lithic clasts (volcanic and mudstone clasts). Hence, we conclude that the thick graded fiamme units are syn-eruptive pyroclastic deposits. Despite being largely composed by juvenile pyroclasts, the thick graded fiamme breccia units show no evidence for hot emplacement. The parallel to bedding compaction of pumice (now fiamme) is more likely to be diagenetic than resulting from welding.

Units of bedded fiamme breccia and sandstone may occur laterally to units of thick graded fiamme breccia and can define sequences that can be more than 50m thick. These units consist on the alternation of massive to normally graded units of fiamme breccia with massive beds of sandstone.

The numerous felsic lavas/domes, intrusions, and pyroclastic units defined relatively small lava-cryptodome-pumice cone volcanoes throughout the VSC. The lava-cryptodome-pumice cone volcanoes of the VSC are rhyolitic (e.g. Neves Corvo, C. Rosa, 2007) or rhyolitic to dacitic (other areas, D., Rosa et al., 2004; 2006) and their facies architecture range widely in complexity. The volcanic centre at Albernoa illustrates the simplest, lava-dominated end member of these volcanoes. It consists mainly of lava(s) (up to 400m thick and >8 km long) and one pyroclastic unit (~20m thick), with restricted lateral extent. In the other end of this range, volcanic centres like Serra Branca can exhibit a much more complex anatomy. At Serra Branca, at least fourteen felsic lavas or domes and cryptodomes, intercalated with pyroclastic units, were recognized.

The pyroclastic units lack extrabasinal- or basin-margin-derived clasts (most non-juvenile clasts are intrabasinal), and are poorly sorted and fiamme-rich (former pumice lapilli), which suggests that the source vents were submerged (Whitham & Sparks, 1986; McPhie & Allen, 2003).

The studied felsic volcanoes range in diameter from >2 km (Neves Corvo), to >5 km (Serra Branca) and their thickest sections vary from >800m (Odiel River) to ~400m (Neves Corvo). The intrusions are cryptodomes and partly-extrusive cryptodomes up to 2 km long and up to 200m thick.

These volcanoes were similar in size and facies associations to the submarine felsic "dome-cryptodome-tuff volcanoes" described by...
Horikoshi (1969) and Kokelaar et al. (1985), the “dome-top tuff cone volcanoes” of Cas et al. (1990), the “cryptodome-tuff volcanoes” studied by Allen et al. (1997), or the “cryptodome-pumice cone volcanoes” described by Stewart & McPhie (2006).

3 GEOCHEMISTRY

It is normally considered that HFSE have an immobile behaviour (e.g. MacLean & Barret, 1993). Despite this, classification of IPB volcanic rocks based on their immobile element contents is not always entirely consistent with phenocryst compositions and assemblages, or with their established tectonic settings. In some cases, as documented by D. Rosa et al. (2004, 2006) rocks plot in the transition between the rhyodacite/dacite field and the andesite field in the Winchester & Floyd (1977) diagram, which does not agree with their abundant quartz and feldspar phenocrysts. This type of misclassification likely reflects crustal fusion under relatively low temperatures, which does not allow for the melting of refractory phases in which HFSE, such as Zr, Y or Nb used in the diagrams, reside. These relatively low temperatures have been confirmed through zircon and monazite geothermometry (D. Rosa et al., 2006) and it can therefore be argued that, had the fission temperature been higher, increased Zr contents would moved these rocks into the correct fields of the above mentioned diagram.

The felsic pyroclastic units appear to have been erupted from vents within the lava-cryptodome-pumice cone volcanoes. This is confirmed by the strong geochemical affinities between some pyroclastic units and the associated lavas/domes, which suggests a common source (D. Rosa et al., 2006).

4 PROXIMAL VS. DISTAL FACIES

The areas containing the thickest intervals of lavas, intrusions and fiamme-rich units are interpreted to be proximal to vent areas. For example, at Neves Corvo proximal facies are approximately 400m thick, whereas in the distal sections of the sequence thickness does not usually exceeds 25m. Felsic lavas or domes in proximal areas are typically dominated by coherent facies and in situ hyaloclastite (Albernoa, Neves Corvo, Serra Branca, Paymogo quarry, Odiel River). The pyroclastic units comprise relatively thick, coarse, and massive or normally graded fiamme-rich breccia that may also contain dense volcanic and sedimentary clasts (Neves Corvo, Serra Branca and Odiel River). The felsic intrusions are characterized by coherent facies, and discordant upper contacts that may be defined by peperite. The partly extrusive cryptodomes often have marginal aprons of resedimented hyaloclastite (Serra Branca).

Areas interpreted to be more distal in relation to the source vents of lavas or domes comprise aprons of resedimented hyaloclastite (Albernoa, Neves Corvo, Serra Branca, Cerro de Andévalo), or even farther from the source vent, crystal-rich sandstone facies, intercalated with mudstone. In very distal areas, the fiamme-rich facies consist of diffusely to well-bedded fiamme-bearing sandstone and mudstone. Hence, the diversity of volcanic facies in the VSC seems to reflect in a large extend the variations in proximity to source vents, and in the volume of eruptions.

The time gap between eruptions within each study area is poorly constrained, except for the Neves Corvo volcanic centre, where the available biostratigraphic data (Oliveira et al., 2004; C. Rosa et al., in prep.) conforms with a time gap of at least 1Ma between the explosive and the subsequent effusive volcanic events. In other areas, relatively thin intervals of mudstone are intercalated within the VSC (e.g. lower part of the Serra Branca VSC), or erosional surfaces have been identified (e.g. Paymogo quarry), which suggest there were some breaks (of unknown significance) during the accumulation of the volcanic successions. In contrast, other sections do not show any evidence for interruptions and may have aggraded both continuously and very rapidly (e.g. Albernoa, El Almendro-Villanueva de los Castillejos, Cerro de Andévalo and upper part of the VS Complex at Serra Branca).

5 MINERALIZATION AND VOLCANIC FACIES

Amongst the study areas, Neves Corvo is the only volcanic centre that hosts VHMS mineralization. The VSC at Neves Corvo consists of relatively thick, widespread fiamme-rich volcanioclastic units overlain by massive sulphide-hosting thick rhyolitic lavas (Rosa et al., 2005; and in prep). Both units were variably affected by massive sulphide-related hydrothermal alteration. Both the massive sulphides and the
felsic lavas at Neves Corvo were dated as late Strunian in age (upper Devonian) (Oliveira et al., 2004; C. Rosa et al., in prep).

Relatively abundant sulphide clasts were identified in some volcaniclastic units at Serra Branca, El Almendro-Villanueva de los Castillejos and Cerro de Andévalo. This is consistent with ore formation on the sea floor in proximity to the felsic volcanic centres, most likely during periods of acquiescence of the volcanism. In the cases where these clasts can be ascribed to massive-sulphide ores, this can be used as an exploration criterion for concealed massive sulphide deposits in this province.

6 CONCLUSIONS

The lava-cryptodome-pumice cone volcanic facies of the IPB are similar to other felsic volcanoes of ancient and modern submarine successions. The composition and close spatial relationship between the felsic lavas/domes and some pyroclastic units suggest that these might have been sourced from the lava/domes.

ACKNOWLEDGEMENTS

This is a contribution to research project ARCHYMÉDES I (POCTI/CTA/41393/2001).

REFERENCES


ABSTRACT: New lead isotope analyses are reported for sediments of the IPB Phyllite-Quartzite Group (PQ) and sulphide ores of the “bornite zone” at the Neves Corvo deposit. PQ rocks have lead isotopic compositions characterized by $^{206}\text{Pb}/^{204}\text{Pb} = 18.639 - 19.466$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.639 - 15.697$ and $^{208}\text{Pb}/^{204}\text{Pb} = 38.908 - 39.965$. The “bornite zone” ores expand the range of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values previously reported for Neves Corvo ores, and form a steep linear trend in $^{206}\text{Pb}/^{204}\text{Pb}$ - $^{207}\text{Pb}/^{204}\text{Pb}$ space, independent from the one defined by cassiterite, with isotopic ratios varying from $^{206}\text{Pb}/^{204}\text{Pb} = 18.13$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.59$ to $^{206}\text{Pb}/^{204}\text{Pb} = 18.43$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.87$. Lead in typical IPB ores could have been derived from the PQ sediments. Extensive fluid mixing occurred near the sites of Neves Corvo ore deposition and the lead isotope compositions of the “bornite zone” ore could reflect input of a magmatic fluid component.

KEYWORDS: Iberian Pyrite Belt, VHMS deposits, Neves Corvo, Lead isotopes, Metal sources

1 INTRODUCTION AND GEOLOGICAL SETTING

In the Iberian Pyrite Belt (IPB) massive sulphide deposition occurred during the waning stages of felsic volcanism within a thin volcanic-siliceous complex (VSC; < 600m; Upper Devonian-Lower Carboniferous). The VSC is overlain by a synorogenic flysch succession (>1600m-thick; Baixo Alentejo Flysch Group; early to middle Carboniferous) and lies on shallow platform siliciclastic sediments (>2000m-thick, base unknown; Phyllite-Quartzite Group – PQ -, upper Devonian and older) (Tornos, 2006; and references therein).

The hybrid regime of metal supply in the IPB has been emphasized by a number of authors, who invoke the participation, besides seawater, of variably significant proportions of connate waters equilibrated with the PQ metasediments, fluids resulting from low-grade metamorphic dewatering, direct contributions of magmatic waters, and/or different combinations of either of these fluids in the IPB fluid budgets (e.g., Tornos, 2006). Lead, strontium and neodymium isotope systematics suggest that most metals in the deposits should have been sourced by the, only partially known, sedimentary sequence that underlies the ore-hosting volcanic-siliceous complex (e.g. Marcoux, 1998). However, direct evidence for this is still lacking after these studies. In addition, in the Neves-Corvo deposit, previous isotopic data indicate a unique history of metal supply embracing multi-sourced metal contributions (Relvas et al., 2001).

Here we include representative lead isotope data for rocks of the PQ Group, and for sulphide ores from the “bornite zone” at Neves Corvo. These data widen the spectrum of lead isotope results reported by Marcoux (1998) and Relvas et al. (2001), providing new insights on the IPB metal sources.

2 PHYLLITE-QUARTZITE GROUP

Four lithofacies – phyllites, siliceous phyllites, quartzwackes and quartzites - have been defined on the basis of the petrographic and
lithogeochemical classification of the PQ rocks, their “protolith” compositions being calculated from averaging the unaltered to least altered samples. Whole-rock geochemistry of these metasediments indicate provenance from granitoid sources and mature homogenization resulting from prominent sedimentary recycling (Jorge et al., 2006).

3 THE NEVES CORVO “BORNITE ZONE”

Bornite-rich, sulphide ores, characterized by high-sulphidation sulphide associations, occur in the Neves orebody of the Neves Corvo deposit. Gold, together with high concentrations of copper and minor Sn, Sb, Se and In, was found in these ores. Tin occurs as cassiterite, stannite and other copper-tin sulphides and sulfohalts, which are similar to the Cu-Sn paragenesis at the South orebody of the Kidd Creek deposit, (Hannington et al., 1999). These peculiar ores were interpreted as resulting either from extreme zone refining effects, or from the late input of an external fluid component (magmatic?) in the Neves Corvo system (Pinto et al., 2005).

4 SAMPLING AND METHODS

The 48 samples used in this study were selected from large sample sets representing the various lithofacies of the PQ Group, both in Portugal and Spain (Jorge et al., 2006), and from drill core intersections and underground workings at Neves Corvo (Pinto et al., 2005). 41 samples of PQ sediments were analysed for major and trace elements. 5 samples of phyllites from the PQ Group, and 7 samples representing the “bornite zone” ores of the Neves Corvo deposit were selected to yield lead isotope data. The analyzed material consists of whole-rock powders.

5 RESULTS

5.1 Lead isotope systematics of the PQ Group

The analysed PQ phyllites are enriched in U (U/Pb = 0.14 – 0.33) and Th (Th/U = 4.57 – 5.65) relative to the continental crust, and Pb isotope values display a total range of 206Pb/204Pb values from 18.639 to 19.466, 207Pb/204Pb values from 15.639 to 15.697 and 208Pb/204Pb = 38.908 to 39.965 (Fig. 1). Plotting PQ lead isotope data with that of Central Iberian and Ossa-Morena Zones Palaeozoic sediments display consistent trends on both U- and Th-radiogenic diagrams, suggesting that the PQ sedimentary rocks were predominantly derived by recycling of (older) basement from the internal zones of the Variscan Chain. Furthermore, the (age corrected; ~350 Ma) PQ isotopic results overlap those of the IPB felsic volcanic rocks (Marcoux, 1998); both PQ sediments and felsic volcanics plot above the orogenic curve of Zartman & Doe (1979) and very close to Stacey & Kramers (1975) model values for contemporaneous lithospheric lead, complying with petrogenetic models that require crustal sources for felsic volcanism in the IPB (e.g. Munhá, 1983). Most of the lead in the PQ rocks was certainly derived from the same crustal sources as were the IPB felsic volcanic rocks.

5.2 Lead isotope distribution in the IPB ores

Lead isotope systematics of several IPB deposits reported by Marcoux (1998) show that (except for Neves Corvo) massive sulphides have a highly homogeneous lead isotopic composition (206Pb/204Pb = 18.133 ± 0.021, 207Pb/204Pb = 15.622 ± 0.015, 208Pb/204Pb = 38.191 ± 0.049), which is similar to that of their felsic volcanic host rocks (Marcoux, 1998). Conversely, Neves Corvo massive sulphides
are relatively heterogeneous ($^{206}\text{Pb}/^{204}\text{Pb} = 18.22 - 18.29$), and early “stringer and massive cassiterite ores” are strongly radiogenic, with their cassiterites varying from values ($^{206}\text{Pb}/^{204}\text{Pb} = 18.50$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.65$) slightly above the massive sulphides to highly radiogenic $^{206}\text{Pb}/^{204}\text{Pb} (= 35.03)$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ($= 16.78$) ratios (Relvas et al., 2001). Our new data expand the range of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values previously reported for the Neves Corvo ores (Fig. 2). The analysed ore samples from the “bornite zone” form a steep linear trend in the $^{206}\text{Pb}/^{204}\text{Pb} - ^{207}\text{Pb}/^{204}\text{Pb}$ diagram, independent from the one defined by cassiterite (Fig. 2), with isotopic ratios varying from $^{206}\text{Pb}/^{204}\text{Pb} = 18.13$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.59$ (typical of IPB sulphides) to $^{206}\text{Pb}/^{204}\text{Pb} = 18.43$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.87$. The lowest $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb} “bornite zone” ore data plot close to the Stacey & Kramers (1975) model Pb-growth curve and have a model age of $\sim 348$ Ma, in agreement with U/Pb-zircon results, which indicate an age range of $345-356$ Ma for IPB sulphide deposition (see, Barrie et al., 2002).

## 6 DISCUSSION AND CONCLUSIONS

Plotting IPB ore lead data together with age corrected (350 Ma) compositions of felsic volcanics and PQ sedimentary rocks (Fig. 2) demonstrates that lead in typical IPB ores could have been derived from both the felsic volcanics and the underlying PQ sediments, as recently suggested by several authors. Furthermore, on-going research shows that many samples of PQ sediments underwent iron, manganese and base metals depletion while interacting with saline basinal waters (Fig. 3).

Lead isotopic compositions also reflect the exceptional nature of the Neves Corvo deposit.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Diagrams of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ for (age corrected) PQ phyllites and IPB felsic volcanics, typical IPB ores, and Neves Corvo stringer and massive cassiterite, massive sulphide and “bornite zone” ores (data from Marcoux, 1998; Relvas et al., 2001; this study).

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Plot showing metal depletion in PQ sediments, accompanied by potassium metassomatism and loss of CaO and Na₂O. The plotted values correspond to normalized ratios against Al₂O₃.

The lead isotopic signature of its “stringer and massive cassiterite ores” compares to that of granite-affiliated cassiterites (Relvas et al., 2001); however, a rigorous characterization of its origin is precluded by the absence of adequate outcropping regional rocks. Some vein and stratabound Sn-W mineralizations have been documented in the IPB (Bajo Corumbel, Spain), but these relate to late-Hercynian intrusives, and hence are unrelated to the VHMS-hosting felsic volcanic cycles (Sáez et al., 1989). Their occurrence, however, speak for the potential of the IPB crustal rock reservoirs to generate Sn-enriched granitoids. External sources are implied by Pb, Os and Nd isotopic signatures preserved in the “stringer and massive cassiterite ores” (Relvas et al., 2001; Munhá et al., 2005); however, the sources for lead in “stringer and massive cassiterite” and “bornite zone” ores were distinct, as indicated
by the widely different slopes of their $^{207}$Pb/$^{206}$Pb - $^{206}$Pb/$^{204}$Pb isotopic trends (0.07 and 0.99, respectively; Fig. 2). “Bornite-zone” ores Stacey & Kramers’ (1975) model date (<348 Ma) corresponds to the time in the past when the Pb was withdrawn from the Stacey-Kramers reservoir and was thereby separated from U and Th during ore deposition; subsequently, this Pb was mixed with radiogenic lead(s). Observed variations in Pb isotopic compositions (Fig. 2) thus reflect ore-forming fluids with different origins and/or traveling along distinct hydrothermal pathways, equilibrated with rocks of different isotopic compositions, and finally mixed at the site of ore deposition. Mixing of different fluids at or near the site of ore deposition is required in order to preserve the isotope distinction between the ore samples, providing further evidence for multiple sourced ore fluids (cf. Relvas et al., 2001). This is demonstrated by the development of distinct mixing arrays (dashed lines in diagrams of Fig. 2) that diverge from the typical IPB massive sulphide composition towards the more radiogenic “stringer and massive cassiterite” and “bornite-zone” ores of Neves Corvo. Expectedly, Pb isotopic compositions of “bornite-zone” ore samples are intermediate between their main end-member lead sources. The lead budget from the less radiogenic end-member was largely dominated by the IPB felsic volcanic and PQ sedimentary components, whereas the high $^{207}$Pb/$^{206}$Pb values (> 15.87) inferred for the more radiogenic end-member require lead sources that are external to the IPB volcano-sedimentary sequence.

The steep $^{207}$Pb/$^{206}$Pb - $^{206}$Pb/$^{204}$Pb isotope trend of “bornite-zone” ores (not accompanied by time-integrated growth of $^{206}$Pb/$^{204}$Pb; Fig. 2) suggests contributions from enriched mantle derived magmas (such as those represented by IPB mafic rocks; Munhá, 1983) that have assimilated old (high $^{207}$Pb/$^{206}$Pb) crustal rocks. Thus, the lead isotope composition inferred for the more radiogenic end-member component in the “bornite zone” ore requires derivation from a distinct (specific) source; indeed, this could reflect late input of a magmatic fluid component in the Neves Corvo system, as suggested by Pinto et al. (2005).

**ACKNOWLEDGEMENTS**

This is a contribution to research project ARCHIMEDES II (POCTI/CTA/45873/2002).

**REFERENCES**


Geology and lithogeochemistry of the unique Las Cruces VMS deposit, Iberian Pyrite Belt.

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ABSTRACT: The Las Cruces deposit is a unique example of supergene enriched massive sulphide deposit in the Iberian Pyrite Belt (IPB). This massive sulphide, is the most easterly in the IPB hosted in shales and fine grain volcanoclastic rocks within the lower Volcano-Sedimentary (VS) Complex. Detailed lithostratigraphic study identifies four units. The footwall comprises a dacitic dome interbedded with sandstone and shale, at the bottom, where the primary mineralization is developed. The hanging wall is formed of three main units, consisting of a complex sequence of volcanoclastic breccias and sandstone, alternating with siltstone and shale, including a pumice-rich breccia. The chemostratigraphic results show a composition between rhyodacite and basalt-andesite with a calc-alkaline affinity. There is no significant geochemical difference within the entire sequence suggesting a unique magmatic pulse. Lastly, the geochemical analysis of the hosted shale suggests local anoxic conditions prevailed during massive sulphide formation.

KEYWORDS: Las Cruces, VHMS, IPB, lithogeochemistry, supergene, gossan, massive sulphide

1 INTRODUCTION

Las Cruces mine hosts the southeasternmost massive sulphide deposit of the IPB. It is the only deposit located within the Guadalquivir Cenozoic basin and is covered by a thick sequence of Neogene marls. The orebody occurs as lenses within the lower part of Volcanic-Sedimentary Complex (VS Complex) (Conde et al. 2003), the late Devonian-early Carboniferous sequence that hosts all the massive sulphide deposits of the IPB.

The deposit was discovered in 1994 by Riomin Exploraciones S.A. (a subsidiary company of Rio Tinto) after a geophysical campaign in the extension of the IPB below Cenozoic sediments. INMET Mining Corporation is currently the owner of the project and the mine is expected to produce the first concentrates in late 2007. The main feature of the Las Cruces deposit is the presence of a pristine zone of supergene alteration that caps the massive sulphides. In all the other deposits of the IPB, supergene enrichment zones have been systematically eroded and/or mined. Supergene enrichment makes Las Cruces one of the richest copper deposits worldwide. The estimated total pre-mining reserves are 30.2 Mt @ 1.15% Cu, 1.19% Pb, 3.51% Zn, 21g/t Ag and 0.3g/t Au for the primary massive sulphides, 16 Mt @ 6.9% Cu, 0.25% Zn and 0.76% Pb for the supergene cementation zone and 1.7 Mt @ 115 g/t Ag and 4.3 g/t Au for the gossan.

Previous work has dealt with a detailed study of mineralization (Knight 2000) or else focused on the mining project (Doyle et al. 1998, Norris 2001). In this abstract we present the first conclusions of an ongoing study of the geology and geochemistry of the deposit. The work deals with the stratigraphy and the geochemistry of the host sequence and the results are based on the detailed logging of 12 drillholes, a petrographic study, and the analysis of representative samples of the host rocks, including both volcanic and sedimentary rocks.

2 GEOLOGICAL SETTING

The primary mineralization of the Las Cruces massive sulphide deposit has a lensoidal morphology, dipping of 45° to the N (Doyle et al. 1998). Mineralization is hosted by shale and fine grain volcanoclastic rocks of the lower VS Complex. Detailed study of the host sequence shows that it occupies the same stratigraphic position of nearby deposits of Aznalcóllar and...
Los Frailes (Conde et al 2003). In this area, the VS Complex is formed of massive volcanic rocks (domes and sills), volcanoclastic breccia and arenite, interbedded with shale and chemical sediments (chert and jasper). Felsic volcanic rocks dominate (dacite and rhyolite) but andesitic and basaltic-andesitic flows and sills are also present in the stratigraphic sequence.

3 LITHOSTRATIGRAPHY OF THE LAS CRUCES DEPOSIT

The host rocks of the deposit can be grouped into four main units (Fig. 1).

The footwall (>300m) consists of a porphyritic dacite dome with associated hyaloclastite and hydrothermal breccias along the margins. These rocks grade upwards into crystal-rich sandstone and dark shale, the latter hosting the primary mineralization (Fig. 1). Rocks beneath the massive sulphides have been affected by a pervasive but highly irregular hydrothermal alteration, consisting of chloritization, sericitization and silicification. The more altered rocks host a mineralized stockwork similar to that found in other deposits of the IPB.

The hanging wall consists of a complex sequence (450-600m) of felsic and intermediate volcanic rocks, including lava, debris flow and pumice-rich breccia alternating with siltstone and shale, which dominate the upper part of the sequence. In the hanging wall, three units can be distinguished. The basal unit, capping the massive sulphides, includes dark shale alternating with epiclastic argillite and arenite. The intermediate unit is a thick package made up of heterogeneous breccias and rich-crystal sandstone (debris flow); here there is a single layer containing pumice rich fragments that has been traced over the whole area (Conde et al. 2003). The uppermost part of the hanging wall is composed of shale and felsic volcanoclastic rocks. A characteristic unit of massive dacite that could either is flow or a sill locally caps these rocks. The hanging wall units show a weak to moderate hydrothermal alteration (chloritization, sericitization, silification, and carbonatization). In the area around Las Cruces these Palaeozoic rocks are capped by about 150m of Neogene conglomerate, sand and marl (Fig. 1).

Both U-Pb isotopic (Barrie et al 2002) and palynological (Oliveira et al 2004) dates of the host rocks at Las Cruces show that the massive sulphides formed during the late Strunian (late Devonian) and contemporaneously with most of the shale-hosted massive sulphide deposits of the southern IPB (Tornos 2006).

In detail, the massive sulphides occurs as stratiform massive and semi-massive sulphides, an irregular copper-rich stockwork, and a zone of supergene alteration including both a cementation zone and an overlying gossan (Knight 2000). The primary massive sulphides are very similar to those found in other deposits of the IPB. They are dominated by fine grained, massive to banded, pyrite with local enrichments in sphalerite, chalcopirite and galena. These massive sulphides show local sedimentary structures such as parallel lamination, as well as a characteristic layer near the footwall and made up of syn-sedimentary breccias with fragments of massive sulphide, shale, chert and jasper. Furthermore, there are evidences of stratiform sulphates being replaced by pyrite (Tornos 2006). All these features indicate that the primary mineralization was exhalative onto the seafloor, probably within a third order anoxic basin.

The secondary mineralization occurs as veins and breccias at the top of the massive sul-
phides and has produced a systematic enrichment in copper and depletion in zinc. The mineralogy of the secondary zone includes chalccocite, covellite, bornite, and enargite.

4 LITHOGEOCHEMICAL

48 samples (25 volcanic rocks and 23 shale) from drillcore were analysed by XRF and ICP techniques for major and trace elements. The shale was also analyzed for total organic carbon and sulphur.

Since many of the rocks show a pervasive alteration, discrimination between lithological groups has been predominantly based on elements traditionally regarded as immobile (Al2O3, TiO2 and Zr) (MacLean & Barret, 1993; Barret & MacLean, 1999).

The volcanic rocks have been plotted in the standard discriminating diagram SiO2 vs. Zr/TiO2. They range in composition between rhyodacite and basalt-andesite without major gaps (Fig 2). The magmatic affinity has been tracked using the La-Yb diagram of Barret & MacLean (1999). La and Yb contents of 7-30 ppm and 1-3 ppm, respectively, define a calc-alkaline trend. The TiO2% vs. Zr and Nb/Zr ratios identifies only one group of volcanic rocks with no major differences, suggesting that all the sequence is derived from a unique magmatic pulse with no dramatic chemical changes.

The chondrite-normalized REE spidergram for felsic and intermediate rocks show similar patterns for all REE except for Eu. The intermediate rocks show either no Eu anomaly or else a positive one whilst the dacite and rhyolite-dacite patterns have no a clear negative Eu anomaly. This may indicate difference in the plagioclase composition. However, this is not reflected in the other REE. This observation, together with the equivalent spidergram for the felsic and mafic rocks, suggests that these rocks have been significantly altered rather than having magmatic sources (Mitjavila et al. 1997).

The degree of hydrothermal alteration can be assessed using the alteration box plot of Large et al (2001). The data confirm that both the footwall and the hanging wall are affected by hydrothermal processes but only the footwall rocks plot into the chl ± py ± (ser) field (Fig 3).

As indicated above, shale is a rather significant component of the whole sequence and the immediate host rock to the orebody. Mineralized shale is enriched in elements typically present in anoxic settings (e.g. V, Cr, Mo and W). The Mn-Fe-V and V/(V+Ni) rates show that this hosted shale are plotted in the anoxic field (0.73-0.89 avg. V/V+Ni). However, the redox conditions change in the barren shale above the massive sulphides where sub-oxic to oxic conditions are established. These different features confirming the evidence found in other massive sulphide deposits of the IPB that the mineralization is related to local anoxic conditions (Tornos et al. 2003).

5 DISCUSSION AND CONCLUSION

The detailed geological and geochemical studies of the host sequence of Las Cruces massive sulphide deposit show that both the ore horizon and the environment of formation were the same as for neighbouring Aznalcôllar and Los Frailes deposits. The host unit is a complex
volcanosedimentary sequence composed of coherent dacite to andesite with associated hyaloclastite, interbedded with volcanoclastic sandstone, siltstone and thick shale units. The lithogeochemical results show that all the volcanic rocks belong to a single sequence showing no major chemical change. The geochemistry also suggests that shale which hosts the primary massive sulphides was deposited in an anoxic setting.

ACKNOWLEDGEMENTS

This work is part of the PhD of C. Conde and it’s a contribution to the Global Comparison of Massive Sulphides project (IGCP 502). The study was supported by BTE2003-0290 DGI-FEDER project and the IGME. We thank Cobre Las Cruces SA for their help for handing and sampling the drill cores.

REFERENCES


Knight FC (2000) The mineralogy, geochemistry and genesis of the secondary sulphide mineralization the Las Cruces deposit, Spain. PhD, University of Wales, Cardiff.


Geochemical factors important in developing genetic models for hydrothermal uranium deposits

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ABSTRACT: Important factors to consider in the formation of hydrothermal uranium deposits are the source of metals, nature and source of transporting fluids, associated metals, mechanisms of transport, and mechanisms of deposition. Uranium is enriched in alkalic igneous rocks, felsic volcanic rocks, organic-rich shales, and phosphatic sedimentary rocks. It is most closely associated with elements of similar large size and high charge in rock-forming and accessory minerals. It occurs in aqueous solution as several different uranyl complexes, however, carbonate and possibly chloride species are most likely responsible for transport. Transport of uranium in the reduced form is unlikely. Deposition may result from increase in pH, reduction of the fluids and/or decrease in pressure and loss of carbon dioxide gas. Decrease in temperature is not an adequate mechanism for precipitation.

KEYWORDS: hydrothermal uranium deposits, carbonate complexing, pH, reduction, alteration, haematite

1 INTRODUCTION

Geochemical factors important in the modeling of hydrothermal uranium deposits are: 1) the source of the metals; 2) nature and source of transporting fluids; i.e magmatic, meteoric, connate or metamorphic; 3) elements consistently associated with uranium; 4) mechanism of hydrothermal transport; and 5) mechanisms of deposition, i.e. heat loss, pH changes, and/or changes in oxidation state.

2. URANIUM DISTRIBUTION AND ELEMENTAL ASSOCIATIONS

Uranium occurs: 1) as a major constituent in its own minerals; 2) substituted as a minor component in rock-forming and accessory minerals; 3) in exchange positions in clays, secondary oxides and zeolites; 4) adsorbed on crystal faces and as coatings in microfractures; and 5) dissolved in intergranular fluids and fluid inclusions. The average crustal abundance is about 2.8 ppm. In primary crustal processes uranium behaves as an incompatible element because of its high charge density. During magmatic differentiation it is progressively enriched in the silicate melt and appears in the highest concentrations in felsic rocks. Uranium is enriched in alkalic rocks over calc-alkalic equivalents; volcanic equivalents generally contain 1.5 to 2 times the uranium as plutonic equivalents. Typical concentrations in mafic rocks are between 1 and 2 ppm, whereas felsic rocks range from 6 to 10 ppm; felsic volcanic glasses typically contain about 10 ppm U. Alkalic rocks may contain 100’s of ppm. In igneous rocks, uranium is associated with elements of similar charge density such as thorium, zirconium, titanium, niobium, tantalum, and rare earth elements.

In sedimentary environments, uranium is fixed by 1) reduction of uranyl (6+) to uranous (4+) and resultant precipitation; 2) adsorption on organic matter, secondary oxides, and fine clays, and subsequently incorporated into rocks during lithification; and 3) precipitation of insoluble uranyl compounds. In sedimentary rocks, uranium is most closely associated with elements of variable oxidation states such as copper, vanadium, arsenic, molybdenum, and selenium. Fine grained elastic rocks average about 3 ppm U, with organic-rich shales containing up to 1000 ppm. Coarse grained quartz
arenites average less than a ppm while limestones contain up to 3 ppm; phosphatic equivalents may contain hundreds of ppm U.

Additional associations observed in various hydrothermal settings are cobalt, nickel, chromium, and beryllium, although these geochemical associations are complex and may result from multiple overlapping hydrothermal events. In metamorphic rocks, there is a general decrease in uranium from low to high grade facies: epidote-amphibolite (3 ppm); amphibolite (1 ppm) low grade granulite (0.9 ppm); high grade granulite (0.4 ppm).

Fig 1: Distribution diagram showing the distribution of uranyl complexes as a function of pH at 200 °C assuming fluoride concentration of 100 ppm, sulphate, 1000 ppm, phosphate, 1 ppm, and 1m NaCl (6 wt%) at a partial pressure of CO₂ of 1 atm. See text for explanation.

3. MECHANISMS OF TRANSPORT

In hydrothermal solutions uranium can occur in as many as 43 different aqueous species, depending of solution composition. Uranium occurs primarily in two oxidation states, U⁴⁺ and U⁶⁺, the latter as uranyl UO₂²⁺, depending on the redox state of the solution, where the uranyl (UO₂²⁺) species are typically soluble and the uranous (U⁴⁺) are not. Thus, uranium will be most mobile under oxidizing conditions and immobile under reducing conditions.

Because of their unusual size and charge, neither uranous nor uranyl commonly occur as free ions in solution, but readily hydrolyze to soluble and insoluble hydroxyl species, or form other aqueous complexes with a wide range of anions, such as CO₃²⁻, SO₄²⁻, F⁻, Cl⁻, HPO₄²⁻, and H₂PO₄⁻. Figure 1 illustrates the proportion of uranium occurring as each of the uranyl complexes in a model hydrothermal solution at 200°C at a partial pressure of carbon dioxide of 1 atm and an oxygen fugacity where the uranyl state would predominate. The composition of the solution was chosen to illustrate approximate limiting conditions under which the various complexes will occur. Order of magnitude changes in the anion concentrations would be required to change the overall distribution. What is apparent in Figure 1 is that the various anions are competing for the uranium in solution.

Carbonate complexes are the most stable and predominate in alkaline solutions where CO₃²⁻ is the dominate carbonate species (UDC – UO₂(CO₃)₂²⁻; UTC – UO₂(CO₃)₃⁺). In acid fluids fluoride complexes are most stable and compete favorably with sulphate and chloride, both present in much higher concentrations. The ramifications of the dominance of phosphate complexes in the near neutral region are not well understood, however, in very low phosphate fluids, 0.01 ppm, this region becomes dominate by carbonate complexes. The affinity of uranyl ion for phosphate carries through to the occurrence of uranium in phos-
phate minerals in certain geologic environments. The concentrations of anions such as fluoride and phosphate are kept low by the insolubility of minerals such as fluorite and apatite, so the importance of these complexes would be enhanced in low calcium fluids, which might be expected in an alkalic system.

As temperature is increased to 300°C, carbonate complexes disappear and the entire pH range is dominated by uranyl hydroxyl species, with the exception of the near neutral region where phosphate complexes predominate.

At low oxygen fugacities, the uranous state does not form carbonate complexes under any conditions of pH or temperature. Over a wide range of pH’s uranous hydroxide complexes predominate, while fluoride complexes may appear at low pH’s in solutions of elevated fluoride concentrations. However, uranous uranium solubilities are so low under reducing conditions that it is unlikely that uranous complexes play any role in uranium transport in hydrothermal systems.

Figure 2 illustrates the solubility of uranium as a function of oxygen fugacity and temperature at pH’s consistent with the coexistence of kaolinite and illite for a partial pressure of carbon dioxide of 0.1 atm and a 20% NaCl solution. Fluid conditions were chosen to show the limiting conditions under which carbonate and chloride complexes might predominate in solutions appropriate for the formation of hydrothermal uranium deposits, based on geochemical studies. The shaded area in the upper right represents the fluid conditions based on mineral assemblages shown in area 3 in Figure 3. Based on an analysis of the relative stability of all uranium complexes, carbonate and chloride complexes are the most likely to occur under natural conditions. The solubilities are superimposed on the relative stability of iron minerals (dashed lines), and the relative stability of the alteration minerals alunite (Alu), kaolinite (Kaol), illite (Ser) and adularia (Ksp) (dot-dashed lines), assuming a potassium concentration of 1000 ppm. The boundary between Mg-montmorillonite (Mg-Mont) and Mg-chlorite (Mg-Chl) is shown as a double dot-dashed line, to show the approximate stability limits of low iron chlorite, a common alteration mineral in some hydrothermal uranium deposits. The relative stability of chalcopyrite (ccpy) and bornite (bn) (fine dashed lines) is shown as proxies for the conditions under which base-metal sulphides would occur.

4. MECHANISMS OF DEPOSITION

Figure 3 shows the relative distribution of uranium complexes and oxides as a function of oxygen fugacity and pH under fluid conditions similar to Figure 1, with phosphate eliminated for simplicity. Also shown are the relative stabilities of iron minerals (dashed lines), and the relative stability of the alteration minerals alunite (Alu), kaolinite (Kaol), illite (Ser) and adularia (Ksp) (dot-dashed lines), assuming a potassium concentration of 1000 ppm. The boundary between Mg-montmorillonite (Mg-Mont) and Mg-chlorite (Mg-Chl) is shown as a double dot-dashed line, to show the approximate stability limits of low iron chlorite, a common alteration mineral in some hydrothermal uranium deposits. The relative stability of chalcopyrite (ccpy) and bornite (bn) (fine dashed lines) is shown as proxies for the conditions under which base-metal sulphides would occur.

Fig. 3: Oxygen fugacity-pH diagram at 200 °C showing the distribution of uranium oxides and iron minerals, distribution of alteration minerals, and solubility of uranium oxides assuming 10 ppm Fe, 100 ppm F, 1000 ppm sulphur, 1000 ppm K 6 wt % NaCl and CO₂ partial pressure of 10 atm. See text for explanation.
Four regions are delineated between two fine lines representing the 10 ppm U (left) and 0.1 ppm U (right) solubilities. The solubility decreases as a result of increase pH and/or reduction towards the lower right. Each area has been established from alteration and gangue mineral assemblages observed in various uranium deposits. For example, area 3 would be typical of an assemblage consisting of chlorite, illite, and haematite. Area 1 would be typical of an assemblage showing illite, bleaching (soluble iron) and/or siderite. However, the diagram also illustrates the unlikely co-precipitation of uranium oxide and metal sulphides unless the fluids were quite acid and reducing. However, the phase relations shown do allow for the deposition of uranium as a result of mixing of fluids, an oxidized uranium transporting fluid, and a reduced fluid.

The diagram illustrates that uranium deposition can indeed occur as a reduction of the transporting fluid. However, in area 3, increase in pH appears more effective, in which case the formation of haematite might be a consequence of the precipitation of uranium according to the reaction:

\[
3\text{UDC}_a + 2\text{H}^+ + 2\text{Fe}^{2+} \rightarrow \text{U}_3\text{O}_8(s) + 6\text{CO}_2(g) + \text{H}_2\text{O} + \text{Fe}_2\text{O}_3(s)
\]

This reaction would also be favored by decrease in pressure and the loss of CO\textsubscript{2}. However, Figure 2 shows that a decrease in temperature will not result in uranium deposition.

4. CONCLUSIONS

Theoretical geochemical considerations of the origin of hydrothermal uranium deposits are consistent with uranium being transported as a uranyl carbonate complex, and deposition occurring as a result of pH and/or temperature increase, reduction, or a combination of these processes, which are not independent of each other. At high temperatures, chloride, phosphate, or hydroxide complexes may also play a role in transport, without altering the mechanisms of deposition. Physical processes that can result in these changes include pressure release and resultant loss of carbon dioxide or other volatile components, reaction of the fluids with the wall rocks, or fluid mixing. Based on alteration and gangue mineral assemblages, it appears as if deposition occurs at near neutral pH’s under oxidizing conditions where haematite is the predominant iron phase.

5. ACKNOWLEDGEMENTS

The author wishes to acknowledge the editing of Irvine Annesley, whose comments have resulted in substantive improvements in this paper, and Michel Cuny and Colin Andrew; without their help this paper would not contain figures.

REFERENCES

Romberger, S.B., 1984, Transport and deposition of uranium in hydrothermal systems at temperatures up to 300 °C: Geologic implications; in Uranium Geochemistry, Mineralogy, Geology, Exploration, and Resources, B. De Vivo, et al. eds; Institute of Mining and Metallurgy (London); p. 12-17.
Romberger, S.B., 2006, Uranium: Metal Transport and Deposit Types: Short Course Notes; Roundup06, Vancouver, B.C. (Canada); 36p.
A specific REE signature of uranium oxides for each type of uranium deposit.

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ABSTRACT: REE analyses were performed by ion microprobe on natural uranium oxides from various types of uranium deposits throughout the world: (i) two unconformity-type deposits from Athabasca Basin (Saskatchewan, Canada): the Sue and the McArthur River deposits, (ii) two vein-type deposits: the perigranitic Pen Ar Ran (Vendée, France) and the Margnac (Limousin, France) deposits, (iii) a volcanic caldera related deposit: Streltsovka, (Tranbaikalia, Russia), (iv) an intrusive type deposit: the Rössing deposit (Namibia). These analyses were conducted to try to characterize each type of deposit from their REE signatures, and to test whether different generations of uranium oxides in the same deposit may be distinguished with respect to their REE composition. In situ analyses of the uranium oxides were performed by Secondary Ion Mass Spectrometry (SIMS) on a Cameca IMS-3f ion microprobe. The Rare Earth Elements are particularly interesting in the case of the uranium oxides because U\(^{4+}\) in eight-fold coordination has a ionic radius close to that of the middle REEs and thus should be much less mobile than lead, which has a much larger radius, to characterize different uranium oxide generations.

KEYWORDS: ion microprobe, uranium oxide, Rare Earth Elements, REE patterns

1 INTRODUCTION

Natural uranium oxides (UO\(_{2+x}\)) can incorporate variable quantities of other elements during their crystallization. The processes of incorporation depend on (i) the element ionic radius, (ii) the physical-chemical characteristics of the mineralizing fluid (temperature, nature of ligands), (iii) the composition of the rocks with which the mineralizing fluid has been equilibrated and (iv) post-depositional reequilibration in relation with later fluid circulations. Rare Earth Elements (REE) represent a particularly interesting set of elements, because their ionic radii are close to that of U\(^{4+}\) in eight-fold coordination and most of them are not sensitive to changes of redox conditions. Hence, these elements may better preserve their primary distribution within uranium oxides. A literature survey of the scarce data about REE distribution in uranium oxides shows that each type of uranium deposit may be characterized by a specific signature (Fryer & Taylor, 1987; Pagel et al., 1987; Hidaka et al., 1992; Hidaka & Lafaye, 2000), although strong variations seem to occur among a specific type of uranium deposits (Fayek & Kyser, 1997).

The purpose of this study was to determine the typical REE signature of uranium oxides from genetically different uranium deposits.

2 ANALYTICAL METHODOLOGY

U-oxides were first examined by optical microscopy, electron microscopy in Back Scattered Electron mode (BSEM) and electron microprobe to select the areas presenting the highest degree of homogeneity. Most ore bearing samples are highly heterogeneous and frequently comprise several generations of U-oxides. Therefore, in situ analyses by SIMS represents one of the most appropriate techniques for the determination of trace element and isotopic compositions of U-oxides with a spatial resolution of 20-40µm.

The determination of REE abundance in natural uranium oxides by SIMS was only recently performed in Japan using a SHRIMP (Takahashi et al., 2002; Horie et al., 2004). The
instrumental conditions employed for REE analyses in uranium oxides using the CAMECA IMS 3f are similar to those described in Fahey et al. (1987) and Hinton (1990). The standard sample was an uraninite from Mistamisk (Kish & Cuney, 1982), the REE composition of which was determined independently by ICP-MS (R. Pik, 2006, CRPG, Nancy, unpublished). REE analyses were performed on the same locations as the U-Pb analyses to make sure that each U oxide generation was distinctly analyzed for their REE contents.

3 REE SIGNATURE OF URANIUM OXIDES FROM UNCONFORMITY-TYPE URANIUM DEPOSITS

REE analyses were conducted on U-oxides from the Sue and McArthur River deposits, located in the western and eastern part of the Athabasca Basin in Canada, respectively. The McArthur River deposit is located within the Wollaston belt of metasediments, which were metamorphosed during the Trans-Hudson Orogeny (1850-1750 Ma). The Sue deposit is located in a brecciated zone, which is composed of rounded argilized sandstone fragments or ‘balls’, wrapped in a clay matrix. The ball zones are considered to be coeval with the formation of structurally controlled uranium unconformity related mineralization (Lorilleux, et al., 2003).

In situ U-Pb dating revealed three ages for the McArthur River deposit, at ca. 1460, 1335 and 1275 Ma, while at Sue the main and oldest stage occurred at ca. 1186 Ma, while altered uraninites yielded an isotopic age of 257 Ma. All chondrite-normalized REE patterns are characterized by bell-shaped curves centered on Tb-Dy. These data concur with literature data for other unconformity-type deposits both in Canada and in Australia. Such REE patterns totally differ from those of uranium oxides from other types of uranium deposits (eg. intrusive-type, vein-type), suggesting that bell-shaped REE patterns may be considered to be an “unconformity-type” signature.

There are however notable differences with respect to: (i) the absolute abundance of REE which can vary by more than one order of magnitude from one phase to another. For instance in the McArthur River sample the cores of the U oxides (dated at 1460 Ma) are significantly poorer in REEs than their rims (dated at 1275 Ma), but the overall shape of the REE pattern is similar. (ii) The variable distribution of light REE (LREE). LREEs are more abundant in the youngest generation of uranium oxides from the Sue deposit, than in the oldest generation. However, since the young uraninites were altered, and given that LREEs are more mobile than HREEs in uraninite, these variations in LREE composition are not syngenetic in origin, but mainly indicate the alteration of the uranium oxides.

4 REE SIGNATURE OF URANIUM OXIDES FROM VOLCANIC-TYPE URANIUM DEPOSIT

The Streltsovka deposit is located in a caldera of 20km in diameter, within the Variscan Mongol-Okhotsky fold belt (Tranbaikalia, Russia), filled by Cretaceous volcano-sediments. Uranium minerals are mainly pitchblende, whose isotopic deposition age was determined at 133 ± 4 Ma (Chernyshev & Golubev, 1996).

The REE patterns of uranium oxides show (i) small abundance variations, what reflects a rather weak uraninite alteration, and (ii) the enrichment in Sm, Eu and Gd, what can be regarded as characteristic of the volcanic-type deposits.

5 REE SIGNATURE OF URANIUM OXIDES FROM VEIN TYPE URANIUM DEPOSIT

The Margnac deposit, Limousin, France, is a vein type deposit hosted within the two mica peraluminous leucogranites of Saint Sylvestre, French Massif Central. The granitic complex of Saint Sylvestre underwent two hydrothermal alteration events, one at 305 Ma (episyenite formation) and one at 275 Ma (uranium ore deposition in the episyenites). The REE patterns of uranium oxides from vein-type deposits illustrated by the Margnac deposit are typically characterized by a decreasing abundance from LREE to HREE, with a weakly negative Ce anomaly. These patterns are similar to the REE patterns of the host leucogranites, but are devoid of the Eu anomaly. Similar REE patterns have been obtained from other deposits in the same granite.

The Pen Ar Ran deposit, Vendée, France is located along an E-W fault, to the north of the
Guérande peraluminous leucogranites, within the so-called “Porphyroïdes” metamorphic unit, close to the contact with graphitic shales and quartzites. The Pen Ar Ran U ore consists of massive uranium oxides deposited on a small quartz comb in fractures at 320 ± 9 Ma ago (Holliger, 1992).

The REE patterns of uranium oxides from Pen Ar Ran are homogeneous and characterized by low REE contents and weakly developed fractionation, except for marked enrichment in Sm, Eu and Gd. Compared to the available REE patterns of uraninites from different types of deposits, the Pen Ar Ran REE patterns are similar to those of pitchblende from the volcanite-related Streltsovskaya uranium deposit (Russia).

The similarities of REE patterns between these two deposits indicate that the uranium from the Pen Ar Ran deposit has not been leached from the nearby two mica granites but from the “Porphyroids” which should have a volcanic origin.

6 REE SIGNATURE OF URANIUM OXIDES FROM INTRUSIVE-TYPE URANIUM DEPOSIT

The Rössing granite-hosted uranium deposit is located in the Central Zone of the Pan-African Damara Orogen (Neoproterozoic – early Palaeozoic) to the south-west of the Rössing Dome, in Namibia. The REE patterns from the Rössing alaskite deposits are characterized by a weak fractionation between the LREE and HREE, with only a small decrease in the HREE. The negative Eu anomaly reflects the preferential trapping of europium from the melt in the plagioclase during magma fractionation. The shape of the REE patterns is characteristic of the intrusive-type deposit: it is typical of uraninite from magmatic high temperature origin.

7 CONCLUSIONS

REE patterns of uranium oxides from different uranium deposit types appear to have a specific signature.

Unconformity-related deposits have a uniform bell-shaped REE pattern centered on Tb, but with variable total REE abundance depending on the uranium oxide generation. Alteration of the U-oxides leads to a strong increase of the lightest REE, but preserves the overall REE signature, which can be used to characterize primary ore deposition.

Uranium oxides from vein-type deposit hosted within leucogranites are characterized by decreasing abundance from LREE to HREE anomalies. However, the Pen Ar Ran vein-type deposit yield a U-oxide REE signature that reflects the nature of the host rock. Because of the similarity of the REE signature of the Pen Ar Ran U-oxide with those from U deposits associated with volcanics, the previously debated origin of the host rock is elucidated here as being of volcanic origin.

Intrusive-related deposits REE patterns seem to be characterized by a weak fractionation associated with a negative Eu anomaly.

ACKNOWLEDGEMENTS

We thank M. Champenois and D. Mangin for the help with electron microprobe analyses and Slava Golubev from IGEM for the REE analysis of the Mistamisk uraninite.

REFERENCES


Cosmochimica Acta, 68, 115-125.


ABSTRACT: The average uranium content in the geological formations of the Ladoga region increases through time. Specific uranium enrichment of the crust was produced by the late Kalevian (1.85-1.8 Ga) and early Riphean (1.65-1.5 Ga) granite intrusions. Most of uranium occurrences are related to the Svecofennian orogeny and to a lower-middle Riphean event. Erosion of uranium-bearing formations, redistribution and accumulation of uranium produce large low-grade deposits during the Caledonian and Hercynian orogeny.

KEYWORDS: uranium, geochemistry, age, Ladoga region

1 INTRODUCTION

The periphery of the Baltic Shield may be considered as a potential area for high-grade uranium deposits related to Mesoproterozoic unconformities, as in the Athabasca Basin (Canada) and Pine-Creek Geosyncline (Australia).

The Ladoga region is located at the border of the Archaean Karelian and the Palaeoproterozoic Ladoga-Bothnian (Svecofennian) domains (Fig. 1). The marginal area between these domains is called Raahe-Ladoga zone. Supercrustal basement of the Ladoga region is overlapped by the vast Mesoproterozoic (Riphean) Pasha-Ladoga sedimentary basin. To the south, the region is covered with Vendian-Palaeozoic sediments of the Eastern-European platform.

2 METHOD

The review given below was compiled from a geochemical data base (over 12000 analyses) collected from published and archive sources. If it is not mentioned specially, U/Pb age determinations of U mineralization were obtained by authors with IMS-3F Cameca at CRPG (Nancy, France). Uraninite from Katanga (Zambia) dated 540 Ma was used as a standard. Analytical protocol was according to Holliger (Holliger, 1988).

3 U CONTENT IN BEDROCKS

There is a gradual increase of the average U content through time in geological formations of the southern margin of the Baltic Shield (Mikhailov 1999) (Fig. 2).

The Archaean is poor in U; regional U Clarke for Mesoarchaean in the area is 0.5 ppm, Neoarchaean – 1.4 ppm. The highest U contents in Neoarchaean are related to the late Lopian persilicic metavolcanites of the Jalonvaara depression (2.95-2.85 Ga) and Jalonvaara granite intrusion (2.6 Ga, Ivaschenko, 1988) to the north of the area, in the Archaean Karelian domain. U content in these rocks is up to 4 ppm.

U abundance in the Palaeoproterozoic formations is 2.5 ppm, but varies much for different epoch. Sumian (2.5-2.4 Ga) and Sariolian (2.4-2.3 Ga) andesite-basalts and sediments of the Karelian domain are poor in U (1.1 ppm).

The average U content in the Jatulian (2.3-2.1 Ga) formation is 1.5 ppm, with enrichment of the basal terrigene horizon up to 6 ppm U and up to 160 ppm Th.

The average U content in the Ludicovian (2.1-1.92 Ga) is 2 ppm, but varies much for the different units. Low U contents in mafic
metavolcanites (less 1 ppm) contrast with high values in carbon-bearing carbonate rocks (up to 8 ppm). Ludicovian formations of the Northern Ladoga area host numerous U-P occurrences.

In Kalevian (1.92-1.8 Ga) the average U content reaches 4 ppm. Graphite-bearing lithologies have 4.8 ppm U in average. Late-orogenic Svecofennian granites (1.85-1.8 Ga) are rich in U: 7 ppm in average. There are numerous U occurrences in migmatites and pegmatoids in granite-gneiss domes of the Northern Ladoga area, related to the Kalevian granitization.

Vepsian (1.8-1.65 Ga) sediments occur to the east from the Ladoga area in the Onega depression of the Karelian domain. Average U content in these rocks is less than 3 ppm. A few uranium occurrences are hosted by Vepsian formations in the vicinity of the Onega Lake. There are no contemporary sedimentary forma-

tions in the Ladoga Lake area, only a few post-orogenic alkaline intrusive massifs to the west from the lake. Average U content in these intrusions is 4.5 ppm.

Riphean (1.65-0.65 Ga) starts with intrusion of series of rapakivi type multiphase massifs. In the Ladoga area they correspond to the Wiborg, Salmi, Ulyalegi and Svir plutons. Subordinate early mafic phases have low U contents (< 1 ppm), but U contents increases with fractionation, up to 7.6 ppm in the latest leucocratic phases. There are several complex ore deposits with U mineralization in the metamorphic rocks surrounding the Salmi pluton. Their origin may be related to the fluids derived from this pluton.

U content in the Mesoproterozoic (Lower-Middle Riphean) formations of the Pasha-Ladoga basin varies from 1 ppm for mafic volcanites, to 5 ppm for Qtz-Fsp sandstones, with an average of 3 ppm. The basal sedimentary layer of the NE slope of the basin (Salmi depression) hosts the Karku unconformity-type

Figure 1. Ladoga region

Figure 2. Evolution of uranium in the Ladoga area.
Vendian (0.65-0.56 Ga) corresponds to the beginning of the sedimentation of the Eastern-European platform. At present they occur in the southern part of the area. Average U content in Vendian sediments is 4 ppm with up to 8.4 ppm in the basal organic-bearing layers.

Average U content in Palaeozoic Formations reaches 8.6 ppm, but it is solely because of the anomalous Lower Ordovician sediments. In Cambrian pelites and psammites average U content is only of 2.2 ppm, in upper Devonian limestones and sandstones – only of 1.2 ppm, but in Lower Ordovician Dictyonema shale it reaches 130 ppm. Overlying Lower Ordovician glauconitic sandstone and clay have an average U content of about 16 ppm, Middle Ordovician limestone and marl – 3.1 ppm. Silurian formations are absent in the Ladoga area.

4 URANIUM OCCURRENCES

From their location, numerous uranium occurrences of the Ladoga area can be subdivided into three groups: occurrences in the basement, in the Riphean cover, in the Vendian-Palaeozoic platform cover.

4.1 Uranium occurrences in the supracrustal basement formations.

They are discovered in the Northern Ladoga area only, along the Raahe-Ladoga zone and belong to several genetic types.

4.1.1 Th-U mineralization in Jatulian.

The earliest U mineralization occurs in a pericraton depression at the margin between the Karelian domain and the Raahe-Ladoga zone in the Maloye Janisjarvi area. There are numerous anomalies in Jatulian quartz conglomerate interlayers with U content up to 120 ppm and up to 7000 ppm of Th. Since the mineralization is considered as syn-sedimentary, its age is presumed to be about 2.3-2.14 Ga.

4.1.2 U-Th-REE occurrences in migmatites and pegmatites of granite-gneiss domes.

These occurrences are localized in AR-PR1 granite-gneiss domes. U mineralization was generated during late Svecofennian migmatisation of the domes. U-Pb age of 1818±27 Ma was obtained for the uraninite concentrations related to the biotite-enriched lenses in the pegmatoids (Sjuskinsaari occurrence, MSWD 3.9). Pitchblende from the blastomylonite zone was dated at 1789±31 Ma (Puttumyaki deposit). Traces of Palaeozoic U redeposition have been established for the same type occurrences (Korennoye deposit) (Shurilov, 2006).

4.1.3 U-P occurrences in Ludicovian carbonate rocks.

U-P occurrences are located mainly along the Ruskeala anticline – an elongated uplift of Palaeoproterozoic basement, parallel to the NW-striking Ruskeala fault zone. The anticline is formed with Ludicovian carbonate rocks (dolomite, carbonate- amphibole schist and marbles) and metavolcanic interlayers. U mineralization mainly consists of finely disseminated pitchblende grains, making their dating difficult. The unique successful previous U/Pb dating gave an age of 1.85 Ga. For the same type of deposits in Finland a U-Pb age of 1876±2 Ma was obtained (Vaasjoki, 1980). New U-Pb dating of pitchblende from the ore veinlet yielded age of 326±21 Ma (Mramornaya Gora deposit, MSWD=8,4). It is a manifestation of late U deposition.

4.1.4 Uranium-polymetallic occurrences in the dome surrounding skarns.

There are few U-polymetallic occurrences on the south-eastern continuation of the Ruskeala fault zone, related to the Ludicovian skarns of granite-gneiss dome frame. Primary U concentrations are syn-sedimentary, but ore concentrations result from the late Svecofennian migmatisation of the domes. Due to the relation of the mineralization with this process, its age is presumed to be between 1.85 and 1.8 Ga.

4.1.5 Complex ore deposits with uranium mineralization around the Salmi rapakivi massif.

Numerous complex ore deposits are located on the contact of the Salmi granite pluton, mainly in the metamorphic rocks of the frame, less in the granites. Sn is the principal component of the ore, associated with Cu, Zn, Fe, Be and overprinted U mineralization. According to the Sm-Nd analyses of the ore hosting skarn and greisen, ore-forming process occurred between 1.55 and 1.49 Ga (Larin, 1991).

4.1.6 Uranium-polymetallic veins.

There are few vein-type U occurrences in the Northern Ladoga area. Ore deposits are localized in breccias zones of supracrustals. U
mineralization is associated with a complex paragenesis (Cu, Bi, Ni, Au etc). The pitchblende mineralization of Varalakhti has Riphean age, between 1.54 and 1.46 Ga (Shurilov, 2006).

4.2 Uranium occurrences in Riphean.
Two types of U occurrences related to the Mesoproterozoic (Lower Riphean) unconformity were discovered in the Salmi depression.

4.2.1 U mineralization related to the Riphean sandstone/basement unconformity.
The most significant one is the Karku U deposit. The ore is hosted within basal Riphean Qtz-Fsp sandstone and – in minor part – within weathered graphite-bearing Palaeoproterozoic metapelites. The deposit results from multi-phase hydrothermal processes. Earliest highest-grade pitchblende mineralization gives a Lower Riphean isotopic U-Pb age of 1405±76 Ma (Shurilov, 2006).

4.2.2 U mineralization in fractured Riphean basalts.
In the Kotalakhti occurrence late pitchblende mineralization in fractures within the Riphean basalts occurred. Its age is 412±73 Ma (Shurilov, 2006).

4.3 Uranium occurrences in Vendian-Palaeozoic platform cover.
4.3.1 U occurrences in Ordovician shales.
The Lower Ordovician Pakerortsky horizon of the Dictyonema shale is continuous from the southern Ladoga area to the Estonia. U abundance is syn-sedimentary and caused by organogenous concentrations with ages of 0.47-45 Ga. Occurrences in this horizon have huge resources of low-grade U mineralization (usually less than 300 ppm).

4.3.2 U occurrences in Vendian sediments.
There are a few deposits and numerous ore showings in the basal horizon of the Vendian sediments. U is related to the Hercynian event. Age of the mineralization is 0.38-0.17 Ga (Mikhailov 1999).

5 CONCLUSIONS
U distribution analysis in the Ladoga area geologic formations demonstrates a gradual increase of their U content though time. Specific U-rich lithologies include the latter phases of late-Svecofennian and early Riphean granites, and organic-bearing sediments of Palaeoproterozoic and Palaeozoic. U accumulation up to ore deposit level took place during four tectonic events: Svecofennian, Riphean, Caledonian and Hercynian. Resources of U deposit tend to increasing with time, but highest-grade ore grade is related to the Riphean (Fig. 2).
The multiple mineralization types demonstrate a good potential of the Ladoga area for the occurrence of U-deposits at different stratigraphic levels.

ACKNOWLEDGEMENTS
This research is financially supported by AREVA NC, France. Personal thanks to Boris Shustov and Vladimir Kushnerenko (Nevsk-geologia, Russia) and Vitaly Mikhailov (VSEGEI, Russia) for discussion.

REFERENCES
ABSTRACT: Intense and purposeful predictive metallogenic and prospecting studies conducted in the Russian part of the Baltic Shield and in the territory abroad lead to discoveries of uranium and complex uranium deposits of different types: unconformity, “sandstone” (bitumen-uranium), quartz-pebble conglomerates, veins, etc., as well as numerous ore-showings, and anomalies. Among numerous ore types of uranium and complex uranium mineralization the most promising are uranium-precious-metals-vanadium ores of fold-fault zones (Srednyaya Padma) formed during the Svecofennian tectonomagmatic activation (TMA) and uranium unconformity-type ores in the vicinity of the Pre-Riphean structural-stratigraphic unconformity (SSU) in the Pasha-Ladoga Graben (Karku) and pre-Vendian SSU (Slavyanka, Ryabinovsky). The role of pre-Early Proterozoic SSU to which numerous ore-showings are confined (Palozero-1, Pachtavuoma and others), are at present underestimated.

KEYWORDS: Uranium, Types of mineralization, Promising areas, SSU

The territory of the studies covers the Kola, Belomorian, Karelian, Ladoga megablocks and suture fold-thrust zones, which divide them: East Karelian and Raakhe-Ladoga (Fig.1).

Intense and purposeful predictive metallogenic and prospecting studies conducted in the Russian part of the Baltic Shield by geologists of various organizations and in the territory abroad by specialists of Finnish, Norwegian, and Swedish geological surveys lead to discoveries of uranium and complex uranium deposits of different ore types (Afanasieva, 2003; Kushnerenko, 2004; Kharlamov, 2000; Mikhailov, 2000). Within the north-west of Russia there are 13 uranium deposits, more than 120 ore showings; their resource potential is more then 2 million tonnes (Kushnerenko, 2004)

Uranium deposits of the Baltic Shield occur in different structural-petrological settings. The most prospective are: uranium-precious-metal (gold-platinum-palladium)-vanadium ores of fold-fault zones (Srednyaya Padma) formed during the Svecofennian tectonomagmatic activation (TMA), uranium unconformity-type ores in the vicinity of the pre-Riphean structural-stratigraphic unconformity (SSU) in the Pasha-Ladoga Graben (Karku) and pre-Vendian SSU (Slavyanka, Ryabinovsky). The role of pre-Early Proterozoic SSU to which numerous ore-showings are confined (Palozero-1, Pachtavuoma and others), are at present underestimated.

The complex deposits are controlled by fold-fault zones, which are very typical for the Onega depression.

Eleven zones were recognized, with five deposits and nine ore-showings, but only four zones have been studied.

The structural map of the Onega depression displays a combination of open brachysynforms and steeply dipping fold-fault zones (FFZ). The FFZ zones comprise strongly elongated anticlinal folds striking north-west, which are complicated by folding of higher orders and longitudinal faults.

The cores of the anticlines are filled with dolomite overlain by siltstone and schungite-bearing shale. Ore-bodies occur along the longitudinal faults (Kosmozero FFD zone), or occur along faults perpendicular to the longitudinal one (Tambitsa fold-fault zone with the Srednyaya Padma deposit, which is the largest one).
As a rule, ore bodies occur in carbon-bearing Ludicovian (2.2 to 1.85 Ma) rocks and are located at the contact between Jatulian (2.4 to 2.2 Ma) dolomite and Ludicovian black shale. Ore zones have been traced from 1 up to 2.7 km; their width varies from 100 to 150 m.

The ore bodies are surrounded by a halo of hydrothermal metasomatic alterations. The external part consists of albitite and ribeckite-phlogopite-albite metasomatites. The intermediate part is composed of carbonate-roscoelite-Cr-phengite (carbonate-micaceous) metasomatites. The inner part consists of Cr-phengite-phlogopite-roscoelite metasomatites (micaceous) and a quartz-carbonate-sulphide-selenide assemblage.

Vanadium is the main metal in the deposit. The vanadium mineralization is represented by roscoelite and V-bearing phlogopite. The average grade is 2.83 wt% V$_2$O$_5$ (in some sections it runs up to 22 wt% V$_2$O$_5$). Mineralization occurs as fine disseminations, disseminated veinlets, disseminated-nest and sometimes as massive ores.

The uranium mineralization mainly occurs within the haloes of the vanadium ores and is represented by pitchblende, uraninite, coffinite, uranium titanates and secondary minerals (uranyle silicates and vanadates). The average uranium grade is 0.133 wt%, up to 1-5 wt% in some sections, with a maximum of 35 wt%.

The occurrence of gold, silver, palladium, and platinum is a peculiarity of the ores. They occur in sulphides, selenides, sulphoselenides of lead, bismuth and copper.

The age of pitchblende is 1730-1770 Ma (U/Pb), (Melnicov, 1993) correspond to the time of primary ore formation. Secondary enrichment of the ores took place in the time interval from 900 ±100 Ma to 270±20 Ma, and their supergene alteration occurred between 150 and 100 Ma.

Estimated resources are 600,000 t V$_2$O$_5$, 169,000 t U and several tens of tonnes Au.

Measured reserves of the Srednyaya Padma deposit are 108,000 t V and 3,000 t U.

Zones of structural-stratigraphic unconformity (SSU) are widespread in the Baltic Shield.

Uranium mineralization with the old uranium-bearing SSU zones are of different grade: high-grade mineralization occur in the pre-Riphean SSU, low-grade ore but with significant reserves in the pre-Vendian SSU zones, low-grade ore in pre-Jatulian SSU zones.

The Preriphean SSU has the greatest potential because the Pasha-Ladoga through hosts the Karku unconformity-type uranium deposit. The SSU results from the deposition of Riphean sediments on folded, metamorphosed and faulted Archaean and Proterozoic rocks. The Riphean sediments and basement rocks are intensively kaolinized, chloritized, and carbonitized. Abundant sulphide and bitumen are recorded. Five ore bodies with lenticular-bedded shape were discovered in the Karku area. They extend over hundreds of m$^2$ and their thickness ranges from 1-2 to 10-20 m. The uranium mineralization - pitchblende and coffinite - is confined to the cement of the sandstone. The uranium grade ranges from 0.03 to 0.2-0.5 wt%, locally up to 19 wt%. Anomalous Zn, Ag, and Pb contents are recorded in the rocks. The uranium mineralization was also found in the basement rocks. The age of the mineralization (Pb/Pb) is 1500-1400, 840-720, 500, 350, 180 Ma (maximum frequency) (Novikov, 2001).

Riphean troughs also occur in the Belomorian block with the Tersky Bereg potential uranium-ore district. In this region Riphean red sediments lies on a heterogeneous early Proterozoic folded and metamorphosed basement. Riphean sediment deposition starts with a conglomerate-gritstone member, overlaid by sandstone and siltstone.

Silicification, fluoritization and chloritization are recorded in the Riphean rocks. The basement is composed of alternating biotite, biotite-cordierite, quartz-biotite-cordierite, quartz-feldspathic gneiss, amphibolite, quartz-feldspar-amphibole, carbonate-amphibole gneisses. Some graphitic matter occurs in the rocks. Migmation is developed in the basement rocks. There are a lot of pegmatite bodies. Carbonate-amphibole and graphite-bearing rocks are characterized by higher uranium contents.

Uranium ore showings and mineralization are located in the Tersky region. The Yulitsa showings are located in albitite and quartz-albite metasomatites. The albitite and quartz-albite metasomatites are deformed and brecciated; the last alteration process corresponds to chloritization, sericitization, and carbonitization. The Kita showing occur in pegmatite and quartz-feldspathic metasomatite, which underwent low-temperature alterations (chloritization, sericitization, albitization). The
estimated resources (Category P₃) are about 63,000 t U.

The Tersky area is characterized by the intensive manifestation of all ore-controlling factors. So there is a good potential for finding uranium deposits in the basement complex.

The locations of the Pre-Vendian unconformity type deposits are controlled by the junction between the Russian Platform and the Baltic Shield. Sandstones and gritstones of the basal Vendian horizon overly early Proterozoic schists and gneisses intruded by numerous bodies of plagioclase-microcline leucocratic granites. A 20-30m thick regolith is developed on the basement. Carbonaceous sandy-clayey sediments represent the host-rocks of the deposits. Anomalous uranium concentrations were also recorded in sandstones and gritstones of the basal horizon and in the regolith. An increase of uranium concentration is recorded along tectonic structures of the basement. Generally higher uranium concentrations zones in the basal layers of the sediments follow of the extension of the radiogeochemical anomalies in the basement. Uranium occurs as pitchblende and sooty uranium oxides and locally coffinite. Uranium grade ranges from 0.03 to 0.1 wt % over 0.5 to 3.5m. Main associated elements are Pb, Mo, Ag. Slavyanka, Ryabinovka, Ratnistky are the major deposits of this type. Their main deposition age is between 350 and 420 Ma, the most common age being 380 Ma. Younger ages (300 to 5 Ma) indicate uranium redistribution.

Pre-Jatulian unconformity is very widespread within the Baltic Shield (Jangozero, Onega). The favorable conditions for the possible occurrence of uranium deposits in the Pre-Jatulian unconformity zones are the following: (1) graphite-bearing rocks varieties in the basement; (2) late Archaean granitoids with high radioactivity which might have been a source for uranium; (3) thick quartz-pebble sequences in the early Proterozoic sediments which may have represented a reservoir for uranium accumulation; (4) high thorium contents in the conglomerate sequences suggesting that uranium was leached out during the mineralization event; (5) permeable fault-fold zones representing the channels for mineralizing fluid migration; (6) contacts between rocks with different rheological properties, such as the Jatulian conglomerate-sandstone sequence and the Ludicovian black-shale sequence which may have acted as barriers for U deposition.

The settings and the variety of structures described do not exhaust the uranium ore potential of the Baltic Shields as to the likelihood of discovering other workable and payable uranium deposits there. Further probing is needed to search for commercial mineralization of the types known for this region: ultra-metamorphic, volcanic, quartz-pebble-conglomerate, metasomatic, phosphorous, sandstone, intrusive and black shale ones. The most prospective of them are metasomatic and black shale types.

Within the Baltic Shield there are a lot of uranium ore showings associated with hydrothermal-metasomatic altered rocks. The Litsa uranium-ore area is a typical example of this type of deposits.

The Litsevskoe ore showing is the most studied. It is located in biotite, biotite-amphibole, amphibole and cordierite-bearing gneisses. Plagiogranite, microcline and porphyrophytic plagioclase-microcline granite of the Litsa-Araguba complex are widespread in the area of the ore showing. Chloritization is the most widespread hydrothermal-metasomatic process there. Besides, in the granite and enclosing gneisses illitization, kaolonitization and montmorillonization also may occur. In the Litsevskoe ore showing, two types of uranium mineralization occur: disseminated veinlet and veinlet types.

Disseminated veinlet ores are confined to areas of closely spaced cracks with up to 1500-2000 ppm U. The mineralization mainly corresponds to disseminated uraninite (?) inclusions into chloritized biotite, with minor amounts of pitchblende I. The veinlet ores are located in small zones with intensive fracturing with U contents exceeding 3000 ppm U. The mineralization corresponds to pitchblende and two coffinite generations. Massive pitchblende fills the central part of the veinlet.

Coffinite-I occurs in the peripheral part of the coffinite-pitchblende vein. At the contact between coffinite and the host rock, chloritized biotite is hosting early uraninite. Coffinite-I aggregates include fine cryptogenic aggregates of native lead. Coffinite-II is the youngest primary uranium minerals because it crosscuts coffinite-I.

In addition to pitchblende and coffinite, abundant secondary uranium minerals are recorded: kasolite, uranophane, sklodowskite, urhyte, schoepite, etc. In the rock there are...
spot-like aggregates of sulphide, chalcopyrite, pyrite, galena, sphalerite as well as minerals of the oxidation zone (chalcosine, bornite, native copper).

The age of the studied ore varies from 1750 to 220 Ma (Savitskii, 1995). According to our data, the uranium mineralization age (U/Pb) is 420±20 Ma (Fig. 2) (Afanasieva, 2006).

The Kuusamo-Pana-Kuolajarvi ore field is very prospective for uranium and complex with uranium mineralization. Within this area there are uranium, gold-uranium ore-showings associated with quartz-feldspathic metasomatites and pegmatites, with albites and albite-carbonate metasomatites (Ozernoe, Lagernoe et al.), with biotite, quartz-biotite metasomatites (Hejkinjarvi, et al.).

With the obvious uranium mineral material deficiency, it seems timely to have a new look at the Lower Ordovician Dyctionemic shale. The Dyctionemic shale represents an environment for V-Mo-U mineralization in carbonaceous shale and clay. Maximum uranium content ranges from 0.019 wt % U with a thickness of 1.2 m to 0.069 wt % U with a thickness of 0.2 m. Beside uranium, the dyctionemic shale contains 0.02 wt % Mo, 0.091 wt % V, 0.016 wt % Ni.

CONCLUSIONS

1. The zones of structural-stratigraphic unconformities and fold-fault zones have the highest potential for with the occurrence of uranium deposits.
2. The Pasha-Ladoga graben (with pre-Riphean unconformity type deposits), the Onega trough (fold-fault zones type deposits) show considerable prospectivity for the discovery of uranium deposits.
3. Regional work should be continued in the Tersky Bereg structure because it is possible to expect uranium deposits in early Proterozoic basement rocks near the contact with Riphean rocks (Australian unconformity related type).
4. It is very important to continue to study the uranium potential of pre-Jatulian unconformities, which are widespread within the Baltic Shield.
5. Areas, hosting uranium deposits in the Archaean-early Proterozoic basement associated with low-temperature hydrothermal alterations also have a great potential (Litsa, Kuusamo-Pana-Kuolajarvi and other areas).
6. Kuusamo-Pana-Kuolajarvi structure is a promising area for uranium and complex (Co-Cu-U) vein-stratiform deposits (Olimpic-Dam type).
7. Lower Ordovician Dyctionemic shale is very potential of uranium, vanadium and molybdenum.

REFERENCES:


Fig. 1. Karelian-Kola ore province

1-2-Riphean: 1-sedimentary, 2-volcanogenic-sedimentary rocks
3-Svecofennian carbonaceous shale filling Raakhe-Ladoja zone of the Ladoga megablock
4-Early Proterozoic depression
5-Late Lopian greenstone structures
6-Karelian megablock
7-Balomorian megablock
8-Kola megablock
9-Vendian cover
10-ore areas
11-surfaces of structural-stratigraphic unconformity: Pre-Vendian (f), Pre-Riphean (b), Pre-Jatulian (c), 12-main types of deposits: black shale (a), Pre-Vendian unconformity (b), Pre-Riphean unconformity (c), Pre-Jatulian unconformity (d), gold in Svecofennian carbonaceous shale (e), in fold-fault dislocation (FFD) zones (f), in quartz-feldspathic metasomatites and pegmatites (g), in chlorite-hydrromica metasomatites (h), in subalkaline and carbonatite intrusive (i), schungites (j), sulfur-pyrite (k), copper-pyrite (l), gold deposits in Late Archean greenstone structures (m), diamond (n)
U-Pb ages of zircon, monazite, and zircon tips in Hudsonian granites at the McArthur River uranium deposit: a record of U mineralizing fluids

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ABSTRACT: U-Pb results are presented here from leucogranite and granitic pegmatite samples near the McArthur River uranium deposit. These provide constraints on the regional stratigraphic correlation and thermotectonic evolution of the sub-Athabasca basement in the McArthur River area. New zircon growth in the form of uraniferous tips probably yields the initial age of U mineralizing fluids in the vicinity of the McArthur River uranium deposit at 1680-1550 Ma.

KEYWORDS: U-Pb geochronology, zircon tips, McArthur River, U mineralizing fluids

1 INTRODUCTION

The McArthur River high-grade uranium deposit is situated in the southeastern part of the Athabasca Basin. The sub-Athabasca basement complex comprises highly deformed Wollaston Group metasediments that are intruded by Hudsonian granitic pegmatites and leucogranites. Previous work (Annesley & Madore 1999, Annesley et al. 1992, 1997, 1999, 2000, 2005) to the NE and SW has documented the presence of both Archaean and Palaeoproterozoic granitoids and orthogneisses, as well as several generations of Hudsonian granitic pegmatites. New, high-quality U-Pb results from fresh basement drill core samples immediately east of the uranium deposit (ca. 200 m) are presented here for regional stratigraphic correlation and thermotectonic evolution of the sub-Athabasca basement in the McArthur River area. The results also provide constraints on the initial age of U mineralizing fluids in the vicinity of the McArthur River uranium deposit, which has yielded an U-Pb upper intercept age of 1598 ± 25 Ma for uraninite (Fayek et al. 2002).

2 GEOLOGICAL SETTING AND MCARTHUR RIVER GEOLOGY

The McArthur River deposit lies between 500 to 640 meters depth within a basement-rooted, southeast-dipping reverse fault structure (i.e. reactivated Hudsonian shear zone) with a maximal vertical displacement of 80 meters.

3 LEUCOGRANITE AND GRANITIC PEGMATITE

One leucogranite (sampled at 628.4-629.0 m) and one granitic pegmatite (sampled at 636.5-636.9m) from drill hole MAC-257 were dated by IDTIMS (for isotope dilution thermal ionization mass spectrometry) methods at the Jack Satterley Geochrology Laboratory. Both samples yielded datable quantities of both high-quality zircon and monazite. Individual grains clad with zircon tips as well as individual zircon tips were analyzed. Additional U-Pb-Th zircon data were obtained by microprobe analyses of individual grains with zircon tips at the Electron Microprobe Laboratory at the University of Saskatchewan.

4 ANALYTICAL PROCEDURES

Zircon and monazite were separated from the rock samples using standard heavy liquid and magnetic separation techniques. All zircon fractions have had an air abrasion treatment (Krogh, 1982); monazite was not abraded. Mineral dissolution followed the procedure of Krogh (1973). The weight of the grains in each fraction was less than 5 micrograms, thus no
chemical separation procedure was needed and the bulk-dissolved sample was analyzed. In the case of monazite, dissolution was achieved using 6N HCl at ca. 40°C for 2 days and chemical separation of U and Pb using anion exchange columns follow the procedure of Krogh (1973), modified by using small anion exchange columns (0.05 ml of resin) that permit the use of reduced acid reagent volumes.

Pb and U were loaded together with silica gel onto outgassed rhenium filaments. The isotopic compositions of Pb and U were measured using a single collector with a Daly pulse counting detector in a solid source VG354 mass spectrometer. Data are corrected for a mass discrimination of 0.14 %/AMU and a deadtime of 21.0 nsec. The thermal source mass discrimination correction is 0.1 %/AMU. The laboratory blanks for Pb and U are usually less than 1.0 and 0.02 pg, respectively. Initial common Pb above 10 pg was estimated using the model of Stacey & Kramer (1975). Error estimates were calculated by propagating known sources of analytical uncertainty for each analysis including ratio variability (within run), uncertainty in the fractionation correction, and uncertainties in the isotopic composition and amount of laboratory blank and initial Pb. Decay constants are those of Jaffey et al. (1971). All age errors quoted in the text and error ellipses in the concordia diagrams are given at the 95 % confidence interval; errors in Tables 1 and 2 are 2σ. Age calculations and concordia diagrams were derived for both samples using the programs of Ludwig (2000) and Davis (1982).

5 HUDSONIAN LEUCOGRANITE: U-PB ISOTOPIC RESULTS

Most zircons are small, metamorphically rounded, cracked, hazy, colorless, 2:1 prismatic grains with small faces. Rare grains show a small amount of overgrowth material. Two single-grain and one multi-grain fractions from the igneous zircon population of the leucogranite were selected for analysis and gave 207Pb/206Pb ages of 1817.1, 1775.6, and 1811.7 Ma that are −0.2, 3.3, and 0.7 % discordant, respectively. The three points are collinear and a regression line analysis yielded an upper intercept age of 1819.4 ±10/−7 Ma and a lower intercept age of 1008 ±114/−97 Ma with a 75 percent probability of fit. Two single-grain fractions of high-U monazite in the sample yielded 207Pb/206Pb ages of 1816 and 1805.4 Ma, and are 0.3 and 0.2 % discordant, respectively. The more precise age of 1816 ±1 Ma is identical within analytical error to the zircon crystallization age. The 1805.4 Ma age indicates some post-crystallization disturbance during Hudsonian thermotectonism, causing Pb loss in monazite but not zircon.

6 HUDSONIAN GRANITIC PEGMATITE: U-PB ISOTOPIC RESULTS

The zircons are elongate and needle-like, colorless, flat and platy grains with very small clear tips. Three zircon fractions yield slightly discordant to discordant data with 207Pb/206Pb ages of 1799.4 ± 38.7 (1.9% discordant), 1789.1 ± 2.4 (2 % discordant), and 1664.3 ± 3.7 Ma (10% discordant), respectively. A regression line calculation through the three zircon data points gives upper and lower intercept ages of 1811.5 ± 5 Ma and 960 ± 27 Ma, respectively, with a 77% probability of fit. The lower intercept age of ca. 1000 Ma is indicated most strongly by the most discordant fraction, which morphologically was flawless, and may be discordant due to a small amount of remaining rim material that was not completely abraded away.

One single-grain fraction of clear, euhedral, multifaceted monazite grains and one single-grain fraction of clear, inclusion-free, yellow monazite grains from a granitic pegmatite yielded 207Pb/206Pb ages of 1815.6 and 1814.2 Ma, and are 0.3 and 0.2 % discordant, respectively. They have a weighted mean 207Pb/206Pb age of 1814.6 ± 1.4 Ma (MSWD of 0.77). The monazite age is slightly older, but well within error of the upper intercept age of the zircon data. The U concentrations in the zircons are extremely high (potential U protore), varying from about 2150 to 3690 ppm, that will have caused metamictization leading to variable Pb loss. If recent Pb loss has more strongly affected the more discordant data, it is possible that the upper intercept age is slightly younger than the true crystallization age. Thus, the best estimate for intrusion and crystallization of the pegmatite is probably given by the weighted mean monazite age of 1814.6 ± 1.4 Ma. The monazite ages are identical within analytical error and fall within the bracket of 1818 to 1805 Ma, the age of peak thermal metamorphism for the Wollaston and Mudjatik domains (Annesley et al. 1997, 1999, 2005). This suggests that granitic pegmatite intrusion, as well as the leucogranite intrusion, in the McArthur River area...
was coeval with peak metamorphism and strong Hudsonian overprinting.

7 ZIRCON TIPS

In both samples, the lower intercept is indicated to be “Grenvillian” age, and there is evidence of new zircon growth in the form of very small tips (Figure 1). Two single grains clad with tips and two zircon tip fractions from the leucogranite were selected for analysis and gave $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1680.8, 1613.9, 1602.4, and 1551.4 Ma that are 5.4, 6.8, 16.9, and 7.4% discordant, respectively (Table 1: Zrn-4, 5, 6, 7).

![Figure 1. Separated single zircons clad with tips. Scale bar is 500 microns.](image)

Interpretation of these data gives 1680-1550 Ma as the approximate timing of the thermal event(s) that produced the new zircon growth with anomalously high uranium values (>1900 ppm; U protore). U-Th-Pb chemical dating by microprobe of six individual zircon grains clad with tips revealed a wide range of ages from 1800 to 450 Ma with distinct age clusters at 1800 to 1700 Ma, 1700 to 1600 Ma, 1550 to 1300 Ma, 1250 to 900 Ma, and 850 to 450 Ma. The highest age cluster correlates within analytical error to the precise crystallization age of 1820 $^{+5/-4}$ Ma. The latter clusters correlate with the far-field thermotectonic events that have affected/reactivated the sub-Athabasca basement structures (Annesley et al. 2000, Fayek et al. 2002) and produced the associated fluid/heat flow responsible for new growth, recrystallization, and/or alteration/isotopic resetting of radiogenic minerals like zircon, monazite, and uraninite.

8 DISCUSSION AND CONCLUSIONS

U-Pb dating of leucogranite yields an upper intercept crystallization age of 1820 $^{+5/-4}$ Ma (94 % fit) from one monazite and three zircon points. Another monazite point yields a 1805.4 $^{\pm}$ 2 Ma age, indicative of some post-crystallization disturbance during strong Hudsonian thermotectonism (Annesley et al. 2005), which caused Pb loss in monazite. Fresh granitic pegmatite yielded an upper intercept age of 1812 $^{\pm}$ 5 Ma; interpreted as its minimum age of crystallization. The best estimate for intrusion and crystallization comes from the weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1814.6 $^{\pm}$ 1.4 Ma from two monazite points.

IDTIMS analysis of the zircon tips in the leucogranite yielded ages from 1680 to 1550 Ma, which are interpreted as the approximate timing of the thermotectonic event(s) and associated fluids that produced the new zircon rich in uranium within essentially fresh rock ca. 200 meters from high-grade U ore. This implies uraniferous fluid flow in the basement, and provides strength to the basement source origin. Also from an uranium exploration perspective, these results suggest Pb isotopes as an important vector tool because of cryptic alteration.

ACKNOWLEDGEMENTS

Funding was provided by the Saskatchewan Research Council, Jack Satterly Geochronology Laboratory, University of Saskatchewan, and the East Athabasca Basin Modeling Project. Special thanks go to Michel Cuney for reviewing this contribution.

REFERENCES


Annesley, I.R., Madore, C., Portella, P. (2005) Geology and thermotectonic evolution of the western margin of the Trans-Hudson Orogen: evidence from the eastern sub-Athabasca basement, Saskatchewan. Special Issue on the Trans-Hudson Orogen of Lithprobe, Ed-

Proceedings of the Ninth Biennial SGA Meeting, Dublin 2007 1127


Fayek, M., Kyser, T.K., Ricuputi, L.R. 2002 U and Pb isotope analyses of uranium minerals by ion microprobe and the geochronology of the McArthur River and Sue zone uranium deposits, Saskatchewan, Canada: Canadian Mineralogist 40: 1553–1569.


Table 1. Isotopic data for MAC-257-628.8 leucogranite.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>U (ppm)</th>
<th>Th/U</th>
<th>PbCom (pg)</th>
<th>207/204</th>
<th>206/238</th>
<th>207/235</th>
<th>207/206</th>
<th>207/206 Age (Ma)</th>
<th>% Disc.</th>
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<td>Zrn-1</td>
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<td>0.7</td>
<td>1200</td>
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<td>0.11075</td>
<td>1811.7</td>
<td>0.7</td>
</tr>
<tr>
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<td>550</td>
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<td>114.7</td>
<td>110</td>
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<td>Mzn-1</td>
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<td>10.2</td>
<td>19603</td>
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<td>19.5</td>
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Table 2. Isotopic data for MAC-257-636.7 granitic pegmatite.

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<th>PbCom (pg)</th>
<th>207/204</th>
<th>206/238</th>
<th>207/235</th>
<th>207/206</th>
<th>207/206 Age (Ma)</th>
<th>% Disc.</th>
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Model Th/U ratio estimated from 208Pb/206Pb ratio and age of sample
Total common Pb in sample, includes initial and blank Pb
207Pb/204Pb corrected for spike and fractionation
Pb/U ratios corrected for spike, fractionation, blank and initial common Pb, using model of Stacey & Kramers (1975)
2D and 3D seismic imaging of high-grade uranium ore deposits in structurally complex environments, in the eastern Athabasca Basin, Canada

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S. Gyorfi, Hungarian Horizon Energy Ltd., Budapest, Hungary
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ABSTRACT: Hardrock environments occur in various geological settings, from modern orogenic systems to Precambrian shields. They are dominated generally by diverse and often strongly deformed assemblages of igneous and metamorphic rocks (Eaton et al. 2003). These crystalline basement rocks are hosting important quantities of mineral resources at variable depth, hence a growing interest to better constrain their subsurface geology. Seismic mapping of such environments is extremely challenging, because they differ radically from sedimentary environments. These differences are evident in all phases of the process from data acquisition to final interpretation. The purpose of the present study is to assess the applicability of seismic methods in mapping subtle subsurface structural and stratigraphic features associated with the McArthur River mining district and the Russell Lake exploration area.

KEYWORDS: seismic, mineral exploration, unconformity-type uranium deposits, data acquisition

1 INTRODUCTION

Since 2000, high-resolution and regional multi-channel seismic reflection investigations were undertaken, first under the auspices of the EXTECH-IV Athabasca Multidisciplinary Uranium Studies Project, more recently by Hathor Exploration Ltd. The overall goals of the seismic program are to develop a functional seismic technique as an efficient tool for uranium exploration, and to contribute to the four-dimensional geoscience framework for uranium exploration within the deeper parts of the Athabasca Basin. The ultimate goal is to determine the seismic signature of a known U deposit.

2 GEOLOGICAL FRAMEWORK

The Mesoproterozoic Athabasca Basin (Figure 1) consists of a maximum 1500m thick succession of mainly fluvial-continental deposits. These clastic sequences are overlying unconformably the medium-to-high grade metamorphic crystalline basement rocks of the Mudjatik and Wollaston domains, deformed under ductile conditions during the Palaeoproterozoic Trans-Hudson Orogeny (1.9-1.8 Ga). Later brittle deformational events have overprinted and partially reactivated the ductile basement structures.
The studied region is located close to the SE margin of the Athabasca Basin (Figure 1). The dominant orientation of regional basement structures is NNE-SSW to NE-SW (Figures 2 and 3). The P2 structural zone, hosting the high-grade uranium occurrences, at the McArthur River site, follows the same trend and is delineated in the study area by more than 50 boreholes. Potential data analysis reveals that the structural trend is comparable, ~50km south, in the Russell Lake area, although direct subsurface control is very limited.

Figure 2. Vertical gradient magnetic map of the McArthur River mining district.

Figure 3. Survey configuration in the Russell Lake area.

Sonic logs show that interval velocities within the silicified sandstone can increase to as high as 5400-5600 m/s, versus the non-silicified section with interval velocities between 4200-4500 m/s. Where not gradational, this boundary can be mapped by seismic technique. Borehole data also indicate that the sandstone basement unconformity is commonly associated with a thick palaeo-weathered zone or a highly fractured breached zone, thus creating major acoustic property and seismic signal changes.

3 DATA ACQUISITION

Because of permitting requirements, most seismic data is collected under extreme winter weather conditions with ambient temperatures as low as -35°C. The high-resolution survey utilized mainly 3 component Vectorseis detectors, and one or two 22,000 kg IVI-2400 Vibroseis units. Geophone group interval is 5m, while vibration interval is 20m. Sweep frequencies ranged from 30-170 Hz (non-linear, 12 dB/octave upsweep). The sweep length is 12 s, the correlated record length being 6 s. The 3D survey has identical acquisition parameters, the only difference being that beside the 600 Vectorseis 3C units additional 960 IO-2000 geophones were employed. In fact, this survey was one of the β-sites for testing the applicability of the Vectorseis 3C recording system in extreme temperature conditions. The acquisition geometry for the 3D survey (Figures 4 and 5) is irregular due to limitations imposed by topographic conditions, the infrastructure related to mine operations and the number of available recording units. This irregular acquisition ge-
ometry has certain impacts on data processing.

![Figure 5. Fold coverage of the 3D data using 10x10m bins; 12 and 14 are 2D profiles.](image)

4 PROCESSING SEQUENCE

The processing sequence for the 2D and 3D surveys is very similar. The processing flow applied includes the following steps: 1) Editing and geometry assignment; 2) Refraction statics (GLI 3D); 3) Data enhancement/filtering (FX decon, FK filter, predictive decon and Eigen-filter); 4) Muting; 5) Velocity analysis (2 iterations); 6) Residual statics (2 iterations); 7) NMO; 9) Post-NMO mute 10) Stacking; 11) 3D DMO; 12) Post DMO velocity analysis; 13) Post-stack Kirchoff time-migration. Residual statics and especially the adopted filtering sequence improved considerably the quality of individual shot-gathers.

In order to avoid spatial biasing (Yilmaz, 2001), the choice of correct bin size is of crucial importance. Parameters considered were: 1) expected dips, 2) average velocities, and 3) maximum frequency of the seismic signal. Based on these parameters, a 10x10m bin size was established. Velocity analysis was difficult due to fluctuating fold coverage and non-uniform offset distribution within CDP gathers. Using available velocity information (sonic logs) and running two iterations (velocity analysis-residual statics), velocity picking became more feasible. Finally, DMO and the post-stack Kirchoff time-migration resulted in considerable improvement of the stacked data.

5 INTERPRETATION

Our processing strategy described in the previous section resulted in final migrated sections of reliable quality. The imaged structures showed good agreement with borehole data and the overall reflectivity was close to the synthetics generated from sonic logs. Interpretation of the 2D high-resolution lines 12 (Figure 6) and 14, oriented sub perpendicular to the P2 structural trend can be summarized as follows: 1) The basement is poorly constrained by borehole data. Its interpretation is conceptual, however constrained by regional geology, results of other regional and high-resolution surveys and analogies. In our interpretation, the basement is made up of interleaved Archaean and Palaeo-proterozoic structural units related to the THO 2) The basement/sandstone unconformity can be correlated reasonably in most places. However structural complexity (intense faulting) and/or absence of the basal weathered horizon can make interpretation difficult; 3) Within the Athabasca sandstones, reflectivity changes laterally and vertically (continental environment, intense faulting, diagenesis etc.), but based on a few borehole data, the different sandstone members could be correlated all along the sections; 4) There are numerous reverse faults affecting the Athabasca Sandstone and the P2 “fault” is in fact a broad zone of compressional deformation. The basement was involved in this late-stage faulting and the seismic data suggest that the brittle deformation is kinematically linked to earlier basement structures formed under ductile conditions; 5) Thickness variations across faults seen in the upper parts of the Athabasca Sandstone (MFe and MFd) are indicative for synsedimentary deformation, offering constraints on the age of compressive deformation; 6) Comparison of lines 12 and 14 also revealed that although the overall style of deformation is similar, individual structural elements are difficult to correlate. Transverse faulting has been documented in boreholes and on vertical gradient maps (Figure 2). Thus the existence of a lateral ramp running between lines 12 and 14 was postulated as the most plausible explanation; 7) The recently processed 3D survey fully supports this idea. Crossline 50 (Figures 2 and 7) running parallel to the P2 trend shows our preliminary interpretation of the structural style. High-angle transt-
Figure 6. Interpreted 2D high-resolution line 12 running perpendicular to the P2 trend.

Figure 7. Preliminary interpretation of crossline 50; this line is parallel with the P2 trend 3D survey.

Figure 8. Seismic profile of line 5 from Russell Lake. Correlation to borehole geology illustrates the stratigraphy complexity at the UC and immediately below it.

Figure 9. Seismic section of line 8 illustrates preservation of ductile deformation in the basement complex at the UC and immediately below it.

6 CONCLUSIONS

The high-resolution 2D and 3D survey met successfully most of the initial objectives. In spite of acquisition difficulties and limitations in the survey geometry and elevated noise levels, the final processed data imaged successfully the intricate and subtle stratigraphic and structural features associated with the P2 productive trend. Further efforts will concentrate on the full 3D interpretation, and study of possible seismic attributes associated with the ore bodies. The Russell Lake seismic profiles (Figures 8 and 9) image the structurally complex basement beneath the unconformity (UC). The seismic data also demonstrate that the complex seismic signatures at the UC are associated with distinct changes in basement lithological units. Our studies demonstrate that the seismic method is an extremely valuable exploration tool in the deeper parts of the Athabasca Basin, and following regional to sub-regional potential geophysical surveys, it can assist in the development of a more efficient drilling program.

ACKNOWLEDGEMENTS

The authors would like to thank Jon Tessman (I/O), Russell Kappius (GMG), Robert Kendall (Veritas DGC), Barrie Taylor and Dana Hackney (Landmark Graphics) for discussions on seismic data processing. We extend our gratitude to all EXTECH-IV participants for their technical and financial support. Landmark Graphics Corp., Schlumberger-GeoQuest Inc., and Hampson-Russell Software Services Ltd. are thanked for generous support of the Seismic Laboratory of the University of Saskatchewan.

REFERENCES

A Two-Stage Thermotectonic Model for the Athabasca Unconformity-Type Uranium Deposits

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ABSTRACT: Regional tectonics and petrology studies of the south-western Canadian Shield suggest that metallogenetic processes involved in the development of Athabasca unconformity-type uranium deposits are controlled by long-lived basement shear zones. Overprinting belts of high- to low-grade metamorphic tectonites record the passage of transcurrent megashears through the middle and upper crust during late Palaeoproterozoic syntectonic exhumation. Uranium-enriched mid-crustal levels of the megashears were overprinted by highly porous greenschist-grade mylonite belts, which hosted active thermal-convection cells. The deposition of the Athabasca Group and the subsequent build-up of a low-permeability carapace of hydrothermally altered clastic strata, led to the development, in places, of “pressure cooker” hydrothermal systems that maximized fluid/rock interaction for effective metal leaching at depth in the basement fault zone and ore precipitation near the Athabasca unconformity.

KEYWORDS: unconformity-type uranium deposits, Palaeoproterozoic, Athabasca Basin, Canadian Shield, transcurrent shear zones, faults

1 INTRODUCTION

Previous, apparently mutually exclusive genetic models for the Athabasca unconformity-type uranium (U) deposits (“magmatic-hydrothermal”; “metamorphic hydrothermal”, “super-gene” and “diagenetic hydrothermal” models) are here reconciled in a thermotectonic two-stage U enrichment model. The model is derived from descriptive geological features and processes common to U deposits and occurrences, integrated with regional tectonics and petrology of basement rocks of the Athabasca Basin and adjacent Canadian Shield (Fig. 1).

2 COMMON U DEPOSIT FEATURES

Athabasca-type U deposits are:

• structurally controlled at all scales: a) the basement underlying or including U deposits is invariably represented by shear zones; b) U ore is localized along brittle faults either within the basement, at the basement unconformity, or within the fractured Athabasca clastic rocks; and c) U ore exists as fracture fillings or disseminations in the wallrock.

• associated with linear zones of metasomatic transfer of elements within basement shear zones and/or from basement into overlying Athabasca Group clastic strata: a) shear zones show variable degrees of metasomatism and retrogression to greenschist and subgreenschist facies rocks, whereas the overlying Athabasca clastic strata are overprinted by plume-like epithermal alteration halos elongated along faults.

Figure 1. Total magnetic field map of the south-western Canadian Shield, showing the location of the main Athabasca unconformity- and vein-type U deposits and prospects, and the tectonic elements mentioned in text.
trending parallel or slightly oblique to the underlying shear zone; and b) the mineralization is polymetallic with mineral assemblages typical for polyphase hydrothermal discharge.

The overlying Mesoproterozoic elastic strata played a key role in the metallogenic processes that generated the richest U deposits on Earth (large reserves and ore grades up to two orders of magnitude higher than other U deposit types).

3 BASEMENT PETROLOGY/TECTONICS

The present erosional level of the southwestern Canadian Shield and the sub-Athabasca unconformity provide a horizontal section through the following zones (Fig. 2):

A) dry continental deep crust formed in the major Late Archean period of crustal growth. Granulite-facies parageneses and associated intrusive rocks are exposed either as extensive areas of dome-and-basin structures in the Mudjatik Domain of the Hearne Province and portions of the Rae Province or as smaller tracts in:

B) linear zones of Palaeoproterozoic tectono-magmatic recycling dominated by amphibolite facies metamorphic tectonites, migmatites, and associated intrusive rocks, including the Taltson (ca. 1.99-1.93 Ga), south Snowbird and Wollaston (ca.1.86-1.80 Ga) tectonomagmatic zones;

C) wide (>10km) belts of amphibolite facies mylonites, occasionally including granulite-facies relics, hundreds of kilometres long, with conspicuous strike-parallel mineral stretching that mark broad domains of continental transcurrent deformation in the Canadian Shield. From west to east, the most prominent exhumed infrastructures of such Palaeoproterozoic megashears are: the Charles Lakes Shear Zone, and the concealed Maybelle River Shear Zone, in the Taltson magmatic zone, the Tazin River Shear Zone near the eastern margin of the Taltson magmatic zone, the Beaverlodge Shear Zone overprinting the Rae terrane, and, on either side of the Mudjatik Domain, the Virgin River-Black Lake Shear Zone, and the Mudjatik-Wollaston “Transition Zone” (Fig. 1);

D) finally, anastomosing belts of low-grade mylonite to cataclasite.

U-Pb geochronology and overprinting relationships are consistent with initial, widespread amphibolite to granulite-facies deformation (B) being gradually concentrated in belts of retrogressed granulite to lower amphibolite facies tectonites (C) during syntectonic exhumation through intermediate crustal levels; greenschist-grade mylonite belts (D) record further retrogression and strain concentration – partitioning – migration within narrower belts during the evolution of shear zones through shallower crust. Classic districts of vein- and unconformity-type U mineralization (e.g., Beaverlodge, Wollaston) are within retrogressive and metasomatic megashears (C), with notoriously U-rich Athabasca unconformity-related deposits formed exclusively within or atop high-porosity, greenschist shear zones (D).

4 URANIUM ENRICHMENT

4.1 Stage I: Primary U enrichment at mid-crustal levels of megashears

The exposed Palaeoproterozoic megashears (C) are kilometres-wide zones of deformation at low to mid-crustal levels that show an elusive transition through strain and hydration gradients to intact adjacent A- and/or B-type crust. These belts of mainly amphibolite facies mylonitic gneiss record creep processes and retrogression associated with quasi-steady state permeabilities higher than those of the surrounding, less rapidly deforming granitoid-granulite crust A and B. Carbonate-impregnated quartzofeldspathic gneiss, synkinematic carbonate and quartz segregations, impure quartzite and feldspathic quartzite, all very common in the Palaeoproterozoic megashears (C), record intense CO₂- and/or SiO₂-rich fluid migration during steady-state ductile deformation. Multiple generations of gabbro-basalt-dolerite and granitic pegmatite dykes, testify to hot-fluid advection and melting along wide linear zones of strain. Similar rocks encountered in mining and drilling operations in the Beaverlodge and Wollaston uraniferous
districts provide a three-dimensional perspective on the extensive shearing, retrogression and metasomatic processes (carbonatization, fenitization, migmatization), and localized magmatism, as well as large-ion lithophile (LIL) elements leaching, all triggered by hot CO$_2$-H$_2$O fluids migration to mid-crustal levels within the megashears. The LIL elements, notably U, Th, K, Rb and REE, have migrated from the lower crust either in:

- partial melts [e.g., uraninite-bearing granitic pegmatites in the Beaverlodge district (Beck, 1985); uraninite-rich leucogranites and pegmatites in the Charlebois area, and the main Wollaston-Mudjatik district (Annesley et al., 2005); K, Th, U and REE-enriched synkinematic granitoids of late Taltson age near Shea Creek (Brouand et al., 2003)]; or

- a mineralized CO$_2$-H$_2$O vapour flux [uraninite-enriched retrogressive amphibolite facies rocks of the Wollaston-Mudjatik district (Dahlkamp, 1978)]. Enriched in radioactive elements, the mid-crustal levels of megashears became zones of high heat production.

4.2 Stage II: secondary U enrichment by fault zone-related hydrothermal activity

The broad amphibolite-facies megashears (C) are overprinted by braided systems of sub-parallel greenschist and subgreenschist facies mylonite belts tens to hundreds of metres wide (D). Concealed by the Athabasca Group, segments of greenschist mylonite belts overprinting amphibolite-grade mylonite gneisses have been identified at each Athabasca unconformity-related uranium deposit and prospect. The greenschist facies mylonites record the passage of these long-lived zones of crustal weakness through the brittle-ductile transition zone; whereas associated hematite/limonite-cemented breccia, cataclasites, and fault gouge record strain localization and water influx at near-surface conditions. This transition from continuous aseismic shearing to the mixture of discontinuous and continuous shearing processes in the seismo-genetic upper crust has major metallogenetic implications.

4.2.1 High porosity greenschist belts

Increased porosities (up to 8%; Onishi & Shimizu, 2005) and permeabilities ($k = 10^{-12}$ m$^2$; Foster & Smith, 1990) of fractured granitoid rocks are considerably more effective than those of massive granite and common sandstone, and orders of magnitude greater than the Athabasca orthoquartzite. The pre- to syn-Athabasca steeply dip-pling belts of greenschist/subgreenschist facies fault rocks constituted a tectonically weak and porous medium that allowed infiltration of connate, diagenetic and meteoric waters with formation of subvertical basement aquifers. Thus, thermal convection-driven hydrodynamic cells have preferentially developed within the fractured basement and involved inflow (infiltration) of externally derived fluids balanced by an upflow of fluid heated at depth in the high radioactivity linear domains now flooring parts of the Athabasca Basin. Fluid advection through subvertical fault aquifers is capable of significant heat transport and large water-rock ratios. Infiltration of surficial waters along steeply dipping fault zones in the Beaverlodge and Wollaston districts is recorded by increased haematitization of strained rocks culminating with brick-red ‘mud gouge’ layers, high oxygen fugacities (haematite field), and high carbonate $\delta^{18}$O values (6‰ to 19‰, SMOW) in the alteration zones associated with U mineralization. The plume-like epithermal alteration halo marks the locus of hydrothermal discharge above the shear/fault zone.

4.2.2 Episodic faulting

The association of mylonitic fabrics interlaced with pseudotachylites and fine-grained, compact gouges marking fault slip domains with multiple generations of hydrothermal fault veins (quartz and/or carbonate) and mineralization pulses recognized in all Athabasca-type U deposits provide spectacular evidence of episodic slip/ fracturing creating permeability and interseismic sealing by mineral precipitation during ongoing deformation and hydrothermal activity. Paragenetic relationships, including multiple generations of U mineral precipitation with phases of remobilization, are consistent with fluid redistribution and related hydrothermal processes being either directly driven or strongly modulated by stress and permeability cycling tied to the earthquake stress cycle of fault zones (e.g., Sibson, 2001). Dated U mineralization phases cannot be directly linked to regional tectonic phases; therefore, they must be local phenomena. The association of U ore in the area of the Athabasca Basin with local small displacement faults may be explained by purely fluid-driven failures without changing
the absolute stress state. In hydrothermal regimes, the influx of fluids can induce spontaneous brittle failure even under constant stress differences ($\sigma_1 - \sigma_3$). An increase in pore fluid pressure ($P_f$) would reduce the effective normal stress ($\sigma_n$) according to the relationship:

$$\sigma_n^{(effective)} = \sigma_n - P_f$$

and implicitly reduce the shear strength ($\tau$) in a rock of certain cohesive strength ($C^*$) according to the Coulomb shear failure criterion:

$$\tau = C^* + \mu \sigma_n^{(effective)}$$

($\mu$ – coefficient of friction)

Thus, ancient fault/shear zones in the basement of the intra-cratonic Athabasca Basin do not need to be tectonically reactivated, instead, they set up the peculiar locus for self-promoting and self-organizing fluid-driven faults. Although of no regional tectonic significance, the intermittent seismic slip on these faults triggered highly efficient suction-pump and fault-valve mineral precipitation mechanisms.

4.2.3 The “pressure-cooker” U-enrichment

Following the deposition of the lower Athabasca strata, an effective lid to the advecting hydro-thermal fluids developed atop the sub-vertical basement shear/fault zone. Hydrothermal plumes infiltrating the Athabasca strata led to the build up of an even less-permeable silicification and/or argillization carapace atop fault zones, which allowed for prolonged interaction between hot hydrothermal fluids and U-enriched basement rocks. Consequently, repeated pulses of fluid in-filtration-overpressuring-failure-discharge would achieve very high fluid/rock ratios and transfer metals into the zone of hydrofracture vein network, which may extend hundreds of metres below the carapace (e.g., Shea Creak and McArthur River deposits). Fracturing of the low permeability carapace triggered by fluid-driven basement faults, provided cross-stratal conduits for occasional outbursts of mineralizing fluid from the overpressured domains of the fault zone aquifer. Ore-sealed fractures and disseminated ore within this altered sandstone carapace make up major sandstone-hosted deposits (e.g., Rabbit Lake and Cigar Lake deposits). The world-class high-grade Athabasca unconformity-type uranium deposits are probably one of the most spectacular examples of hydrothermal fault-valve action.

ACKNOWLEDGEMENTS

Thanks go to Reg Olson, Charlie Jefferson, and Ken Wheatley for very stimulating discussions.

REFERENCES


Fluid mixing and uranium deposition in unconformity type deposits (Saskatchewan, Canada, Northern Territory, Australia)

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ABSTRACT: The richest U-deposits occur in both Australia (McArthur Basin, Northern Territory) and Canada (Athabasca Basin, Saskatchewan) at the unconformity between middle Proterozoic sedimentary basins, and Archaean to lower Proterozoic basement. This study shows how detailed analysis of palaeofluids may further the understanding of the genesis of these deposits. Fluids inclusions were studied in both silicified sandstones and hydrothermal quartz considered to be pre- and post-U ore cements in breccias associated with the deposits. The methodology employed in this study is a combination of microthermometry, Raman microspectroscopy and Laser Induced Breakdown Spectroscopy (LIBS). Results show that cation ratios (Na/Ca, Na/Mg) and chlorinity may be used to discriminate different types of brines, and to decipher the mixing, or dilution, processes between brines and more dilute waters. Mixing processes are considered to have played a prominent role in the formation of the U-deposits.

KEYWORDS: Unconformity-type uranium deposits, fluid mixing, brines, Athabasca, Kombolgie

1 INTRODUCTION

Unconformity-type uranium deposits are the most profitable source of uranium because of their exceptionally high grade and large tonnage. At least 10 unconformity-type uranium deposits have been discovered in the Athabasca Basin, northern Saskatchewan, Canada since the Rabbit Lake deposit was discovered in 1968. In unconformity-type uranium deposits, the ore is located close to the intersection of the unconformable contact between Archaean to lower Proterozoic metamorphic rocks and a middle Proterozoic sandstone cover, with reverse faults that are rooted in the basement in graphitic metasediments.

The first model suggested that uranium deposition resulted from a mixing between oxidized basinal brines with basement-derived reduced fluids (Pagel 1975; Hoeve & Quirt 1987; Kotzer & Kyser 1995; Fayek & Kyser 1997). The second model proposed the interaction of basinal brines with reduced basement lithologies to explain U deposition (Hoeve and Quirt 1984; Komninou & Šverjensky 1996; Fayek & Kyser 1997). Although brines were described in previous fluid inclusion studies (Pagel 1975; Pagel et al 1980; Kotzer & Kyser, 1995), no detailed fluid compositions are available. The present study, therefore, addresses five key questions: i) How many fluids have circulated in the vicinity of the unconformity-type U deposits and what major elements do they contain? ii) Are the brines, the silicification and mineralization events genetically related? iii) Do the different fluid types have similar origins? iv) Did the Proterozoic basins undergo pressure and temperature variations from diagenesis to the ore forming event? v) Are the fluid events similar in the Canadian and Australian deposits?

2 METHODOLOGY

Detailed determination of the composition of individual fluid inclusions in the H2O-NaCl-Ca(Mg)-Cl2 system from microthermometry data may be difficult because (i) the melting of salt hydrates is often unclear, (ii) salts or salt hydrates are often metastable, and iii) eutectic temperatures are often difficult to precisely determine due to a unique salt-water system.
These problems can be overcome by using a Raman microprobe to identify the salt hydrates and to measure the chlorinity, and by using Laser Induced Breakdown Spectroscopy (LIBS) to determine cation ratios (Fabre et al. 1999). Data are cross-checked at each step in the determination of the fluid inclusion composition. Data collection is then completed by the crush-leach technique on bulk samples.

3 RESULTS

The above methodology was applied to several case studies, 1) mineralized faults and associated breccias from the Alligator River Uranium Field (middle Proterozoic Kombolgie Subgroup, Northern Territory, Australia), and 2) the McArthur river Uranium deposit (Saskatchewan, Canada).

3.1 Jabiluka & Nabarlek, Australia

The studied faults in the Jabiluka, Nabarlek area are cemented by euhedral quartz containing a variety of fluid inclusions with a wide range of ice-melting temperatures, from near 0°C to about -50°C. The results identify three types of fluids (Derome et al. 2007).

1) A calcium-rich brine, with about 1-8 wt% NaCl, 14-23 wt% CaCl₂ and no detectable MgCl₂ with the exception of one inclusion. This end-member primarily corresponds to fluid inclusions with Tmice around -30°C when no hydrohalite is observed.

2) A sodium-rich brine, with about 10-19 wt% NaCl, 4-11 wt% CaCl₂, and 0-6 wt% MgCl₂. This fluid corresponds to fluid inclusions with Tmice of around -21 to -28°C and also to those in which hydrohalite melting was observed after Tmice.

3) A Na-Ca-Mg fluid, which contains about 3-13 wt% NaCl, 1-13 wt% CaCl₂, and 0 – 0.6 wt% MgCl₂. This fluid corresponds to fluid inclusions with Tmice ranging from -6 to -15°C.

Recent studies (Polito et al. 2005) claim that U-ore fluids were distinct from those related to the main silicification events affecting the studied faults. At Jabiluka, however, all the fluid types were found in close relation with the ores within the basement, and the U-ore fluid compositions falls within the range of the mixing trend between the two first fluid types above-mentioned. We, therefore, consider that both fluids were present during the main U event.

3.2 McArthur River, Saskatchewan

Several studies have been carried out recently on this deposit (Derome 2002, Derome et al. 2005). The results of these are summarized below:

1) Two main types of brines were distinguished for the first time in the Athabasca sandstones and the underlying basement in the vicinity of U-mineralization: a hot (minimum 190°C) NaCl-rich brine (about 25 wt% NaCl, up to 14 wt% CaCl₂, and 1 wt% MgCl₂) and a cooler (approximately 140°C) CaCl₂-rich brine (5 to 8 wt% NaCl, up to 20 wt% CaCl₂ and up to 11 wt% MgCl₂). This differs from previous works (Pagel 1975; Kotzer & Kyser 1995), who considered only one type of brine circulating at a temperature of about 200°C.

2) Quartz cementation at the base of the Athabasca basin occurred in three stages with an early diagenetic cementation synchronous with the NaCl-rich basal brine and a later cementation event (Qz²-Qz³) corresponding to a first brecciation event that was synchronous with the input of the CaCl₂-rich brine. This “calcic-brine episode” was probably related to the reactivation of basement faults such as the P2 structure.

3) According to petrographic relationships, the NaCl-rich brine is the earliest basal fluid in the McArthur River area, and was still present during and after uranium deposition. The NaCl-rich brine is the regional basal fluid, as it was observed all over the Athabasca basin. Then, a cooler NaCl-rich brine, coming from upper levels of the Athabasca Basin, percolated into the basement lithologies, where Na is exchanged with Ca to form the CaCl₂-rich brine. As pressure decreased, the CaCl₂-rich brine migrated into the sandstone and was trapped during the pervasive silicification event (Qz²) as well as in Qz³ from the breccia bodies, where it mixed with the NaCl-rich brine. The predomiance of the CaCl₂-rich brine in Qz² and Qz³ suggests that this brine was injected into faults zones after the Qz¹ stage, during which the NaCl-rich brine was dominant, and that the CaCl₂-rich brine was the main fluid during the growth of Qz² and Qz³. The NaCl-rich brine again became dominant during the quartz Qz⁴, suggesting that the amount of CaCl₂-rich brine decreased during the growth of Qz². We conclude that the “calcic-brine episode” is characteristic of the pre-to syn-ore Qz² and Qz³ cementation events. This “calcic-brine episode” is
probably one of the key factors in the process of uranium mobilization and transportation; the evolution of the redox conditions during these process could not be constrained from the present study.

4 CONCLUSIONS: A COMPARISON BETWEEN FLUID COMPOSITION IN CANADIAN AND AUSTRALIAN U-DEPOSITS

4.1 Brine compositions

In both deposits, brines are interpreted as primary formation waters that were expelled from bedded evaporates. The CaCl₂-rich brine is considered to have formed during the interaction between the NaCl-rich brine and Ca-rich minerals in the basement. It was introduced into the fault system and mixed with the NaCl-rich brine during the critical stage of U-deposition.

4.2 Fluid sources

The brines are enriched in Br, and are interpreted as residual brines probably linked to the evaporite layers. Such layers are present within the McArthur Basin in Australia (Sweet et al., 1999). Brines evolved chemically during their interaction with the Proterozoic basement and the mid-Proterozoic siliciclastic sediments, as the Ca concentrations are likely to be due to the interaction of the Na-brine and Ca-rich lithologies. The Ca-enrichment probably occurred when the fluid migrated from shallow levels in the basin down to the contact with the basement along and below the unconformity.

4.3 Fluid mixing

The results of this study identify three types of fluids in the Kombolgie deposits, and two main fluid types in Saskatchewan deposits. In both cases, the Ca and Na brines mixed with each other. The main differences between the two cases, is the mixing of the brines with a less saline brine, which took place during the latest stages of the fluid evolution in Australian deposits.

4.4 Dynamics of fluid movements

A wide range of compositions between the end-members suggest that fluid mixing occurred in the breccias zone during periods of fluid influx; no complete homogenization of the fluids compositions occurred.

The fault zones and the breccia bodies at the base of the sandstone basins represent active drainage zones where different fluid reservoirs were connected, and thus a highly favourable location for fluid mixing. Temperature and pressure changes, combined with the effects of brine mixing, appear to be key-factors in the main stages of quartz cementation and U-deposition in studied deposits. These fluid movements are considered to be related to the main processes that were responsible for the U-mineralization at or below the unconformity.

ACKNOWLEDGEMENTS

The AREVA Company is gratefully thanked for the financial support and for providing samples for the fluid inclusion study from the Alligator Rivers Uranium Field (ARUF), whilst CAMECO and AREVA are acknowledged for permitting the study of the McArthur deposit in Canada. The GDR Transmet and CEA are acknowledged for the financial support of the analytical development of the LIBS technique.

REFERENCES


Hoeve J, Quirt D 1987 A stationary redox front as a critical factor in the formation of high grade, unconformity-type uranium ores in the Athabasca Basin,

Komninou A, Sverjensky DA 1996 Geochemical modeling on the formation of an unconformity-type uranium deposit. Econ. Geol., 91, 590-606


Alteration of monazite and zircon as the indication of uranium mobilization within the Pasha – Ladoga volcanic-sedimentary basin and its basement (Baltic shield, Russia). Inferences on the genesis of unconformity related uranium deposits

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ABSTRACT: Large-scale rare-earth elements, yttrium, uranium, migration has been evidenced in the Mesoproterozoic siliciclastic sediments of the Pasha – Ladoga basin (Russia), in its basement composed of Archaean – Palaeoproterozoic metamorphic rocks and Mesoproterozoic anorogenic rapakivi granites. In the vicinity of the unconformity surface at the northeastern margin of the Pasha – Ladoga basin the Karku uranium deposit has been discovered. REE, U and Y migration is in relation with extensive alteration of zircon and to a lesser extend of monazite. The same type of alteration is observed in the basement outside the Pasha – Ladoga basin, which confirm a much larger extension of this basin and correspondingly the possible existence of basement-hosted unconformity related deposits as those observed in the Athabasca (Canada) and more especially in the East Alligator River (Australia) district.

KEYWORDS: uranium, unconformity related deposits, sandstones, Mesoproterozoic basin, hydrothermal alteration, monazite, zircon.

1 INTRODUCTION

Mesoproterozoic unconformity related uranium deposits are the largest uranium resource presently mined in the world (Jefferson et al., 2005; Thomas et al., 2000). Unconformity related uranium deposits from the Athabasca basin (Saskatchewan, Canada) represent the world richest uranium ore bodies. The search of new unconformity related uranium deposits in similar geological environments, as the Athabasca or the East Alligator River district in Australia is a major exploration deal. During the last 10 – 15 years abundant research projects have been conducted on some of the best-known deposits but only a few new deposits and prospective areas have been discovered.

Unconformity-related uranium deposits are spatially related to the intersection of an unconformity between large and thick Mesoproterozoic siliciclastic highly oxidized sandstone basins, overlying Palaeoproterozoic to Archaean crystalline basement, with graphite-rich reverse faults. The source of uranium for these deposits is still a matter of debate.

Understanding the mechanisms leading to the formation of such high-grade uranium ore at that time represents a major scientific challenge. Numerous recent studies have been performed on these deposits and their environment (i.e.: Fayek & Kyser, 1997; Thomas et al., 2000; Cuney et al., 2003). Recent studies have been specifically devoted to the distribution of uranium and other trace elements in the two major possible source rocks: the sandstone cover and the basement lithologies) to identify the mechanisms of its leaching from accessory minerals (Cuney & Mathieu, 2000; Hecht & Cuney, 2000; Mathieu et al., 2001; Hecht et al., 2003; Cuney et al., 2003).

The aim of the present paper is to characterize accessory mineral alteration and associated trace elements migration at the scale of the Mesoproterozoic Pasha – Ladoga basin and the Archaean – Proterozoic basement below the basin and beyond its present extension preserved from erosion.
2 GEOLOGICAL SETTING

The Ladoga Lake area is located in the southeastern part of the Fennoscandian (Baltic) shield at the northwestern margin of the East-European platform.

Crystalline basement of the Northern Ladoga Lake area consists of Archaean granite-gneiss domes, rimmed by Palaeoproterozoic supracrustal rocks metamorphosed in the amphibolite facies, with incipient migmatization and transformed into plagioclase-biotite gneisses, marbles, calcsilicates, amphibolites and quartz-biotite-(graphite) schists (Baltybaev et al., 2002).

Only Palaeoproterozoic metamorphic and plutonic rocks represent crystalline basement of the Western Ladoga Lake area. Palaeoproterozoic supracrustal rocks comprise a metasedimentary assemblage of schists, gneisses and calc-silicate rocks. They are divided into two major blocks separated by the NW trending Priozersk shear zone. To the north of the Priozersk shear zone high temperature-low pressure granulite and amphibolite facies rocks with abundant tonalitic-trondhjemitic migmatites and diatectites are common, while towards the south there is an area of pronounced granitic migmatization (Konopelko & Eklund, 2003).

Intrusive magmatic series in the NW Ladoga Lake region comprise up to 40% of the present surface. The oldest complexes (1881 – 1878 Ma) include syn-kinematic norite-enderbite series and tonalite-granodiorite intrusions with associated gabbroic rocks (Glebovitsky et al., 2001). Syn-orogenic highly potassic granitic complexes (1840 – 1815 Ma) are very abundant and enriched in Th, U and REE (Konopelko & Eklund, 2003). Post-orogenic bimodal intrusions (ca. 1800 Ma) represent shoshonitic series (from ultramafic, mafic potassium-rich lamprophyres to peraluminous granites) strongly enriched in P, F, U, Th and LREE (Eklund et al., 1998).

During Mesoproterozoic (1645-1530 Ma) extension-related anorogenic Vyborg and Salmi rapakivi granite intrusions were emplaced in the northeastern and western parts of the Ladoga Lake area. In contrast to the Archaean – Palaeoproterozoic rocks, the rapakivi granites did not undergo any metamorphism, but have suffered intense postmagmatic hydrothermal processes (Vaasjoki et al., 1991, Amelin et al., 1997).

Pasha-Ladoga Mesoproterozoic Riphean siliciclastic, oxidized, generally coarse grained and immature, sediments with two major interlayed basaltic sequences were deposited into a Ladoga Lake trough. The present extension of the Pasha – Ladoga basin is about 150km in diameter and roughly coincides with the coastline of the Lake Ladoga (Amantov et al., 1996). Mesoproterozoic Vendian sedimentary deposits of Western European platform are completely overlaid the basement and Pasha-Ladoga basin rocks in the southeastern part of the Ladoga Lake area.

3 ANALYTICAL PROCEDURES

Petrographic and mineralogical characteristics of the Pasha-Ladoga sandstone and basement rocks were determined by transmitted and reflected light microscopy. Accessory minerals were more specifically studied through optical microscopy and with SEM in BSEM mode (Hitachi S2500 Kevex SEM, Henri Poincaré Univ., Nancy, France and CamScan MX 2500S SEM, VSEGEI, Saint-Petersburg).

Quantitative chemical composition of the main accessory minerals has been determined with a CAMECA SX-100 electron microprobe (EMP) at the Henri Poincaré University.

4 MONAZITE ALTERATION

Monazite, in the sandstone cover and in the altered sections of the basement of the Athabasca area in Canada (Hecht & Cuney, 2000), in the East Alligator River district in Australia (Cuney et al., 2000) and in the Franceville basin, Gabon, (Mathieu et al., 2001) has been submitted to incongruent leaching of U, REE and P by highly saline Ca-Na oxidizing diagenetic fluids despite its well known refractory behavior in most geological processes. Some uranium was retained in-situ with thorium, which was nearly immobile, within the structure of tiny crystals of uranothorite, which locally still mimic the former monazite crystal shape. Another part of the uranium liberated from monazite alteration has been adsorbed on Fe-Ti oxides and substituted in the altered part of zircon. Finally a residual undetermined part of the uranium may have transported by the diagenetic fluid. P and LREE recrystallized together with Al, Ca, LREE, S and Sr to form Al-phosphates-sulphates of the crandallite-goyoazite-florenclite group, which are regionally.

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observed in the Athabasca and Kombolgie sandstones (Hecht et al., 2003, Gaboreau et al., 2007).

In the basement of the Northern Ladoga Lake area, below the sedimentary basin and beyond its present limits, the degree of monazite alteration is generally very weak. Non altered, idiomorphic monazite is especially abundant in the Palaeoproterozoic quartz - biotite graphitic schists (Lobaev et al., 2005), whereas in the Athabasca basement rocks incipient monazite alteration has been observed even in quite fresh rocks (Hecht et al., 2003).

In the basement of the Western Ladoga Lake area near the sedimentary basin boundaries the degree of monazite alteration is very weak, but some evidences also exist locally. Accessory minerals in the Palaeoproterozoic plutonic rocks of the Western Ladoga area are more abundant than in the Northern Ladoga area and are typically represented by abundant zircon and monazite, uranothorite, allanite, REE carbonate and in one case – uraninite.

In the Pasha – Ladoga sandstone preserved detrital monazite crystals are commonly observed not only where included in detrital quartz grains unlike the Athabasca basin. Monazite with clear corrosion figures is abundant in the clay matrix associated with Ti-oxides. This indicates that monazite from the Pasha – Ladoga sandstones has been altered probably by the diagenetic fluids but with a weaker intensity compared to the Athabasca sandstones (Hecht & Cuney, 2000). Consequently Al-phosphate-sulfate neoformation is also much more limited. Th, which is a weakly mobile element, initially essentially contained in the monazite crystals, crystallizes as rare newly formed uranothorite crystals and/or as a microcrystalline Th-silicate phase with very low concentrations of U and LREE in the Pasha – Ladoga sandstone.

5  ZIRCON ALTERATION

Zircon is the most common and abundant accessory mineral in the sandstones and in the basement rocks. In the basal sandstone of the Athabasca basin well-rounded zircons show very complex internal structures indicating several magmatic crystallization or alteration stages. Rounded cores are common with one to two zoned rims. In BSEM image, cores are usually bright light and rims are frequently grey to dark-grey. The grey parts correspond to altered zones with lower average atomic number, where Zr and Si were substituted mainly by Ca, REE, Y, Sr, Al, P, U. The degree of substitutions may reach up 17 % of the cations of the zircon structural formula. Most of these elements are also characteristic of the Al-phosphates. It means that alteration of zircon should occur synchronously with monazite alteration and neoformation of Al-phosphates-sulphates. The uranium content in the zircon grains ranges from a few hundred ppm to several thousands ppm, the highest contents occurring in the altered zones.

In the Ladoga Lake basement preserved zircon grains show also very complex internal structures, indicating several magmatic crystallization stages especially in the rapakivi granites. Zircon alteration is also commonly observed in the zircon crystals from the basement. Alteration occurs from the edges of the crystals to their core.

Alterations of zircon crystals in basement rocks are observed not only in the vicinity of the unconformity surface below the Pasha - Ladoga basin, but also in basement rocks beyond the present basin limits. Such an alteration has been detected up to 20 to 30 kilometers from the Pasha – Ladoga basin margin, in the western part of the Salmi rapakivi granite batholith and up to 5-10 kilometers in the Palaeoproterozoic graphitic schists. The occurrence of similar zircon alteration below and outside the basin demonstrates that the Mesoproterozoic Pasha – Ladoga basin was extending over a much larger area that its present one and indicate that basement hosted unconformity related deposits may exist at least at several tens kilometer distance from the present limits of the Pasha Ladoga basin.

6  CONCLUSIONS

Geological and mineralogical studies of the Mesoproterozoic rocks of the Pasha – Ladoga basin (Russia) and Archaean – Paleoproterozoic basement have shown that the area share similarities with the classical unconformity-related uranium deposits of the Athabasca (Canada) and East Alligator Rivers (Australia), but also significant differences. Evidence of zircon and monazite alteration with formation of Al-phosphates of the crandallite-goyazite-florencite group, in both basement and basinal formations represent an efficient way for estimating the favourability of an area for the pres-
ence of unconformity related uranium mineralization. An important conclusion is the much larger former extension of the Pasha - Ladoga Mesoproterozoic sedimentary basin indicating the possible existence of basement-hosted unconformity related deposits as those observed in the Athabasca and East Alligator River districts.

ACKNOWLEDGEMENTS

The authors thank AREVA (France) for the financial support of this project, All-Russia Geological Research Institute (VSEGEI, Russia) and Urangeologorazvedka enterprise (Russia) for help in analytical works and permission for the sampling.

REFERENCES


First insights into the inorganic chemistry of ‘carbon phases’ from basement rocks to uranium deposits in the Athabasca Basin, Canada

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ABSTRACT: The work presented here examines the inorganic chemistry of ‘carbon phases’ (both graphite and carbonaceous matter) from the basement rocks of uranium deposits in the Athabasca Basin, Canada using micron-scale synchrotron-based XRF. The results indicate that these phases are not just combinations of C-H-O±S, but instead have an interesting and complex inorganic chemistry including K, Ca, Ti, V, Cr, Fe, Ni, Cu, Zn, Ga, Br, Y, Zr, Mo, Nb, Th, and U. Not only is the presence of these metals interesting, but also their elemental distribution patterns and associations as revealed by 2D elemental mapping. This mapping indicates significant intra- and inter-sample heterogeneity. Two main end-member styles of elemental occurrences are identified: discrete point sources (nano-particles) and diffusive.

KEYWORDS: graphite, inorganic chemistry, Athabasca Basin, synchrotron

1 INTRODUCTION

‘Organics’ either graphite and carbonaceous matter (including hydrocarbons, bitumen) are commonly associated with many different styles of ore deposits globally (e.g. unconformity-type uranium, sediment-hosted base metal, and gold deposits) (see reviews by Parnell 1988, Giordano et al 2000). Indeed in many cases, the occurrence of these ‘organics’ have been linked to ore genesis.

While there has been a vast amount of work devoted to their organic geochemistry (Large & Gize 1996), little or no work has been devoted to their inorganic chemistry: after all they are for the most part combinations of C-H-O±S. Furthermore, most of this inorganic work has examined solid inclusions within the ‘organics’ (e.g. McCready et al 1999, 2003). Only a few workers have examined the inorganic geochemistry (e.g. Drennan et al 1999, Kucha & Przybylowicz 1999). Consequently, there is a need to understand this aspect.

Here we examine the geochemistry of graphite and carbonaceous matter from the basement rocks of uranium deposits and exploration plays in the Athabasca Basin, using micron-scale, synchrotron-based XRF. Not only is this issue important for understanding uranium deposits in Canada and globally, it also has applications to many other metallogenic systems. The ultimate aim is to develop this technique as an exploration tool for identifying prospective areas for mineralization.

2 ANALYTICAL TECHNIQUES

Due to trace element impurities being present in normal thin-section glass and mounting resin (e.g. Ti, V, Cr, Cu), the samples could not be analysed in-situ on a normal thin section. Furthermore, due to the high penetration of the x-ray beam, polished blocks can not be used. Consequently, a 50 µm thick polished or doubly wafer was made for each sample.

Each wafer was examined using a microscope equipped with a 40x lens to establish that no macro-mineral grains, such as pyrite were present. These free-standing wafers were then analyzed using synchrotron-based µXRF.

All data were acquired at beam line L at the Hamburger Synchrotronstrahlungslabor (HASYLAB) in Germany using monochromatic light with an excitation energy of 29
In order to process the data collected (e.g. deconvolution of the spectra, dead-time correction, element identification), the data were processed using either the AXIL or GEOPIXE software packages.

3 SINGLE POINT ANALYSIS

Single point spectral results indicate that all organics studied are not merely combinations of C-H-O±S (Fig. 1a,b). Instead, they contain a plethora of metals. These metals include both those that commonly show positive correlations with carbon in many rocks, such as Fe, Ti, V, Mo, and those more exotic elements that generally do not show a positive correlation with carbon, such as Pb, Cr, Rb, Br, and Sr. Furthermore, in many instances, it is highly probable that REE, Th, and U are present in small amounts, but are hidden due to complex peak-overlaps. The results show significant intra-sample and inter-sample heterogeneity to be present. To date over 25 different elements have been identified.

4 2D ELEMENTAL DISTRIBUTION MAPPING

Two dimensional mapping was undertaken on 4 samples. The results of two of these are shown in Figs. 2 and 3. Again, the results show significant intra-sample and inter-sample heterogeneity. Within the dataset, two end-member styles of elemental occurrences are identified: discrete point sources or ‘nano-particles’, and wide-spread or diffusive. However, certain elements may occur in different styles within different samples. Some of these associations are described in greater detail below.

Titanium is present as distinct, discrete accumulations, possibly indicating the presence of rutile, anatase or brookite nano-particles. Titanium shows intra-sample heterogeneity with respect to V; in one sample they behave like compatible elements (Fig. 3), while in another sample they behave like incompatible elements (Fig. 2).

Iron and S show a bivariate pattern within a single sample. In one instance, they show a similar distribution pattern, suggesting the presence of nano-pyrite crystals. However in another area, the most intense concentration of Fe does not correlate with the highest concentration of S. In contrast, the highest concentration of Fe correlates with the highest concentration of As and Se.

Zirconium and Y show similar distribution patterns, suggesting the possibility of zircon nano-grains. Both Th and U show broadly similar distribution patterns as Zr-Y, but Th appears to be more widespread than U.

In one sample (Fig. 3), Zn does not show a correlation with any other base / transition metals including Fe, whereas in Fig. 2, Zn does show a similar distribution to Fe and Co.

Neither Ni or Cu, show similar distribution patterns as As or Se, suggesting these elements are not present as arsenides or selenides. In contrast, Ni and Cu show differencing behaviour with respect to S; the former shows a positive correlation suggesting a nickel sulphide, where the latter shows the opposite, suggesting instead it is present in elemental form.

A number of elements do not show any relationships (e.g., Mo, Nb, Pb), suggesting they occur in elemental form.

5 CONCLUSIONS

The work presented here indicates that carbon material (graphite and carbonaceous mat-
ter) from the basement rocks of uranium deposits in the Athabasca is not merely a combination of C-H-O±S, but instead contains various metals. The 2D mapping indicates significant intra- and inter-sample heterogeneity, and highlights several interesting elemental associations. Two main end-member styles of elemental occurrences identified: discrete point sources or 'nano-particles' and wide-spread or diffusive. However, certain elements may occur in different styles within different samples. Future work will also focus on the quantification of the qualitative data presented here and assessing its possibility as a new geochemical vector to mineralization can be applied to a number of metallogenic systems (e.g. gold and base metals).

5 ACKNOWLEDGEMENTS

We would like to thank the SRC for financial support during this project. We also thank the SRC for permission to publish the study. We are indebted to the staff of beam line L, for all their help, both during data collection in Hamburg and for answering our numerous emails. We also thank Dr Chris Ryan from CSIRO, Australia, for his help with the GEPIXE package.

REFERENCES


schiefer, Poland. Economic Geology 94: 1137-1162.


Figure 3. Elemental distribution map of metals within carbonaceous matter from the basement of the Athabasca Basin.

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ABSTRACT: The North Australian Proterozoic hosts a large number of economic and sub-economic uranium deposits. The deposits occur in three districts: Alligator Rivers, Westmoreland and Mount Isa. Deposits of the Alligator Rivers and Westmoreland districts can be classified as unconformity-type, the deposits of Mount Isa, however, have seen little modern research and their origins remain more uncertain. The assemblage U-Zr-P-Ti suggests a carbonatitic fluid was involved. This is at odds with theories for genesis of the Alligator Rivers and Westmoreland deposits, which commonly invoke a role for basinal brines. More research is needed on the enigmatic Mount Isa deposits, particularly geochronology. The region remains exceptionally prospective for uranium deposits given virtual inactivity since the nineteen sixties.

KEYWORDS: Uranium, unconformity-type, carbonatite, North Australia

1 INTRODUCTION

Proterozoic unconformity-type uranium deposits account for a large proportion of global uranium production. There are three main areas of occurrence, the Athabasca Basin of northern Canada, the Proterozoic terranes of northern Australia, and Gabon in Central Africa. Deposits of northern Australia occur in three districts: Alligator Rivers, Westmoreland and Mount Isa.

Deposits of the Alligator River and Westmoreland districts can be classed as unconformity-type, based on proximity to a prominent unconformity dividing deformed Lower Proterozoic meta-sedimentary basement rocks from a cover of Middle Proterozoic coarse clastic rocks. A common feature of the orebodies is their obvious structural control. A major difference between the Australian and Canadian deposits is that the latter typically have much higher grades. The Nabarlek deposit is the highest grade uranium deposit yet found in Australia at 1.86% U₃O₈, while other Australian deposits range from 0.04% U₃O₈ to 0.52% U₃O₈ and average 0.34% U₃O₈.

2 MINERALIZATION

The Alligator Rivers and Westmoreland districts contain five major uranium deposits: Jabiluka, Ranger, Koongarra, Nabarlek and Westmoreland, and a number of lesser deposits and occurrences. Exploration was intense during the nineteen seventies but tailed off in the eighties and subsequently as the result of declining uranium price, creation of the Kakadu National Park and aboriginal land rights issues. Consequently the potential for major discoveries remains high.

The deposits are dominated by uraninite located in structural traps at, or close to, the unconformity between mainly flat-lying sandstone of the Middle Proterozoic Kambalda Formation and older Proterozoic meta-sediments and amphibolite. At Jabiluka and Koongarra uranium is locally accompanied by economic gold grades, and elevated Pd has been recognized at Jabiluka. Host-rocks are graphitic metasediments of the basement, or amphibolite in the case of Nabarlek. The deposits are hosted in areas of intense hydrothermal alteration that involved almost complete replacement of quartz and formation of magnesian chlorites (including sudoite) and white-micas. A variety of phosphate minerals are also locally enriched. The deposits of the Alligator Rivers district are hosted in greenschist facies metamorphic rocks that typically display prominent schistosity,
close to an unconformity with overlying sandstone of the Kombolgie Formation. The schistose rocks may have deformed by shear along schistosity planes rather than by fracturing. It is noteworthy that the Nabarlek deposit, which is almost an order of magnitude richer than the other Australian deposits, is hosted in massive amphibolite rather than schist.

The Coronation Hill deposit is perhaps an end-member of the unconformity-type in which the economic value of gold and the platinum-group elements outstrips that of uranium. This association has been rationalized as the product of co-transport in an oxidized, chloride-rich brine as preserved in fluid inclusions (Wilde et al., 1989; Mernagh et al., 1994). Discrete uranium and gold ore-forming events could also explain the association.

The auriferous Westmoreland deposit is hosted entirely within the Westmoreland Conglomerate, a lateral equivalent of the Kombolgie Formation. There are also numerous small occurrences hosted by the overlying Seigal Volcanics, typically containing high gold concentrations (e.g. Cobar II, El Hussen). The Pandanus Creek deposit hosted by felsic volcanic rocks is perhaps equivalent to Coronation Hill and in places contains spectacular gold grades. No deposits are known in the basement rocks beneath the Westmoreland Conglomerate, despite somewhat similar geological setting to the South Alligator Valley. This may be because of the paucity of outcropping greenschist to amphibolite facies meta-sediments similar to the Cahill Formation of the Alligator Rivers region.

3 MOUNT ISA DISTRICT

The Mount Isa District is the least studied of the three districts but contains Australia’s second largest undeveloped resource at Valhalla (41,500 tonnes U₃O₈) and one of its most productive mines at Mary Kathleen with production estimated at 12,000 tonnes U₃O₈.

Valhalla is hosted by meta-basalt and intercalated meta-sediment of the Eastern Creek Volcanics. Recent unpublished work by Geoscience Australia suggests that this is a lateral equivalent of the Seigal Volcanics.

A substantial portion of the uranium at Valhalla is present as fine uraninite inclusions in allanite. REE enrichment is a feature of the ore and a potential REE resource exists in tailings at the now-abandoned mine.

The smaller Anderson’s Lode deposit is hosted by magnetite-rich meta-sedimentary interlayers of the Eastern Creek Volcanic basalt sequence. Uranium occurs as Y-rich brannerite, and is associated with anatase andapatite (Gregory et al., 2005). Post-replacement deformation has concentrated brannerite and anatase into pressure dissolution seams rimmed by apatite. These pressure dissolution seams are cut by quartz-chlorite veins, which are in turn cut by the metamorphic cleavage defined by biotite and chlorite that is attributed to the peak of the Isan Orogeny. A positive correlation between gold and uranium grades has also been recognized but the paragenetic relationship between the two elements is currently unknown.

At the Mount Kelly copper deposit, copper is superimposed on an early uranium-phosphate association, which may be an indication that the later copper deposition utilized pre-existing structural pathways.

4 GENETIC MODELS

Geochemical process models for the Alligator Rivers and Westmoreland deposits typically involve oxidized ore-forming brines derived from the cover rocks, with contributions from halite dissolution, bittern brines and/or atmospheric oxygen (e.g. Wilde et al., 1989). Some authors, however, have proposed that fluids emanating from the basement rocks are being crucial to ore formation.

The deposits of Mount Isa appear superficially different to those of the Alligator Rivers and Westmoreland districts. The distinct association of U with Zr, P, CO₃ and Ti suggests the possible involvement of carbonatitic fluids. This raises the question of whether carbonatitic fluids were involved in the genesis of the unconformity-related deposits. Lack of geochronological data for the Mount Isa deposits precludes a definitive answer to this question.

Hypotheses concerning the depositional process vary from wall-rock reaction (reduction) to mixing, and remain controversial. Mixing fails to account for the common association between unconformity-type deposits and redundant rocks since host-rock lithology is chemically unimportant if mixing is the key chemical process, which implies that exploration should
focus on specific rock-types. Paradoxically, mixing of chemically contrasting fluids is perhaps inevitable in such a geological environment. Mixing is unlikely to occur in the absence of rock, so rock buffering is likely to be critical even if mixing of chemically distinct fluids was occurring.

Little attention has apparently been devoted to the role of deformation and rock mechanics in ore genesis, some authors preferring to regard ore deposition as a consequence of basin evolution, and therefore perhaps representing an equivalent of the Palaeozoic sandstone-type deposits. Canadian examples are hosted in meta-sediments that have experienced a higher metamorphic grade and as a result are more mechanically isotropic. This may account for higher grades seen there.

Deposits of Gabon, including the famed Oklo deposit, and vein-type deposits of the Erzgebirge of Eastern Europe share some of the key characteristics of the unconformity-type, and thus such deposits may be more widespread than commonly supposed. The deposits of Gabon as well as those of Westmoreland show that deposits can be expected well above the unconformity as well as below it, and that the term unconformity-type or unconformity-related needs reconsideration.

ACKNOWLEDGEMENTS

Some of the work on uranium Mount Isa deposits presented here was conducted under the auspices of the predictive mineral discovery CRC. I acknowledge the contribution to this work of Melissa Gregory and Peter Jones on mineralogical and structural aspects, particularly.

REFERENCES


Geochemistry of Sandstone-Type Uranium Deposits in the Mesozoic Ordos Basin, North China

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ABSTRACT: A genetic model is proposed for uranium mineralization in the Ordos Basin in North China based on lithogeochemical as well as C and O isotope analyses of uraniferous sand- and mudstone samples, as well as carbonate cement within the sandstone. A positive correlation between uranium content and the concentrations of LREEs, Ti, V, Zr, Mo, Au, and highly variable, but generally very low Th/U ratios point to a post-depositional, low-temperature hydrothermal origin of the U-mineralization from oxidizing surface waters that were heated up due to Cretaceous magmatism. Higher Th/U ratios reflect a minor contribution from pre-existing detrital U-minerals in the sandstone. The $\delta^{13}$C$_{PDB}$ and $\delta^{18}$O$_{SMOW}$ ratios of matrix carbonate range from -4.2‰ to -23.62‰, and 10.32‰ to 19.52‰, respectively. These results support a hydrothermal model and point to a variable contributions from biogenic C, which was mobilized from deeper stratigraphic units.

KEYWORDS: sandstone-type uranium deposit; carbon and oxygen stable isotopes; Ordos Basin

1 INTRODUCTION

The Mesozoic Ordos Basin in northern China covers an area of approximately $2.5 \times 10^7$ km$^2$. It is bordered by the Yimeng Uplift in the north, the Weibei Uplift in the south, the Western Fold and Fault Belt in the west, and the Western Shanxi Flexure Belt in the east (Fig. 1). With oil and gas resources of $86 \times 10^8$ tons and $11 \times 10^{12}$ cm$^3$, respectively, it is the third most important basin in terms of multi-energy resources in China (Liu 2005).

Recent exploration programmes have led to the discovery of a number of in-situ leachable (ISL) sandstone-hosted uranium deposits in the Ordos Basin. This includes the Dongsheng uranium deposit, which has the potential of becoming a world-class ISL uranium deposit (Di 2002; Chen 2002; Xiao et al. 2004a, b; Yang et al. 2006).

The genesis of the uranium deposits, however, remains unresolved. In this study, we present new lithogeochemical, and C and O stable isotopic data to elucidate the formation of the uranium deposits in the basin.

2 BASIN EVOLUTION

The Mesozoic strata of the Ordos Basin are underlain by a typical sequence of North China Block Palaeozoic passive margin and cratonic sedimentary rocks. Studies of the sedimentary geology of the basin, supported by a new method of reconstruction for younger deformation, demonstrate that the basin filled from three sides by fluvial, lacustrine-deltaic and alluvial fan depositional systems (Ritts et al. 2004).

The evolution of the Ordos Basin is related to gradual uplift along the eastern margin of a precursor basin after the late Jurassic, in response to syn-Himalayan tectonic movement, which led to the progressive shifting of the eastern basin boundary towards the west. As a result, the former sediments were eroded. The residual basin remained deeper in the west and shallower in the east until the late Jurassic. Sedimentation in the Ordos Basin ceased in the early Cretaceous when the entire region was uplifted.

Most of the deformation that accompanied the initial widening and eventual shrinking, of
the basin took place along the basin margin, while internal basin deformation was subordinate (Liu 1998; 2005; Zhang 2004; Darby & Ritts 2002; Ritts et al. 2004). Fluid inclusion data from the uranium-bearing sandstone indicate a post-depositional low-temperature alteration of the basin fill, which was probably related to the formation of the uranium deposits (Yang et al. 2006).

4  RESULTS

4.1  REE and trace elements

Scanning electron microscopy and electron microprobe analyses show that most of the uranium minerals occur as minute (<1 µm) inclusions within potassic feldspar, quartz, muscovite and the intergranular cement with the uranium contents of 1 to several percents. In addition a few larger particles (>100µm) of uraninite and monazite were also observed in the sandstone.

The U bearing minerals are also rich in Th and REE (Yang et al. 2007). Whole rock ΣREE contents range from 57.3 to 804.2 µg/g; mudstone samples generally have a higher REE content than the sandstone samples. Relative to the European Continental Shale composite (ESCC), the analyzed samples show an enrichment in LREE (La-Nd), a mild depletion in middle MREE (Sm-Ho) and strong depletion in the HREE (Er-Lu). Most of the samples display a positive Eu anomaly. In addition to U and LREE, there is a pronounced enrichment of Rb and Pb. The latter is most likely due a radiogenic Pb component; U reaches up to 150 µg/g (on average 67 µg/g) in the analyzed samples. A positive correlation exists between U and Ti, V, Zr, Mo and Au, whereas Sr negatively correlates with U. While some of these correlations can be explained by differential elemental mobility within a single hydrothermal fluid, the U-Zr and U-Ti correlation might suggest that some of the uranium is present within the detrital phases, although a high U-Ti correlation may also suggest that some of the uranium is present as uranium titanates within the sandstone (UTi2O6), however, we have not detected this mineral with SEM scan, nor the other investigators.

Thorium concentrations correlate well with ΣREE concentrations. The Th/U ratio varies

Carbon and oxygen stable isotopic measurements were carried out on the the carbonate cement of sandstone samples using the conventional phosphoric acid treatment method of McCrea (1950). The isotope ratios were measured using a Delta+ mass spectrometer at the School of Earth and Space Sciences, University of Science and Technology of China. The PDB and V-SMOW standards were used, and an overall analytical precision of better than ± 0.2‰ was achieved for the δ13C and δ18O measurements.

Figure 1. Schematic map of the Ordos Basin and its position in China.

3  ANALYTICAL TECHNIQUES

Whole rock geochemistry was carries out on a total of 46 samples of sandstone and mudstone. Ground sample powders were dissolved in 5 ml of mixed HNO3 and HF (1:5) following the method of Liu et al. (1996). In the late stage of dissolution, 0.5 ml HCl was added. The solutions where then analyzed for their trace, including rare earth element (REE) concentrations using a Thermo VG Elemental high precision ICP-MS Plasma Quad 3 instrument in the Physical-Chemical Lab Center of the University of Science and Technology of China. The analytical errors are within 2-5%, as determined by routine analyses of the Chinese standards GSR-4 (quartz sandstone) and GSR-5 (shale).
greatly from 0.04 to 10.6, but is generally low to very low (Fig. 2). These high Th/U ratios support a low-temperature hydrothermal introduction of most U into the host rocks, whereas, these low Th-U ratios may also similar to bulk crustal values.

4.2 C-O stable isotopes

The total C content of the carbonate-bearing sandstone matrix ranges from 0.5 to 16.1 wt%. Isotopic analysis of carbonate cement from the weakly uraniferous sandstone reveals relatively large variations in $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$, from -4.2 to -23.62 ‰, and from 10.32 to 19.52 ‰, respectively (Fig. 3). The lower $\delta^{13}C_{PDB}$ values (-10 ‰ to -23.62%) can be explained by the addition of bitumen during low-grade hydrothermal alteration of the sandstones. The positive relationship between carbon contents and U contents are seen.

5 CONCLUSIONS

On the basis of new lithogeochemical and stable isotope data on the U-bearing sandstones and mudstones in the Ordos Basin, two major conclusions on the genesis of the U mineralization are drawn:

(i) Introduction of U into the host sandstone was largely due to post-depositional low-temperature hydrothermal infiltration that results in an enrichment of Rb, V, Mo, and Au. The presence of U in detrital heavy mineral phases also contributes to the overall uranium budget.

(ii) The mineralizing fluid was oxidizing in composition. this fluid was probably derived from the circulation of surface waters and ground water that was heated by Cretaceous magmatic activity. The hydrothermal introduction of U was accompanied by carbonate precipitation in the host sandstone. The mineralizing fluid also carried variable proportions of biogenic bitumen. The source of the bitumen is speculated to be the lower part of the sedimentary rocks in Ordos Basin, i.e. Ordovician carbonate rocks that are rich in oil and natural gas.

ACKNOWLEDGEMENTS

This study is supported by the China 973 National Key Research and Development Program (2003CB214606).

REFERENCES


Di Y (2002) Preliminary discussion on prospecting potential for sandstone-type uranium deposits in Meso-Cenozoic basins, northern Ordo. Uranium...


Reactive transport modeling of roll front (sandstone) uranium deposits.

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ABSTRACT: This study presents the results of a fluid flow-thermal-chemical reactive transport model of roll front uranium deposits, using some South Australian deposits as an example. This model simulates fluid flow from a topographic high, consisting of granite rich in uranium, to an area of topographic low, within a palaeochannel which consists of reduced clays and oxidized sand and gravel layers. This model shows that oxidized fluid strips uranium from the granite and transports it along the palaeochannel. At reduced environments within the palaeochannel uranium is deposited as uraninite. The resulting deposition and associated alteration assemblages within the model reproduce what is observed within roll front deposits, showing how reactive transport modeling can result in improved genetic concepts and lead to more predictive mineral exploration.

KEYWORDS: uranium, roll front, reactive transport, modeling

1 INTRODUCTION

Australia is now the world’s second largest producer of uranium with 4.4% of its resources coming from roll front (sandstone) type deposits (Geoscience Australia: AusGeo News 80). Well known examples of these include Beverley and Honeymoon in the Frome Embayment field, South Australia. Roll front deposits are also the second most important source of U.S. reserves in Uranium (Adams 1991).

Current genetic models from the U.S suggest that uranium was derived from oxidized tuffaceous sediments, dissolved as bicarbonate complexes, transported by compaction and gravity flow, and precipitated as insoluble tetravalent oxides in reducing zones. Genetic models for South Australian deposits suggest that the uranium may be sourced from granites with high levels of uranium. Equilibrium chemical modeling and reactive transport modeling are powerful tools that can be used to understand the key processes involved in forming roll front uranium deposits. Using a 2D cross section of a palaeochannel, reactive transport modeling will allow us to test and potentially rank host lithologies and/or reductants, predict areas of focused flow, and assess the likelihood of a given horizon or lithology to be an economic host, leading to a more predictive approach to mineral exploration. To illustrate this approach, a reactive transport model based on roll front deposits of South Australia with topographical fluid flow and reactions associated with uranium-bearing granite and palaeochannel is presented.

2 METHODOLOGY OF MODELING

2.1 Initial chemical modeling

The oxygen activity and the pH of the fluid are considered the most important factors controlling uranium solubility. Geochemical modeling was undertaken using The Geochemist Workbench (Bethke, 2002) to calculate stability diagrams to show the stability of uranyl species and uraninite in the presence of rain water (equilibrated with felsic material). The Geochemist Workbench utilizes the thermodynamic data set entitled “thermo.dat” based on Wolery (1992) to calculate and plot stability diagrams on pH and fugacity axes. Figure 1 shows that uranyl carbonate complexes are the most stable in oxidised waters with the $a[\text{U}]=10^{-5}$, $a[\text{H}_2\text{O}]=1$, $a[\text{HCO}_3^-]=10^{-2.046}$, $a[\text{Cl}]=10^{-3.699}$,
\(a_{[SO_4^-]}=10^{-5.505}\) at 25°C and 1 bar, to represent the fluid associated with roll front deposits. This diagram shows that uranium will be transported by an oxidized fluid as a carbonate complex and precipitate from solution as uraninite as the fluid becomes reduced.

This diagram represents a 12 x 2.35km cross section (Fig. 2) consisting of a high heat producing oxidized granite at the topographic high, an oxidized basement and a palaeochannel high, an oxidized basement and a palaeochannel filled with various layers of sandstones, reducing clays and gravel.

2.2 Reactive transport modeling

Reactive transport modeling incorporates the coupling between fluid flow, heat, transport and chemical reaction processes. PmdPyRT (P. Hornby, pers. Comm., Cleverley et al., 2006) is the code used in this study. This code consists of a collection of programs specifying physical parameters, and couples a partial differential equations solver with WinGibbs, a Gibbs Energy minimization solver (Shvarov & Bastaakov, 1999) to solve for equilibrium chemistry using finite element geometry.

Within the program the initial chemistry is defined as solids in terms of volume fraction of minerals (non solid solutions) and fluids as moles or molality in the fluid phase. Within this model topographic fluid flow is imposed by fluid pressure gradients. Heat is transported by conduction and convection (in the moving fluid phase). Solute transport is by diffusion and advection with fluid being equilibrated with the rock after each fluid flow step.

3 A REACTIVE TRANSPORT MODEL OF URANIUM ROLL FRONT DEPOSITS

3.1 Model specifications

The reactive transport model presented here represents a 12 x 2.35km cross section (Fig. 2) consisting of a high heat producing oxidized granite at the topographic high, an oxidized basement and a palaeochannel filled with various layers of sandstones, reducing clays and gravel.

The model is initialized with the top boundary fixed at a pore pressure of 0.1 MPa with a hydrostatic pore pressure gradient and a temperature of 25°C to represent conditions at the surface. The fluid flow paths are shown in Fig. 3. A radiogenetic heat component of \(2.23E-9\) W/kg is added to the granite region to represent the high heat producing granites of the Hiltaba suite (considered to be the source of uranium). The heat flux is allowed to equilibrate with the surrounding geotherm, so that the resulting geotherm is slightly raised in the area of the granite. The initial permeability of the model is shown in Fig. 4. The permeability is calculated as a function of depth based on experimental data and calculations of Shmonov et al (2003).

The initial mineralogy of the rock units was as follows, Oxidised basin: quartz, haematite, kaolinite, clinochlore and chamosite; Granite: quartz, K-feldspar, uranium, anorthite, albite, magnetite and muscovite. The initial fluid composition in the granite and basin regions is oxidized Ca-Na-bearing brine that is equilibrated with the initial mineralogy of the granite. The initial palaeochannel mineralogy consists of Oxidized sands: quartz, haematite, muscovite, and kaolinite; Gravel: quartz, hematite, muscovite, kaolinite and clinochlore. These regions are in equilibrium with a fluid containing H\(_2\)O and NaCl. The palaeochannel also consists of regions of Reduced sands: quartz, K-feldspar, muscovite, kaolinite, pyrite, calcite; and Re
Fig. 3 Vector arrows that indicate the general direction of topographically driven fluid flow. It is shown that recharge occurs at topographical highs and discharge occurs at topographical lows. The scale of the model is in km.

Fig. 4: Permeability values across the model. The scale of the model is in meters.

Reduced clay: quartz, graphite, albite, anorthite in equilibrium with a fluid containing H₂O, NaCl and H₂S.

3.2 Alteration assemblages and uraninite precipitation patterns

Figure 5 shows the concentration of uraninite, at three different points, along the reduced clay layer of the palaeochannel over time. Point A is closest to the granite, and so the oxidized uranium-bearing fluid encounters this reducing environment early in the evolution of the model. Rapid increase in uraninite concentrations occur, until the infiltrating fluid consumes the last of the reductant. At this time conditions become oxidized so that the uraninite is dissolved by the fluid and transported down the hydrological gradient, until it encounters a more reduced environment. For example, in Fig. 5 it is shown that at a later time (approximately 4000 years) uraninite is deposited at Point B (located down the hydrological gradient from point A) and concentrated until conditions are oxidised and uraninite is dissolved. Finally, in Fig. 5, at point C (which is down the hydrological gradient from point B) it is shown that uraninite is deposited at approximately 2000 years but does not reach its highest concentrations until approximately 10 000 years.

The change in mineral assemblage at point C (where uraninite is being deposited within the reduced clay layer of the palaeochannel), over 30 000 years is shown in Fig. 6. As the fluid reacts with the rocks and deposits uraninite it also alters the mineral assemblage. Over time hematite modes increase while siderite disappears when uraninite concentrations are at their highest. At the initial stage of uraninite deposition (approximately 2000 years), albite and clinochlore modes increase, although both are not present after 10 000 years. Kaolinite is stable after approximately 8 000 years, when uraninite concentration is at its highest. Quartz modes are not shown in Fig. 6; initially there are 13.38 moles of quartz, this steadily increases over time to 19.9 moles at approximately 9000 years. These alteration assemblages and migrating rollfronts along the palaeochannel (down the hydrological gradient) over time reproduce...
the features of roll front deposits observed in nature (Adams, 1991).

Fig. 6. Mineral assemblage within clay layer of palaeo-channel, coordinate (5.691, 1.698), over time. The abundance of quartz is not shown here.

4 CONCLUDING REMARKS

Uraninite deposition in roll front type deposits is controlled by fluid flow and chemical processes. This involves reactions at redox fronts where an oxidized uranium-bearing fluid encounters a reducing agent so that uraninite precipitates from the fluid. It is shown that reactive transport modeling is a powerful tool that can be used to further our understanding of the processes which form roll-front deposits. Importantly greater understanding of fluid flow and the chemical processes involved in uranium transport and deposition will lead to more a predictive approach to exploration. This will be achieved by: predicting downstream and upstream alteration mineral assemblages; and predicting the consequences of lateral oxidation (produced by infiltration of oxidized uranium-bearing fluid) versus vertical weathering.

ACKNOWLEDGEMENTS

The Predictive Mineral Discovery cooperative Research Centre and PIRSA are thanked for their financial support.

REFERENCES

ABSTRACT: Uranium is concentrated in granite sheets in the Central Zone of the Damara Orogen at Rössing, Valencia, the Ida Dome, and Goanikontes. The alaskites range in composition from tonalite to alkali-feldspar granite. There are six types (A-F). Early pre-D3 types (A-C) are barren while post-D3 alaskites (D-F), which are more prospective for uranium, were emplaced post-D3 extensional fabric development and dome formation at upper-amphibolite facies. There is a stratigraphic control on the location of the mineralized alaskites close to the Khan-Rössing Formation boundary or to the Khan-Chuos boundary where the Rössing Formation is absent or highly attenuated. Structural controls on emplacement appear to be related to the transition from ductile to brittle deformation.

KEYWORDS: Namibia, uranium, controls on mineralization, leucogranites

1 REGIONAL OVERVIEW

Uranium-bearing granites in Namibia occur within the Central Zone of the Neoproterozoic Pan-African Damara Orogen, a polydeformed and polymetamorphic orogenic belt with a N-S trending coastal belt and an intracontinental branch trending northeastwards from the Atlantic coast (Fig. 1). The Central Zone is characterised by more than 300 granitoid intrusions which crop out over an area of at least 75 000 km². It is considered to represent the root zone of a volcanic arc associated with a subduction zone (Stannistreet et al., 1991). A NE trending structural grain dominates the Central Zone with a prominent elongate dome and basin pattern that developed during D3 deformation (Fig. 2). The Abbabis and Palmenhorst domes are cored by Abbabbis basement granite gneiss, while other domal structures consist either of Damaran sediments (e.g. Rössing Dome; Oliver & Kinnaird, 1996) or Damaran granites (Namibfontein Dome; Poli & Oliver, 2001) or combinations of the two (Palmenhorst Dome; Tack & Bowden, 1999).

Geochronological studies of the gneisses have resulted in various ages including c.2 Ga and c.1 Ga with a Pan-African overprint c. 560 Ma (Jacob et al., 1978; Kroner et al., 1991).
The upper Damara sediments (Swakop Group) comprise a basal pelitic schist (Chuos Formation) which is overlain by a major thickness of glacial diamictite, that is regarded as the Sturtian glaciation (Hoffman, 2005). Regional metamorphic grade increases towards the Atlantic coast. Early metamorphism was of upper amphibolite facies at < 4 kbar. Garnet-biotite geothermometry gives temperatures in the range 519-720°C (Nex et al., 2001b). Peak regional metamorphism probably occurred between 530-523 Ma at conditions of 750°C and 5-6 kbar (Jung & Mezger, 2003). A higher temperature granulite facies event which overprinted the D3 extensional fabric (Nex et al., 2001a) was probably induced by voluminous magmatism and was associated with significant amounts of partial melting of pelitic facies in the extreme west of the orogen (Masberg, 2000; Jung & Mezger, 2003).

2. PRIMARY URANIUM OCCURRENCES

The Rössing deposit, which now produces 7% of the world’s uranium, is the major primary deposit. However, other primary sheeted granite-hosted anomalies occur which are currently under exploration and evaluation at Valencia, the Ida Dome, and Goanikontes (Figure 3). There are six types of granite sheet shown in (A-F), three are barren of U mineralization and were pre-D3 while post-D3 alaskites are more prospective for uranium (Nex et al., 2001). The granites range from tonalite to alkali-feldspar granite in composition, in texture from granophyric, aplitic and fine-, grained to pegmatitic and in colour from white, through cream, to grey or pink. Sheets vary in size from a few cms in width to > 100 m across. Mineralogically, the leucogranites consist of quartz and a combination of microcline, albite or oligoclase, with <5% mafic minerals. Accessory minerals are varied although rarely abundant. The timing of granite intrusion and uranium mineralization at Goanikontes is indistinguishable (monazite and uraninite U-Pb ages of 508 ± 2 Ma and 509 ± 1 Ma respectively, Briqueu et al., 1980).

Uraninite is the dominant primary U-bearing mineral in the leucogranites with minor beta-fite, a Ti-rich pyrochlore, (Ca,Na,U,REE)_{16-x} (Nb,Ti)_{16} O_{48} (O,OH,F)_{8-y} zH_{2}O), and other pyrochlore-group minerals. In addition brannerite [(U,Ca,Ce) (Ti,Fe)_{2}O_{3}OH] and davidite [(Fe^{2+},REE,U,Ca,Zr,Th)_{6} (Ti,Fe^{3+},V,Cr)_{15} (O,OH)_{30}] may be present.

3. CONTROLS ON LOCATION OF MINERALIZED SHEETED GRANITES

There is a fundamental lithostratigraphic control on the location of all significant U-rich leucogranites. They are preferentially located close to the Khan-Rössing Formation boundary or the Khan-Chuos Formation boundary where the Rössing Formation is absent or highly attenuated. At Rössing Mine the open pit is subdivided by the Khan-Rössing Fm boundary. In
both the SH anomaly to the west of the pit and the SK anomaly to the east, the mineralized sheets also intruded at this stratigraphic level. At Goanikontes south, the Rössing Formation is largely absent. Here, the mineralized sheets are constrained stratigraphically to the upper part of the Khan Fm and the lower part of the Chuos Fm. At Goanikontes north, remnant Rössing Formation marble and calcsilicate occurs in contact with Khan Formation biotite-amphibole schist and this is where a significant U-anomaly is associated with abundant type E sheeted leucogranites. At Valencia, uraniferous granites cross-cut the Khan-Rössing Formation boundary and a small stock is emplaced primarily within the lower Chuos Formation (Rossner & Schreuder, 1998). On the east side of the Ida Dome, the uraniferous sheeted leucogranites are also located at the top of the Khan Formation.

The structural controls on emplacement of sheeted leucogranites varies with individual deposits, however, they all appear to be related to the transition from ductile to brittle deformation. At Rössing, U-bearing sheets are concentrated to the south and southeast of the Rössing Dome where alaskites are linked to late ductile to brittle deformation synchronous with sinistral transpression (Basson & Greenway, 2004). This occurred during anti-clockwise rotation of the Rössing Dome within bounding N-NE D4 faults with U-rich sheets emplaced in dilational sites during dome rotation. At Goanikontes, both mineralized and unmineralized sheeted leucogranites are confined to a high strain zone exhibiting ductile constrictional deformation adjacent to the basement-cover contact (Marlow, 1981; Nex, 1997). The high-strain zone is cross-cut by mineralized anastomosing composite sheets trending NE and dip steeply to the NW. The emplacement of the alaskites is believed to result from extension during orogenic collapse (Nex, 1997).

At Valencia, the main granite body occurs on the SE margin of a basement dome and intrudes across the Damaran stratigraphy in the core of an antiform on the NW limb of a major synform (Marlow, 1981: and maps in Roesner & Schreuder, 1992. At the Ida Mine, U-bearing sheets have intruded parallel to the contact of the metasediments and the basement dome. A later shear zone is coincident with these intrusions resulting in a significant amount of secondary uranium minerals. Fluid compositional controls on uranium deposition are linked to the change in lithology at the Khan-Rössing boundary. At this boundary between metapelites below and calcsilicate lithologies above, there is a change in redox potential. Uranium deposition occurred as granite sheets cross-cut methane-bearing Khan pelites and encountered the overlying Rössing marbles, which caused decarbonation and increased CO2 concentration in the vapour phase, leading to the boiling of the magma. Fluid extraction analysis showed that there is a contrast in the fluid compositions between the betafite-dominant SH area to the west of Rössing and the uraninite-dominant pit. Uraninite-bearing pit samples showed a total fluid content in excess of 10 µmoles/gm (typically 20-40 µmoles/gm) and low CO2/NC (non-condensibles), whereas fluid content in betafite-bearing SH samples was consistently low, typically 3-5 µmoles per gram with lower concentrations of NC phases and much higher CO2/H2O ratios (>3) (Herd, 1996; Nex et al., 2002). It is envisaged that betafite crystallisation was favoured by the CO2 flux that occurred in the roof of the small SH pluton which was emplaced close to the Khan-Rössing boundary. For Rössing pit, where the proportion of secondary minerals is higher than elsewhere, there is a greater amount of water-dominated total trapped fluids compared to betafite-bearing samples where the non-condensable component is lower and CO2/H2O ratios are much higher.

4. CONCLUSIONS

Uranium mineralization is associated with post-D3 granite sheets, which are predominantly alkali feldspar granite. Structural controls on alaskite emplacement appear to be related to the transition from ductile to brittle deformation. There is a stratigraphic control on the location of the mineralized sheets close to the Khan-Rössing Formation boundary or to the Khan-Chuos Formation boundary, where the Rössing Formation is absent or highly attenuated. Uranium deposition occurred as granite sheets cross-cut methane-bearing Khan Formation metasedimentary lithologies. Deposition was also favoured as alaskites encountered marbles which caused decarbonation, and thus increased CO2 concentration in the vapour phase, leading to the boiling of the magma. For Rössing, where the proportion of secondary minerals is higher than elsewhere, there is a greater amount of water-dominated total trapped fluids compared to betafite-bearing
samples where the non-condensable component is lower and \( \text{CO}_2/\text{H}_2\text{O} \) ratios are much higher.

ACKNOWLEDGEMENTS

Special thanks to the staff at Rossing Mine for their enthusiastic support and encouragement and especially to Jim Gorman who first initiated our research.

REFERENCES


Jung, S., and Mezger, K. 2003 U-Pb garnet chronometry in high-grade rocks - case studies from the central Damara orogen (Namibia) and implications for the interpretation of Sm-Nd garnet ages and the role of high U-Th inclusions. *Contributions to Mineralogy and Petrology* 146: 382-396.


Source characteristics of U-enriched leucogranites of the Svecofennian orogen in southern Finland

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ABSTRACT: Palaeoproterozoic late orogenic leucogranites (~1.85-1.79 Ga) of the Svecofennian orogen in southern Finland are typical U-enriched leucogranites with U values grossly in excess of average upper crustal values. These rocks are mildly peraluminous and strongly heterogeneous, both in terms of texture and elemental composition. Their initial Nd isotope composition reveals varying mixtures of metavolcanic and metasedimentary source components, Pb isotopes imply a source enriched in U.

KEYWORDS: leucogranite, uranium, Nd isotopes, Pb isotopes, Finland.

1 INTRODUCTION

Peraluminous leucogranites worldwide are a potential source for uranium (e.g., Friedrich et al., 1987 and references therein). They are considered to represent crustal melts and their inherent petrographic and geochemical heterogeneity has been ascribed to inadequately blended melt batches extracted from a range of metasedimentary sources (Kemp & Hawkesworth, 2003 and references therein). Uraniferous leucogranites are enriched in U and Th relative to upper crustal values (2.7 ppm and 10.5 ppm, respectively; Rudnick & Gao, 2003) by an order of magnitude or so. Their major primary carriers of U are zircon, monazite, apatite, uraninite, and uranothorite. The low Th/U character of most uraniumiferous leucogranites indicates that a major part of U resides in uraninite, which is an early precipitate in reduced peraluminous melts. We present Nd-Pb isotope and elemental geochemical data for a suite of leucogranites from the Svecofennian orogen in southern Finland. These high U leucogranites were presumably crystallized from magmas with high and quite varying uranogenic Pb isotope ratios, necessitating a high U source.

2 GEOLOGIC SETTING

The bedrock of southernmost Finland (Fig. 1) is dominated by K-rich, migmatizing, anatectic leucogranites (the late Svecofennian granite-migmatite zone; LSGM zone; Ehlers et al., 1993) that were emplaced between 1.85 and 1.79 Ga (Kurhila et al., 2005 and references therein). LSGM zone is probably related to a collision that took place after the 1.89-1.87 Ga peak of the Svecofennian orogeny (e.g., Lahtinen et al., 2005 and references therein). The host rocks for the granites are Svecofennian 1.89-1.87 Ga volcano-sedimentary and plutonic rocks. Three low P/high T metamorphic domes are found in the LSGM zone and have peak metamorphic ages coinciding with the crystallization ages of the leucogranites (Korsman et al., 1984; Mouri et al., 2005). The LSGM zone is composed of relatively small granite intrusions, dykes and pods, as well as mm- to cm-scale in situ granitic leucosomes. Contacts to the surrounding rocks may be gradational or sharp and partly digested xenoliths are common. The leucogranites have also been deformed after emplacement (e.g., Stålfors & Ehlers, 2006).

3 GEOCHEMISTRY OF THE LSGM ZONE LEUCOGRANITES

3.1 Whole-rock geochemistry

The SiO$_2$ content of the samples in this study spans a relatively wide range, from 67 to 78 wt.%, with the lowest values probably resulting
from episyenitization. The leucogranites are peraluminous (A/CNK 1.04-1.55) and leuco-
cratic (FeO* + MgO + TiO₂ 1.3-3.7 wt.%). Most trace elements have wide ranges of values (e.g., Ba 45-1693 ppm, Rb 85-290 ppm, Sr 40-
230 ppm, Zr 20-435 ppm, total REE 56-616 ppm). These granites are strongly enriched in U (6-791 ppm, median 31 ppm) and moderately
enriched in Th (1.6-180 ppm, median 42 ppm). Most of the samples show low Th/U (≤ 1).

3.2 Isotope geochemistry

3.2.1 Nd isotopes

The twelve samples analysed for Nd iso-
topes have quite varying ¹⁴⁷Sm/¹⁴⁴Nd ratios (0.0991-0.2703), eNd (at 1830 Ma) values (from -11.3 to +1.7; Fig. 1) and TDM model ages (De-
Paolo, 1981) (from 1974 to 3434 Ma). Nine of
the eNd (at 1830 Ma) values fall into two
groups, with averages at -2.5 and -0.5. In a Sm-
Nd isochron diagram (Fig. 2), the groups define
trends that correspond to ages that match the
overall crystallization age of the leucogranites.
Three other samples have either higher (+1.7)
or lower (-3.5 and -11.3) eNd (at 1830 Ma) val-
ues.

3.2.2 Pb isotopes

Pb isotope compositions of leached K-
feldspar fractions from the twelve samples are
presented in Fig. 3. Overall, the uranogenic Pb
isotope ratios of the granites are extremely variable: ²⁰⁶Pb/²⁰⁴Pb ranges from 16.092 to
24.205 and ²⁰⁷Pb/²⁰⁴Pb from 15.383 to 16.797
(Fig. 3A). In contrast, the thorogenic ratio is
almost constant, ²⁰⁸Pb/²⁰⁴Pb values are between
35.289 and 35.617, except for the low eNd gra-
nite that has ²⁰⁸Pb/²⁰⁴Pb ratio of 36.875 (Fig.
3B). The spread in the initial uranogenic Pb iso-

Figure 1. Schematic geologic map of the LSGM zone in southern Finland. Modified from Korsman et al. (1997).

Figure 2. Sm-Nd isochron diagram showing Nd isotope composition of twelve leucogranites from the
LSGM zone. Trends and corresponding ages for two granite subgroups are shown, as are compositions of 
Palaeoproterozoic metasedimentary and metavolcanic rocks from the Svecofennian orogen (Kähkönen,
2005).
The two \( \varepsilon_{\text{Nd}} \) groups (-2.5 and -0.5) yield Sm-Nd isochrons with ages that are compatible with the overall U-Pb ages of the LSGM zone granites (cf. Kurhila et al., 2005). The initial Nd isotope compositions of the groups probably reflect slight source variation. Fig. 2 also shows the Nd isotope composition of 29 metasedimentary rocks and 9 silicic and intermediate metavolcanic rocks from the Finnish Svecofennian. The former have \( \varepsilon_{\text{Nd}} \) (at 1830 Ma) values between -4.1 and +0.4 (median -2.2), the latter between -1.5 and +2.5 (median +1.9). The leucogranites of the less radiogenic group (\( \varepsilon_{\text{Nd}} \)-2.5) thus have Nd isotope compositions that match a Palaeoproterozoic metasedimentary source. The higher \( \varepsilon_{\text{Nd}} \) group (-0.5) is slightly more radiogenic and, therefore, implies a somewhat more radiogenic source, and possibly also a larger volcanic source component.

The Pb isotope composition of galena from veins and pods associated with Svecofennian supracrustal rocks (Vaasjoki, 1981) form a tight cluster near the ~1.8 Ga segment of the Stacey and Kramers growth curves (Fig. 3A, B). According to Vaasjoki, these galenas represent a regionally representative, well-mixed crustal component of the Svecofennian orogeny. The leucogranite feldspars have evidently preserved the initial heterogeneities of Svecofennian crustal units and provide a window to see through the orogenic mixing processes that homogenized the isotope composition of Pb incorporated into the galenas.

**REFERENCES**


Tectogenesis of the uranium-rich Paralana Mineral System within the Mt Painter Inlier, South Australia

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ABSTRACT: A method known as tectogenetic analysis applied in the areas of existing uranium occurrences within the Mt Painter Inlier has led to the identification of structural controls on mineralization. Geological mechanisms during the mineralizing processes, which are also tectonic of nature, produced tectonic breccias and other extensional structures. These were propagated from the basement concurrently with the development of the epigenetic hydrothermal processes allowing the formation of the uranium-rich zones. Based on tectogenetic analysis, a predictive exploration model of the area was developed allowing the identification of the Paralana Mineral System. It is now considered as a major uranium-rich ore system in Australia. Investigation of ore genesis found uraninite as the main ore mineral in the system. The tectogenetic predictive model that was developed indicates the location and geometry of structural features controlling the uranium distribution, including grade variability and thickness of U-rich zones, and potential location of unknown areas of mineralization within the Paralana Mineral System.

KEYWORDS: U-ore system, tectogenetic analysis, tectonic genesis, hydrothermal, basement tectonics, predictive model

1. INTRODUCTION

The uranium-rich Paralana Mineral System (PMS) is located in South Australia, where suitable geological and ore forming processes have led to the formation of major uranium deposits, including Olympic Dam (Cu-U-Au) with the largest U concentration in the world, and the Beverley sandstone-hosted type deposit, which is an ISL extraction operation placed within top 10 uranium mines in the world (Fig. 1).

The PMS appears in an area historically known as Mt Gee or Mt Painter in the SW part of the northeasterly trending Mt Painter Inlier. It represents Proterozoic and Palaeozoic rocks of the NW margin of the Curnamona Craton, which is a host to world-class Broken Hill Pb-Zn and other deposits (Fig. 2).

2. EXPLORATION BACKGROUND

Presence of uranium in the Mt Painter Inlier was reported from almost the beginning of the 20th century, however, in the last 50-60 years the area has been intensively explored. An extensive geological and drilling database was generated by the government and a number of exploration companies. Historical exploration
work and interpretation provided important information on the geology and indicated the presence of U-mineralization (Fig. 3). As a result, a number of localized near-surface uranium occurrences throughout the area were identified, from which small amounts of high-grade uranium ore were mined. Despite intensive drilling and small scale mining a number of geological and mineralization factors remain unexplained. These include the geological criteria and mechanisms governing the development and distribution of uranium mineralization. Hence, the exploration potential of the area has never been satisfactorily explained.

A hypothesis exists that localized uranium occurrences of the Mt Painter area are related to the middle Palaeozoic stages of magmatism, particularly Ordovician, granite intrusive and thermal activities (Drexler & Major 1990, McLaren et al 2002, Elburg et al 2003, Bakker, & Elburg 2006). These developed alteration and uranium mineralizing processes within a Proterozoic granite/gneiss suite (the host rock). Although the alteration processes of the host crystalline rocks display a progressive change into hydrothermal activities (Bakker & Elburg 2006), there is no evidence or data, which in this view would suggest a role of tectonic deformation or structural control on U-mineralizing and ore system forming process.

### 3. METHOD OF INVESTIGATION

A method of tectogenetic analysis of the U occurrence area in the SW part of the Mt Painter Inlier has been used in this study to provide a better understanding of the geological processes leading to the uranium mineralization. This analysis is an alternative method of investigating the tectonic deformation of host rock to determine the controls on a mineralized system. It has been applied successfully in many projects for a number of commodities. In this study, application of the tectogenetic analysis was aimed at providing the understanding for, and explanation of:

- the geological nature of the mineral system and its relationship to the host rock,
- the criteria governing the distribution of mineralized zones,
- the controls on uranium mineralization and grade distribution,
- the mineral composition and ore genesis of the mineral system,
- the exploration and resource potential of the PMS, and
- the regional exploration potential in the NW part of the Curnamona Craton.

Results of the tectogenetic investigations have allowed revision of hypotheses suggesting the localized and dominant role of granite alteration-related mineralizing processes, and provided evidence that the PMS is a major structurally controlled U-carrying mineral system (Figs. 3 & 4). At present, it is considered as one of the largest uranium-rich mineral systems in Australia.
4. TECTONIC GENESIS OF THE PARA-LANA MINERAL SYSTEM

The tectogenetic analysis has demonstrated that PMS extends SW–NE over a distance of at least 11-12km and its origin is closely linked with the formation of the Paralana Fault System (PFS). The PFS is a principal tectonic feature of the Mt Painter Inlier. It displays a SW–NE trend, parallel to the Mt Painter Inlier, and multiphase development. The PFS was propagated as a reverse-slip tectonic structure, NW up/SE down, with a sinistral horizontal component of movement (Fig. 4). It is interpreted that the development of a SW–NE oriented regional deep crustal tectonic break in the basement of the Mt Painter Inlier is a tectonic reason for the PFS formation and its multistage development.

The formation of the PMS was associated with secondary tectonic processes taking part in the PFS development. These processes were propagated using pre-existing tectonic structures produced during earlier metamorphic recrystallisation and tectonic evolution phases of the Proterozoic host rock. As a result, migration and deposition of uraniferous fluids in tectonic breccia zones and zones of tectonic extension (veins and extensional openings) produced the structurally controlled Paralana ore/mineral system (Bogacz 2006). The system displays its own specific geometry and Kinematics (Fig. 4). Tectonic processes and accompanied mineralization were progressively developed from the deeper basement upwards and from NE towards SW. The maximum development is observed in the SW part of the PMS in an area with the most intensive gradients of a negative gravity anomaly (2.5 mgal) identified beneath the SW-NE extent of the PMS. Here Marathon Resources documented, defined and re-discovered the Mt Gee deposit, with further exploration potential open in all directions. Current estimates indicate an Inferred Resource 59 Mt uranium mineralization with 0.062% U₃O₈ average grade containing near 37,000t (about 80 M lb) uranium oxide.

Based on tectogenetic analysis a conceptual geometric model for the system was developed and applied in the exploration strategy (Fig. 4). As a result of exploration and drilling, apart from Mt Gee, other structurally controlled uranium deposits and prospects of the PMS were defined or re-discovered, including the Hodgkinson and Armchair deposits. The tectogenetic model suggests a significant exploration and resource potential in the near surface zones and in deeper levels of the PMS. This is consistent with the directions of propagation of the PFS due to a deep basement fracture activity during the mineralizing processes. This supports a hypothesis that the PMS is predominantly an epigenetic hydrothermal system developed in a basement propagated extensional tectonic regime.

5. GENESIS OF ORE

Analysis of the historically generated petrological database indicates that the dominant host rocks of the PMS, apart from a less important Palaeoproterozoic metasediments, are Mezoproterozoic crystalline rocks, granite/gneiss, syeno-granite and syenite intrusives containing magnetite, monazite, haematite and other mineralogical components. During the
processes forming the PFS/PMS, multiphase tectonic breccias and extensional tectonic deformation zones such as the extensional fault network and the fracture and microfracture zones, accompanied by uranium mineralization stage(s), developed. The U-rich breccias and extensional structures containing haematite, chlorite and minor sericite, quartz, chalcedony and carbonates, essentially form the PMS. Uraninite and pitchblende are dominant ore minerals of the PMS (Fig. 5). In some areas the uraninite is accompanied by much less frequently observed coffinite (Fig. 6).

Dating of unusually large uraninite crystals from the Mt Gee deposit, up to 6 mm size and containing more than 20 zones of observed growth, suggests multistage U-mineralizing processes and their late Palaeozoic, about 290 Ma age. The historical evidence indicates a middle-late Palaeozoic age for the mineralization (McLaren et al 2002, Elburg et al 2003, Bakker & Elburg 2006).

6. CONCLUSIONS

(1) Application of tectogenetic analysis has led to the identification of the PMS within the Mt Painter Inlier, and the re-establishment of the area as a major uranium-rich province.

(2) The study results indicate that the PMS is an epigenetic hydrothermal ore system. It is controlled by breccias and secondary extensional structures of the PFS, which is a SW–NE trending basement-propagated fault system.

(3) The PMS is dominated by uraninite. The ore system’s geometry, the thickness of ore zones, and the ore grade distribution are strongly determined by a specific tectonic structure pattern. The proposed tectogenetic model yielded predictive structural criteria used in the PMS exploration strategy. Consequently, the very large Mt Gee deposit and a number of other uranium deposits and prospects of the PMS were identified.

(4) The tectogenetic analysis is a powerful method of investigation and data interpretation, leading to the understanding of structurally controlled deposits.

ACKNOWLEDGEMENTS

The authors wish to thank Marathon Resources for permission to publish and for funding this research. We also thank Dr John Santich (Marathon Resources) and Dr Phil Dight (Coffey Mining) for their discussions.

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
Petrogenesis of the Mt Gee Uranium Deposit of the Paralana Mineral System, South Australia

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ABSTRACT: The Mt Gee deposit is located within an area of intensive uranium mineralization described as the Paralana Mineral System (PMS). Significant resources of uranium, ca. 37,000 tonnes of contained U₃O₈ with an average grade of 620 ppm and thickness varying from 1.5m to 60m, have been demonstrated in the deposit. The main host of uranium within the deposit is a haematite-chlorite-quartz breccia and microbreccia. The major uranium minerals are uraninite, pitchblende, lesser amounts of coffinite, and minor torbernite; the first three of these control the uranium budget. Uraninite forms euhedral crystals with size up to 6mm. In the early stage, euhedral uraninite is often brecciated and forms a component of the micro-breccias. The PbO content of the uraninite varies from 3.35 to 4.13 wt.%, with an average of 3.77 wt.% for 73 microprobe measurements, in large, euhedral uraninite grain. This PbO content corresponds to an average chemical age of ca 290 Ma.

KEYWORDS: uraninite, coffinite, haematite breccias, alteration, oxidation, reduction

1. GENERAL GEOLOGY

The Mt Gee deposit is part of a major uranium-rich mineral system, the Paralana Mineral System (PMS). The PMS is structurally controlled ore system developed in the Mt Painter Inlier in the NW periphery of the Proterozoic Curnamona Craton, South Australia (Bogacz, 2006, Bogacz et al., 2007). The Mt Gee deposit and PMS area is composed of Early to Middle Proterozoic metasediments and metavolcanics intruded by a Middle Proterozoic granite (older granite suite, Drexel 7 Major 1990), and/or syenite-syenogranite series forming a geological unit known as the Mount Painter Complex. This complex is intruded by amphibolite dykes (late Proterozoic?) and early Palaeozoic granites and pegmatites (younger granite suite). More information on general geology of the area can be found in Drexel & Major (1990).

The Mt Painter area was subjected to deformation and high-T/low-P metamorphism associated with the Dalmerian Orogeny (about 500 Ma). These resulted in metamorphic recrystallisation, and intensive shearing and faulting, followed by magmatic-hydrothermal event at about 440 Ma (Elburg et al., 2003). Extensive breccias and quartz-haematite veins, which are the predominant hosts for U-mineralization, formed later in the history of the deposit. The magmatic event occurred at about 510°C and was followed by a hydrothermal stage at 350-200°C, which was interrupted by brecciation and subsequent quartz-haematite±chlorite alteration event at 140-100°C temperatures (Bakker & Elburg, 2006).

1.1 Granites

This is the most common rock-type in the area. It is moderately to strongly altered and brecciated locally with schistose breccias (probably gneisses) and red haematite staining. The matrix cement is composed of quartz, sericite, and carbonate ± haematite. The original rock composition is estimated to be (vol.%): quartz 10-25, K-feldspar 35-80, muscovite 1-15, plagioclase trace-15, brown biotite trace-3, and primary monazite trace~3.

The rock is altered by albitisation, sericitisation, chloritisation, ± haematitisation ±
carbonisation ± argilisation processes. Plagioclases are usually replaced by sericite. Alteration and tectonic shearing gives a schistose appearance to the rock: such altered and deformed sections host uranium minerals in fractures.

The P content varies from 65 to 2400 ppm (apatite and monazite), La contents vary form 15 to 5100 ppm (uraninite, coffinite), and Th contents vary from 4 to 330 ppm (monazite-huttonite). The highest metal contents are observed in brecciated sections cemented with 3 to 12 wt.% of Fe³⁺.

1.2 Metamorphic rocks (metasediments?)

Abundant angular to subrounded clasts with foliated textures are common in some quartz veins. These clasts represent probably metasediments.

1.3 Sediments

Abundant angular to subrounded clasts of siltstones, which are composed almost entirely of cryptocrystalline quartz and minor argillaceous admixture, are present as clasts within the breccias. This rock type is also common within the flanking sediments.

1.4 Breccias

Breccias may be composed of clasts of all the rocks present in the area, including the hydrothermal lithologies. Some of the breccias have a haematite-chlorite matrix and contain uranium mineralization. Some of breccias have a matrix containing alunite and sulphides.

1.5 Pegmatite

Rare pegmatites are composed mainly of K-feldspar, lesser amounts of quartz, and minor amounts of albite, monazite, magnetite, muscovite and pyrite. The alteration assemblage includes albite-magnetite-quartz, phyllite (muscovite-illite) and chlorite-rutile-clay.

1.6 Hydrothermal Lithologies (Quartz Veins & Quartz Vein Breccias)

The main vein and clast material is quartz, which has undergone multiphase brecciation and quartz cementation events. The quartz is accompanied by K-feldspar, haematite (magnetite often completely replaced by haematite), hydrothermal monazite ± clays ± pyrite ± tourmaline ± smectite ± rutile and chlorite ± apatite ± carbonates ± zeolite ± malachite ± kaolinite ± solid hydrocarbons. Some veins are dominated by sulphides (pyrite, chalcopyrite, chalcocite, covellite, molybdenite, Cu-selenides) or magnetite, haematite with Au inclusions, and monazite, or diopside-titanite (Bakker & Elburg, 2006).

2 URANIUM MINERALOGY AND GEOCHEMISTRY

The major uranium minerals are uraninite, pitchblende (U₃O₈), lesser amounts of coffinite, and minor torbernite. The three first minerals control uranium budget. Uraninite forms euhedral crystals up to 6mm in size. Euhedral uraninite is often brecciated and locally forms an important micro-breccia component. The PbO content of large uraninites containing over 20 growth zones (Fig. 1) varies from 3.35 to 4.13 wt.%, with average of 3.77 wt.% for 73 microprobe measurements. This corresponds to a chemical age of ca 290Ma. However, precise isotopic age dating is required.

![Fig. 1. Part of large, euhedral uraninite grain containing inclusions of haematite (h), and minor monazite I (m), and solid hydrocarbons (sh, black). Sample CiD3A.](image)

Haematite inclusions within the uraninite grains defines it’s growth zones (Fig. 1). The uraninites also incorporated the earliest monazite (monazite I) during the replacement of haematite-chlorite matrix of the breccia. Many of the euhedral uraninite grains show three stages of fracturing, marked up by solid hydrocarbons.

Smaller uraninite grains forming small clasts...
within the haematite microbreccia from different parts of the orebody have lead contents that range from 3.09 to 5.35 wt.% PbO. Clasts that yield chemical higher ages may be due to older uraninite grains originally within the granite-syenite that was subsequently replaced by the younger haematite microbreccia. The uraninites contain inclusions of haematite (Fig. 1), monazite I and II, clausthalite, chalcopyrite, Cu-selenides, molybdenite, hydrocarbons rich in oxygen and locally greenockite.

Some uranium has been detected within xenotime, and monazite-huttonite series minerals with dull internal reflections, which are due to metamict decay caused by uranium radiation. These U-bearing minerals are rare.

Other minerals present include: four types of haematite, two types of magnetite, solid hydrocarbons O-poor in rock matrix and O-rich in uraninite, and pyrite I and II, Cu-Fe-selenides, clausthalite, barite, fluorite, calcite and gypsum.

3 URANIUM-BEARING LITHOLOGIES

The best host for uranium mineralization are red colored micro-breccias whose matrix is composed of quartz, fine-grained haematite, haematite-chlorite and haematite replacing magnetite. These rocks contain from 300 to 5100 ppm U₃O₈. The main uranium minerals here are large uraninite grains rich in inclusions of paragenetically earlier minerals.

Granite-syenite breccias contain 1050 to 1100 ppm of U₃O₈ (two bulk analyses). They also contain magnetite replaced by haematite, a few percent of earthy haematite, and massive sericite ± fine haematite that may reach up to 25%.

Massive, non-brecciated adamellites contain up to 1550 ppm U₃O₈. The uranium mineralization in these lithologies is associated with dispersed haematite that replaces magnetite or ilmenite. The main uranium mineral is coffinite along with minor amounts of uraninite.

4 ALTERATION TYPES ASSOCIATED WITH URANIUM MINERALIZATION

The presence of uranium may be associated with the following alteration types:

1) Haematitization, which occurs mainly as a product of the oxidation of magnetite to haematite, and less frequently of ferrous silicates to haematite and ilmenite to haematite + rutile. The primary content of magnetite in the rock may define the capacity of the host to accumulate uranium. This type of U accumulation would rely on the reduction of soluble U⁶⁺ to insoluble U⁴⁺ with simultaneous oxidation of Fe²⁺ to Fe³⁺ staining the host rock red.

2) Oxidation of pyrite, which occurs in two steps, firstly to oxysulphides and finally to...
limonite (goethite). The first oxidation process takes place under limited oxygen conditions (hypogenic) and introduces uranium minerals. The second type of oxidation, which may take place under hypergenic conditions (including recent) and may remobilize the uranium and re-deposit it is as torbernite.

3) Sericitisation of feldspars, in which the sericitisation of K-feldspars is sympathetic with uranium minerals, whereas the sericitisation of Ca-Na-feldspars is antipathetic. Sericitisation appears to release silica to form coffinite.

4) Chloritisation, which affects both Fe-bearing and K-feldspars. Increased \( \gamma \)-counts in chlorite-rich sections are related to small uraninite inclusions and sub-microscopic U accumulations. The connection between chlorite and U may be related to the oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) present in the chlorite structure.

PARAGENETIC SEQUENCE OF MINERALS AND ALTERATION

The study area shows complex geological features and alteration products that can be grouped in four stages.

1) Greisenisation-albitisation and pegmatitisation that introduced the zircon-monazite-huttonite-rutile association.

2) Hydrothermal stage of the porphyry-type, which introduced chalcopyrite, pyrite I, molybdenite, galena, Cu-selenides, sphalerite, Bi-minerals and probably also Au and REE enrichment that can be related to the activity of younger granite (Bakker & Elburg 2006).

3) Brecciation stage that is responsible for the hydrothermal mineralization and low temperature alteration assemblage composed of uraninite-coffinite-chlorite-haematite II & III (redox type of reactions). This is the main stage of mineralization and is controlled by brecciation and formation of the extensional structures of the PMS, identified by tectogenetic analysis (Bogacz 2006, Bogacz et al. 2007).

4) The last hydrothermal stage is responsible for vug fillings, final alteration and hypergenic oxidation (illite – kaolinite, Fe-hydroxides, Fe-phosphates and gypsum).

CONCLUSIONS

1) The ore-grade mineralization is hosted by reddened haematitic breccias and micro-breccias. The red colour + \( \gamma \)-radiation are therefore good exploration vectors.

2) The main U mineral is uraninite (up to 6mm in size) and the largest crystals can be seen in hand specimens. The second most important U mineral is coffinite (up to 1 mm in size). Due to a lack of distinct optical properties it is unlikely to be seen in unpolished sections.

3) Large haematite laths, earthy haematite and chlorites are the main minerals accompanying uranium. They can be distinguished in hand specimens. This mineral assemblage is of hydrothermal origin.

4) A combination of the three methods – radiography, reflected light microscopy and SEM allow the fast and reliable identification of complex uranium mineralogy and its connections with rock-forming minerals.

5) Euclidean uraninite shows three types of micro- and nano-fractures that probably correspond to the tectonic stresses (and hydraulic jacking?) present during the deposit formation (Bogacz et al., 2007).

ACKNOWLEDGEMENTS

We are indebted to Marathon Resources for permission to publish this note, and for financial support of the research.

REFERENCES


Bogacz WV, Younger A, Kucha H, Piestrzynski A (2007) Tectogenesis of the uranium-rich Paralana Mineral System at the Mt Painter Inlier, South Australia. (this volume)

A Granulitic Crustal Source for Late-Tectonic, U-Th-REE-Mo-Nb-enriched Grenvillian Pegmatites of the Southwestern Grenville Province, Canada: Strontium Isotopic Evidence

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ABSTRACT: The low $^{87}\text{Sr}/^{86}\text{Sr}$ (0.703 to 0.709) for U-Th-REE-Mo-Nb-enriched, late-tectonic Grenvillian pegmatites (~1000 to 1050 Ma), based on earlier whole-rock Rb-Sr dating and confirmed by Sr isotope tracer studies, was used to support a mantle derivation for these magmas. However, this is inconsistent with their crustal A-type characteristics, and the oxygen isotopic signatures (> 10‰). Therefore, Rb-Sr ages for various Grenvillian rocks in the southwestern Grenville Province were compiled then the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio was recalculated (R') at an estimated maximum age of pegmatite formation (~1050 Ma) and a lower whole-rock Sr closure temperature (~950 Ma). This data shows that many Grenvillian gneisses have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at these times, in part because of their low Rb contents resulting from earlier episodes of partial melting and granulite grade metamorphism consistent with a crustal derivation for these uraniferous magmas.

KEYWORDS: uranium, Sr isotope, pegmatite, granulite, Grenville

1 INTRODUCTION

The late-tectonic, U-, Th-, REE-, Mo-, and Nb-enriched granitic pegmatites occur throughout much of the Grenville Province, hosted in rocks that had achieved middle amphibolite- to granulite-grade conditions during the latter part of the Grenville Orogenic Cycle (Ottawan Orogeny; Easton 1986). The initial Sr isotopic ratio for most of these rare-element-bearing pegmatites in the southwestern Grenville Province is low; $^{87}\text{Sr}/^{86}\text{Sr}$ is approximately to 0.702 to 0.709 (without errors), based on whole-rock Rb-Sr extrapolations (Fowler & Doig 1983) and $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.704 to 0.7055 for most pegmatites, based on Sr isotopic determinations on calcite and anhydrite from the cores of these pegmatites (Rimsaite 1982; Lentz 1996, 1998).

These initial Sr isotopic values are low compared to most rare-element pegmatite systems, which usually have more radiogenic signatures (Clark 1982). Fowler & Doig (1983) postulated a mantle derivation for these pegmatites, because the Sr isotopic compositions of some Grenvillian gneisses was thought to be too high to form partial melts that would give rise to these isotopically primitive pegmatites. However, these subalkaline granitic pegmatites have a many other characteristics consistent with crustally derived A-type granitic magmas, including their heavier $^{18}\text{O}$ signature (> 10‰) (Lentz 1996). Some A-type (anorogenic) igneous rocks have been postulated to originate from volatile-undersaturated partial melting in granulite-grade rocks at higher temperatures accounting for their relatively low large-ion-lithophile-element (LILE) contents, as well as their elevated F and high-field-strength-element (HFSE) contents (Collins et al. 1982). Therefore, a literature review of Rb-Sr whole-rock ages from various rocks in the southwestern Grenville Province was undertaken in order to re-examine whether there were any possible crustal source protoliths for these isotopically primitive A-type granitic (pegmatite) magmas.

2 PEGMATITE AGE CONSTRAINTS

The U-Th-REE-Mo-bearing pegmatites in the southwestern Grenville of Ontario and Québec have primary emplacement ages ranging from 1050 to 1000 Ma, based on U-Pb dating on primary zircons, titanites, other U-Th-bearing phases (see compilation of Easton 1986) and Re-Os dating of molybdenite (Lentz 2005). These ages are younger than the Otta-
wan Orogeny (ca. 1100 to 1090 Ma; Easton 1986), but generally precede thermal denuda-
tion of most parts of the southwestern Grenville Province to temperatures less than 500°C, based on $^{40}$Ar/$^{39}$Ar on hornblende, muscovite, and biotite; Therefore, the term late-tectonic peg-
mattites, which is consistent with their relatively undeformed nature and emplacement in the vi-
cinity of late crustal-scale shear zones. How-
ever, the Rb-Sr whole-rock ages from these pegmatites are usually less than 1000 Ma (Fowler & Doig 1983) as are most earlier Rb-Sr mineral ages from the same suite of pegmatite-
related deposits (see compilation of Easton 1986), although the upper error limits on the ages approach the emplacement ages. These Rb-Sr ages are similar to the range of ages on the host Grenville rocks obtained by the $^{40}$Ar/$^{39}$Ar technique mentioned earlier. There-
fore, probably became closed-systems to Sr dif-
fusion as the ambient metamorphic temperature decreased below 500°C (ca. 920 to 980 Ma),
i.e. 20 to 80 Ma later depending on the age of emplacement and individual terrane exhu-
amura (1992b) such that early formed radiogenic $^{87}$Sr was able to move out of the Rb-rich miner-
als, and possibly the rocks, by either simple dif-
fusion and (or) hydrothermal processes so as to continually reset the Rb-Sr chronometer (Clark 1982; Clark & Cerný 1987). For an individual pegmatite or pegmatite suite, the closure tem-
perature for Sr diffusion is a function of the relative abundance of Rb, its distribution in various phases, the relative abundance of these phases, and, for the simple diffusion model, the relative grain size distribution. Also important is the degree of U and Th enrichment, which would produce local thermal perturbations around mineralized pegmatites due to radioac-
tive heat generation. Therefore, considering the difficulty in sampling pegmatites, especially the extreme grainsize variations, it isn't surprising that the Rb-Sr ages obtained are some what discordant with large errors, possibly even repre-
senting pseudochrons because of the difficulty in sampling rocks with the same initial $^{87}$Sr/$^{86}$Sr ratio even in a small area.

Nonetheless, the initial Sr isotopic ratios calculated for these pegmatites is still quite

primitive ($^{87}$Sr/$^{86}$Sr$_i$ = 0.7028 to 0.709) probably because of the overall high relative Sr abundance in these pegmatites (50 to 1000 ppm; Lentz 1992a, 1996). The Rb/Sr ratio of these pegmatites and associated aplites and granites varies considerably from 0.05 to 7, with a mean of approximately 1, which is very low considering the degree of compositional evolution reflected in the rare-metal enrichment of these pegmatites. The Rb-Ba-Sr systematics indicates that Sr, like Ca, is partially enriched in these pegmatites by assimilation or hybridi-
zation processes that were locally extensive in the mineralized pegmatites systems (Lentz 1992a, 1996), therefore, in some cases, inher-
ting the Sr isotopic composition of the host gneisses. With either mechanism, local inheri-
tance or reflecting the original source protolith, it is important to ascertain the Sr isotopic com-
position of the gneisses at the time of formation of these mineralized pegmatites to see if they possibly have crustal signatures.

3 GRENVILLIAN GNEISSES: STRONTIUM ISOTOPES

The Sr isotopic compositions of the Grenvil-
lian gneisses are variable and dependant on Rb and Sr abundance, which reflects the original protolith, and, of course, its closure age that usually represents metamorphic resetting. Available data has been collected on the Rb-Sr ages and initial Sr isotope ratios of various rocks in the southwestern Grenville Province (see Lentz 1992a). Using published whole-rock Rb-Sr ages, average $^{87}$Sr/$^{86}$Sr contents were calculated to a hypothetical time of pegmatite emplacement (1050 Ma; Fig. 1a) and closure (950 Ma; Fig. 1b) using the calculated initial Sr isotopic ratio, the last age of homogenization (Rb-Sr age), and the average Rb/Sr ratio of the rock dated (Table 6.4 in Lentz 1992a). The Grenvillian gneisses commonly have a wide range of Rb contents, therefore, at the time of emplacement the pegmatites had variable Sr isotopic signatures. The partial melting process would tend to homogenize the Sr isotopic sig-
nature of a particular source protolith. In addi-
tion to determining possible protoliths for the pegmatite melts, this data may also be used to evaluate the numerous possible wall rock mixing end-members for the pegmatite-derived hydrothermal fluid, which was involved in associated mineralized skarn-, vein-, and carbon-
ate dyke-forming reactions (Lentz 1991a, b,
Low Sr isotopic ratios are associated with upper amphibolitic to granulitic mafic to felsic igneous gneisses with short residence times in the crust (i.e., before pegmatite emplacement) and (or) had undergone previous episodes of partial melting and granulite grade metamorphism (i.e., removing incompatible Rb). Of the 45 examples of Sr isotopic data surveyed from the southern Grenville Province, 14 granitoid rocks and gneisses have average 1050 Ma initial ratios (R') ($^{87}$Sr/$^{86}$Sr ratio) less than 0.705 (Fig. 1a), which is in the range observed for these late-tectonic granitic pegmatites. In general, the more radiogenic Sr isotopic ratios are associated with gneisses, which had longer residence times in the crust and (or) were Rb richer, although only 20% had original $^{87}$Sr/$^{86}$Sr greater than 0.71.

The calculated $^{87}$Sr/$^{86}$Sr ratio (at 950 Ma R') is used as a lower limit for the open-system behaviour of these pegmatites. The younger Rb-Sr ages of the pegmatites (< 1000 Ma) indicate Sr diffusion after pegmatite crystallization to < 950 Ma, although the minimal amount of radiogenic Sr produced between the emplacement age and closure would not affect the initial Sr isotopic ratio, because of the high Rb/Sr contents typical of these pegmatites.

4 CONCLUSIONS

The low $^{87}$Sr/$^{86}$Sr (0.703 to 0.709) of these pegmatites probably resulted from a combination of partial melting low Rb granulitic felsic to intermediate gneisses (see Dostal & Capedri 1978) and (or) hybridization reactions with other isotopically primitive gneisses during and possibly after pegmatite emplacement, which is consistent with many other crustal A-type features of these granitic pegmatites, especially their low LILE contents including Rb (cf. Cerný & Erict, 2005). Adiabatic uplift of parts of the Grenville, possibly combined with frictional heating associated with fault development, probably contributed to the volatile-undersaturated partial melting at deeper crustal levels, which attained granulite grade and subsequent crystal fractionation of these partial melts during emplacement (Lentz 1996).

ACKNOWLEDGEMENTS

The work represents part of my Ph.D thesis supported by a post-graduate NSERC grant and NSERC grants to Ralph Kretz and Tony Fowler. I thank Tony Fowler and John Blenkinsop for support and encouragement with this project and reviewing the thesis version of this contribution.

REFERENCES


Easton RM (1986) Geochronology of the Grenville Prov-


ABSTRACT: A palaeostress analysis based on inversion of fault-slip data has been conducted in the Abu Hawis area to characterize the direction and state of stress controlling the uranium anomalies along NE-SW shear zones. The analysis and relative chronology studies indicate that the area had passed since the emplacement of the Younger Granite, by eleven compressional and extensional regimes. The extensional regimes prevailed most of the time (seven events) while the compressional regime have shorter duration. Direct and indirect chronologic criteria enabled arranging them according to a relative chronologic sequence. A Palaeostress analysis of the Abu Hawis area indicates a good relation between extensional events and uranium migration trends. The NE-SW, E-W and NW-SE trends are the dominant ones of the mobility map (eU-eTh/3.5), they correspond to NW-SE, N-S and NE-SW extensional events. So, the uranium mobility map is quite helpful in defining the trends of U migration whereas palaeostress analysis of brittle deformation revealed its importance for the determination of the extensional events which control the location of the most mineralized areas.

KEYWORDS: shear zone, palaeostress analysis, inherited faults, neoformed faults

1. INTRODUCTION

The Abu Hawis area is located in the Central Eastern Desert of Egypt, directly north to Qena-Safaga road at the sign 35 km from Safaga City, between latitudes of 26° 44' 15" N- 26° 47' 15" N and longitudes of 33° 34' 37" E- 33° 39' 13" E (Fig. 1).

The Abu Hawis granite is dissected by many faults of different directions; the widest is a NE-SW shear zone. This zone extends over a length of 500m and is 5-10m wide. This trend obviously seems to be re-activated many times during the injection of basic and acidic dykes and deposition of three generations of quartz veins with different colours. The rocks within this zone are sheared, brecciated and highly altered. Some radioactive anomalies are recorded along the NE-SW shear zone with up to 78 ppm eU, encouraging the development of more detailed work in this zone.

It is very important to determine the structural traps which may control the presence of U-mineralization, such as traps along the basic dykes or along parallel structures in the enclosing granite. This study has been mainly conducted to determine the structures controlling U-mineralization within the Abu Hawis granite.

2. GEOLOGY

The Abu Hawis granite forms a peak reaching 800 meter above sea level. It represents a small body (8 km²) with an oval shape (Fig. 1).
of Younger Granite intruded in gneissose granite, tonalite, and quartz-diorite. The granite is pink to red, medium- to coarse-grained and is mainly composed of potash feldspar, quartz, plagioclase, biotite and secondary muscovite is quite common. Small amounts of primary muscovite are recorded. Accessory minerals are represented by opaques, apatite, zircon and alalanite. Chlorite, epidote, sericite and kaolinite are the main alteration minerals (Mostafa, in press). The area is dissected by basic dikes, quartz veins and faults of different trends (Fig. 1). The best U-mineralization is along a basic dike about 5-10m thick and striking N55°E. Clay alteration and iron oxide staining are strongly developed. A silicified zone, up to 1m thick, runs parallel to the dike orientation in the vicinity of the mineralized zone.

3. PALAEOSTRESS TENSOR ANALYSIS

3.1 Palaeostress determined from fault-slip data

Palaeostress tensors were calculated according to the method of Angelier (1984, 1990, and 1994). Assuming that the direction of the maximum shear stress was parallel to the observed striae, the direction of slip on a fault plane depends on the orientation of the maximum ($\sigma_1$), intermediate ($\sigma_2$), and minimum ($\sigma_3$) principal stress axes and on the ratio $\Phi = (\sigma_2-\sigma_3)/(\sigma_1-\sigma_3)$.

Palaeostress tensor analyses have been conducted in the Abu Hawis based on crosscutting and geometrical relationships between faults and dikes. About 230 slip data were measured in the area, distributed in different stations; their analysis revealed the calculation of 36 tensors; Figs. (2 & 3).

3.2 Extensional stress regime

Fault data indicating extensional deformation were found in many sites (Fig. 2). The geometry of the two major fault sets is rather homogeneous from north to south, but oblique-slip faults are also recorded, suggesting frequent reactivation of earlier weakness planes. However, faults recording N-S striking extension are found to the south and centre of the area (site 2). The faults recording NW-SE striking extension are mainly found in the central part of the area (sites 3, 13, 19, and 34), where the high radioactive anomalies along the shear zone have been recorded. The faults recording NE-SW-striking extension are mainly found along the shear zone (sites 21, 30, 33, 36 and 39). Few faults recording nearly E-W-striking extension are recorded in two sites (9 and 24). The average orientations of $\sigma_3$ axes are N180° for N-S-striking extension, N-57° for NW-SE extension, N-126° for NE-SW extension and N-284° for E-S extension. NW-SE and NE-SW-striking extension show a homogenous stress field orientation over the area while $\sigma_3$ axes of the N-S-striking extension show varying from NNE-SSW to N-S orientations (site 2).

Several NE-SW-trending dip-slip faults related to NW-SE-striking extension have been reactivated in oblique-slip faults during N-S-striking extension (site 29), suggesting that the latter is youngest. Also, N-S-striking extension reactivate inherited strike-slip faults (sites 4, and 32) revealing earlier tectonic episodes. So, the study area was affected by seven extensional events which are from the oldest to the youngest: N-S, E-W, NE-SW, NW-SE, N-S.
and E-W. The first E-W extension event occurred prior or during the emplacement of the younger granite.

3.3 Compressional stress regime

Compressional deformation has been defined by using 129 faults strike slip shear system and/or reverse pure compression system in all the 18 measured sites. These systems define four different compressional events: NE-SW, N-S, E-W and NW-SE.

![Figure 3. Lower-hemisphere Schmidt projection of fault slips data corresponding tensor for compressional phases in Abu Hawis area. Symbols: as in Fig. 2. Large black arrows = directions of extension or compression.](image)

The geometry of these fault populations is homogenous in some sites but is complex and varies from site to site. Oblique faulting is common where slip movements were initiated along pre-existing fault planes. For instance, some NNE-SSW-trending strike-slip faults have been reactivated into oblique-slip dextral faults (sites 35, 37 and 38). Some extensional veins and normal faults formed during NW-SE-striking extension have been reactivated into dextral faults (site 11, Fig. 3). Pure compressional regime ($\sigma_3$ vertical with horizontal $\sigma_1$ and $\sigma_2$) is only found in one site (15) whereas pure strike-slip regime ($\sigma_2$ vertical with horizontal $\sigma_1$ and $\sigma_3$) occurs in 17 sites. E-W-striking compression is detected from two conjugate strike-slip fault systems (1, 11, 16 & 22, Fig. 3). The orientations of $\sigma_1$ axis are 283°, 97°, 108° and 257° respectively. The NE-SW compressional event (sites 18, 25, 35, 37, 38 & 4) have orientation of $\sigma_1$ in 65°, 207°, 216°, 20°, 208°, and 229° directions. In site 37, the NE-SW compression overprints the strike slip slickensides on N-S inherited normal fault system. This indicates that this event is younger than the E-W extensional event. Also, from site 18 (Fig. 3), strike-slip slickenside on NE-SW inherited dip-slip fault system indicates that the NW-SE compressional event is younger than the NW-SE extensional event. The N-S compressional event is detected only from strike-slip systems (sites 10 and 12). The computed $\sigma_1$ for this system plunges 20° and 8° and strikes 164° and 188°. The NW-SE compressional event represents pure strike-slip phases (sites 5, 6, 8, & 27). The computed $\sigma_1$ for these systems are between 126° and 291° with plunges from 4° to 20°.

4. Palaeostress analyses and mobility ratio map

The (eU-(eTh/3.5)) mobilization ratio contour map (Abdel Meguid et al., 2003) (Fig.4) shows a good coincidence with high eU concentrations. There are U-anomalies up to 30 ppm eU along the sheared, NE-SW, basic dike. The red arrows shown on figure (4) represent the possible directions of uranium mobilization (Mostafa, in press). The process of uranium mobilization towards the sheared basic dike is very
important because it shows that this altered rock is subjected to mineralization-bearing solutions.

The correlation between the extensional events in the area and the trends of the eU-eTh/3.5 (mobility) map shows that the NE-SW, E-W and NW-SE trends are the dominant trends of the mobility map, which correspond to the NW-SE, N-S and NE-SW extensional events. The NW-SE trend of the mobility map is represented by the NW-SE tension fractures and normal faults which are due to NE-SW extensional events and reactivation of this trend is due to NNE-SSW and N-S extensional events.

5. DISCUSSION AND CONCLUSION

Uranium is largely mobile elements in oxidizing environment, so the paleoclimate, palaeotopography and stress directions are very important parameters controlling uranium mobility until its accumulation as economic deposits. So, when we discuss the uranium mobility we have to consider those factors.

The palaeo-climate, which was prevailing over most Egypt during Permo-Triassic, Lower Cretaceous and Palaeocene-Eocene times led to the formation of continental to fluvial and deltaic sedimentation. In these conditions redistribution of uranium and newly-formed uranium minerals would have the age of the activation event and secondary uranium minerals along the active extensional fractures will migrate and deposit.

Three different U-Pb ages (162, 120 and 54 Ma) have been obtained for U-mineralization in the El-Missikat granite, central Eastern Desert, associated with silica vein in ENE-WSW fractures (Abu-Deif, 1992). This means that the U-mineralized fractures could have been reactivated three times.

Therefore, palaeo-climatic conditions associated with extensional events may represent important factors for uranium accumulation. They are effective uranium-mobilizing agents, which leach uranium dispersed in the granite of Abu Hawis, and then is concentrated within traps. These geological processes control the reapated mobilization of uranium and its concentration along permeable structures. The long duration of the uranium mineralization processes is another important factor for uranium accumulation. Where the processes have had a longer duration with repeated mobilization, larger uranium deposits can be formed.

The (eU-(eTh/3.5)) mobilization ratio contour map (Fig. 4) shows a good coincidence with high eU values. There are anomalies up to 30 ppm mainly occurring over the sheared basic dike trending NE-SW. The red arrows shown on Fig. 4 represent the possible directions of uranium mobilization. The process of uranium mobilization towards the sheared basic dike indicate the direction of the mineralization-bearing solutions.

The eU-eTh/3.5 map allows defining the trends of U migration and paleostress analysis of brittle deformation allows to determine the extensional events. Coupling of the two techniques led to the identification of the most promising U-mineralized areas. So, U mobility and paleostress analysis are important tools in U exploration.

REFERENCES


ABSTRACT: The study of the Younger Granites plutons from the Eastern Desert in fifteen areas revealed that they represent high temperature, highly fractionated mantle derived melts of slightly peraluminous composition called High K-Calc-Alkaline (HKCA) granites. In such type of granite plutons there is one to several phases with specific characteristics. The less differentiated phase has low Rb, Nb, Ta, Hf, U and Th but high in Sr, Zr and mafic minerals. While the more differentiated phase has opposite characteristics. Moderately fractionated phases with intermediate characteristics may also occur. These granitic plutons have been classified according to their favourability for hosting uranium deposits as follows: the less differentiated phase with low U-favourability, the highly differentiated phase also with low U-favourability, and moderately differentiated phase with medium to high U-favourability. These results represent diagnostic features now routinely used as a uranium exploration guide.

KEYWORDS: granites, high K-calc-alkaline granites, uranium, exploration guide
Owing to the high U and Th contents of many of these granites, the uranothorite, uraninite, monazite, Rare Earth Elements (REEs) silico-phosphates and/or Nb-Ti-U oxides are common (Abdel-Meguid et al., 2003) as in the Um Ara (UA) and El Missikat (EM) plutons. Pitchblende has been identified in hydrothermally altered structures in the ES and EM plutons. The thorium content of some analyzed monazite crystals varies from high-Th monazite as in KA and low-Th monazite as in ES granites. Mangano-columbite or columbo-tantalites have been identified in the UA pluton. Betafite, zirkelite, ningyoite and caryocerite were recorded in QA, KA, NU and ES plutons.

3 GEOCHEMISTRY OF THE EASTERN DESERT GRANITES

According to the classification of Debon & Le Fort (1983), in the Q-P diagram, most the YG have compositions ranging from potassium-rich adamellites to granites (Fig. 1). They derive from high temperature melts with HKCA geochemical characteristics and the most fractionated terms may be slightly peraluminous. The location of the NU granite in the granodiorite field results from its highly albite character.

All plutons plot between the Rb/Sr ratios 1 to 100 (Fig. 2). The highly fractionated Rare Metal Granites (UN, MU and NU) have Rb/Sr ratios high than 100.

The YG can be classified into three groups according to their Th-content: low Th-content (< 10ppm), moderate Th-content (10 - 20ppm) and high Th-content (> 20ppm) granites. Based on their Th-content, KA granite can be further classified into two phases: a (10 - 20ppm) coarse granite phase and (> 20ppm) medium to fine granite phase. The episyenite plots at the level of the fine-grained but has Th/U ratio about 1 (Fig.3), indicating that the episyenite, derived from the fine-grained granite, was enriched in uranium. Although the QA pluton has Th/U ratios higher than 1, it does not show evidences of significant uranium remobilization.

4 URANIUM FAVOURABILITY OF EASTERN DESERT GRANITES

In HKCA plutons the less differentiated phase has low Rb, Nb, Ta, U, Th and Hf but high Sr, Zr and mafic minerals. While the more differentiated phase has high Rb, Nb, Ta, U, Th and Hf but low in Sr, Zr. Accordingly the studied granitic plutons can be classified into:

4.1 Low U-favourable granites

Low U-favourable granites include the less and most differentiated phases. The less differentiated phases have a too low degree of uranium enrichment to have a significant part of uranium located in easily leachable minerals and thus such granites cannot represent a source for further hydrothermal or supergene U-concentration as in the Ribdab (RI), Nugroub (NG), Khudaa (KH) and Thamela (TH) plutons.

The most differentiated phases have a low but unexpected U-favourability for the follow-
1. In highly fractionated peralkaline melts, such as the Um Naggat (UN) pluton, Th and REEs are highly soluble, and thus are not fractionated by early crystallization of accessory minerals. During magmatic differentiation uranium is enriched simultaneously with Th, REEs and other incompatible elements. Therefore, uranium will be strongly held in the structure of refractory minerals and will not be easily leachable by hydrothermal solutions especially if they circulate closely after magma emplacement and crystallization (Cuney & Friedrich, 1987). The northern part of UN granite presents an example of a U-enrichment in the albite-rich rim of a peralkaline pluton (up to 200 ppm), but U is mainly bound to refractory mineral phases such as uranothorite and euxenite. Hence, despite this important uranium enrichment, it is highly improbable to discover U richer occurrences at depth.

2. In the case of the HKCA plutons the most fractionated phases generally have a very small size (NU, MU). So, such small granitic units do not have a sufficient volume to represent a source of large U-mineralization even if important brittle structures associated hydrothermal alteration favourable for uranium trapping are present.

The moderately differentiated phase which generally represents the second phase of HKCA plutons, can be classified, according to their accessory mineral paragenesis in addition to the other favourability criteria, into highly favourable granite and medium favourable granite for the presence of U-deposits.

4.2 Medium U-favourable granites

El Missikat (EM) and Gattar plutons (GA) belong to this category. The EM pluton is composed of three phases of HKCA, low biotite (%), and rare muscovite granites with low Ca contents and Th/U ratios of about 2.5. The first phases is slightly metaluminous and the other ones became slightly peraluminous with fractionation. The GA pluton is a leucocratic HKCA to alkaline granite. According to their Th/U ratio of 2.4, uranium in EM and GA plutons is dominantly incorporated in refractory minerals, but 20 to 30% is held in more easily leachable phases. Consequently, owing to their large volume these plutons may represent a significant source for U-deposits. The presence of numerous and wider alteration zones in the EM granites increase its favorability for liberating more U with respect to the GA granite, where most alteration zones are very narrow. Few meters away from mineralized fractures the GA granite lacks micro-fractures and alteration features and thus has a low porosity, limiting the chances for U-leaching and consequently for the presence of large U-deposits.

4.3 High U-favourable granites

This category includes the KA and ES pluton which represent HKCA granites.

The KA granites has two different phases: the two-mica medium-grained leucogranite crosscuts the biotite coarse-grained granite. A small granitic plug located 1.5 km SE of the main pluton present widespread episyenitisation. This development episyenite body is controlled by increased microfracturing, which has enabled the percolation of the hydrothermal fluids. NW striking pegmatite dikes and greisen pockets, mainly occur in the eastern and southwestern parts of the episyenite body. The highest radioactive spots with the highest U/Th ratio occur along the contact between an episyenite with free vugs and one with calcite filling.

The ES pluton is very large (80km²) and composed of two-mica granites. Among the numerous magmatic injections which have been recorded in the area, the fine-grained granites are the most enriched in uranium. In the ES granites uranothorianite and high U-monazite as the main U-bearing accessory minerals. These accessories were completely and/or partly leached or corroded as indicated by the petrographic and mineral chemistry studies, in-
indicating a high U-favourability for the area.

Several types of uranium showings have been recorded mainly located along a 9km long anomalously radioactive structure:

(i) A clay-rich radioactive anomaly with 3000ppm eU and high eTh content (250 ppm), compared to much lower background values in enclosing granites (35 to 40ppm), indicates that the clay may derive from the alteration of a former late magmatic dike, enriched in Th.

(ii) Lamprophyre dikes with large crystals of K-feldspar present uranium enrichment embedded in the fine argilized groundmass. Such basic dikes may have an important role in the fixation of uranium in the area.

(iii) Bostonite dikes were also associated with high fluids circulations as indicated by bleached alteration haloes enriched in uranium at their margins.

5 CONCLUSION

Most of the Egyptian Younger Granites belong to HKCA granites. The more fractionated phases also derive from HKCA granites and have a slightly peraluminous nature. While some other plutons represent transitional types between HKCA and alkaline granites. According to their accessory mineral paragenesis and Th/U ratios these granitic plutons have been classified according to their uranium favourability point of view: (i) the less differentiated phases (low U-favourability), the highly differentiated phases (low U-favourability), and the moderately differentiated phases (medium to high U-favourability). These criteria are used as diagnostic features routinely used as a uranium exploration guide in the Eastern Desert of Egypt.

REFERENCES


Uranium Deposits in Mongolia: Emplacement patterns and potential

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ABSTRACT: Exploration maturity, geotectonic position of Mongolia in the structures of the Central Asiatic belt and major uranium mineralization emplacement patterns are discussed. Uranium-ore formations, main ore-bearing provinces and areas are briefly characterized with the assessment of their metallogenic potential. Prospective structures are outlined and recommendations for further studies are given.

KEYWORDS: Uranium, emplacement patterns, promising structures, RAR, EAR-1, IAEA

The exploration history of uranium mineralization in Mongolia may be divided into three stages on the basis of scientific grounds, equipment availability and effectiveness.

The first stage was a kind of reconnaissance work when no uranium deposit was discovered. Nevertheless, detecting anomalous radioactivity in the Gorikho pegmatite, Tumen-Tsogta greisen and of the brown coals from Choibalsan, Nilgin, Uldzuitin depressions enabled recognizing regular association of uranium showings with Mesozoic rocks and suggesting that uranium mineralization may be connected with stratabound oxidation zones in southern Mongolia. The second stage was uranium prospecting works in Mongolia sponsored by the USSR Ministry of Geology under the Intergovernmental Agreement of June 9, 1970. As a result, a uranium mineral resource base was developed including proved reserves in the Dornot ore field, hydrogenous (sandstone type) deposits in Sainshandian and East-Gobi areas and uranium-promising structures in other areas. Predicted uranium reserves of Mongolia were first estimated as 1470 thousand tons (Mironov, 2006a). The third stage was a cooperation between the mineral resource users and foreign companies to search for uranium in licensed areas already known for proved uranium resources. The prospecting work resulted in the discovery of more uranium deposits.

The initial principles for revealing regularity in uranium mineralization distribution were, first of all, radioactive elements distribution in the regional rocks, regional scale geochemical zonation as well as radiogeochemical zonation features. It was found that the processes resulting in uranium concentrations and their periodic recurrence were synchronous with the emplacement of radiogeochemically specialized magmatic units. General orientation of the specialized magmatic units have induced a longitudinal radiogeochmical zonation. Some evidences of uranium specialization occurring in north-west regional structures are associated with linear volcano-tectonic complexes and leucocratic massifs assemblages rich in radioactive elements. Economic uranium mineralization distribution in the region is correlated with the abundance of rare element specialized rocks. These evidences support the fact that large commercial uranium objects are located in radiogeochemically differentiated zones in the various rocks and that there is a clear dependence of uranium ore genesis with the extent of rare element redistribution and extraction from the basement rocks. These conclusions are ascertained by the mining experience gained in the Trans-Baikalian region and Mongolia. The Dornot, Zhanchublin, East-Gobi and Berkhin ore fields, are located in the blocks of the crystalline basement with low radioactive elements grades. The above regularity can and must be taken into account for further exploration of uranium.
mineralization in Mongolia.

Mongolia is a unique region in having its geological structure and metallogeny determined by their position at the junction of several major geotectonic structures:

a) Siberian and Chinese old platforms,  
b) systems of Palaeozoic terrains of the Central Asia mobile belt,  
c) tectono-magmatic structures connected with the development of the Pacific Ocean mobile belt,  
d) superimposed Cenozoic sedimentation structures which resulted from a collision event during the development of the Gimalaid and Tienshanid belts (Marinov, 1973).

Each of these major structures is characterized with the formation of a proper type of uranium mineralization (Mironov, 2006b):

- the Precambrian platform basement is promising for discovering uranium deposits of the structure-stratigraphic unconformity type;  
- the Palaeozoic terrains resulting from tectonic diastrophism of the Central Asia mobile belt are promising for discovering deposits due to synsedimentary uranium accumulation in carboniferous cherty rocks and redistribution during later metamorphism;  
- The structures produced by the Mesozoic tectono-magmatic event resulting from the development of the Pacific Ocean mobile belt, within the old shields and the Paleozoic terrains contain volcanogenic hydrothermal uranium deposits.  
- Associated with the rifting attributed to the Mesozoic-Cenozoic collision stage resulting in the development of the Gimalaid and Tienshanid belts are exogene-epigenetic uranium deposits in the stratal and ground oxidation zones (sandstone roll type), as well as uranium-coal occurrences and uranium deposits in crushed zones of leucogranites.

Altogether, over 10 uranium deposits, roughly 100 ore occurrences and about 1500 showings of different genetic types were discovered in Mongolian structures of various ages. As the long-term experience shows, the most efficient method for radioactive ore concentrations discovery is ore-formation analysis to determine the relations between enclosing rocks and their associated ore concentrations. The proposed approach permits reducing uranium deposits and occurrences to the following main uranium ore genetic types:

- uranium deposits in terrigenous sediments in paleovalleys (Vitimian type);  
- uranium deposits in terrigenous sediments in depressions (Kharatian type);  
- uranium deposits in coal-bearing rocks (Koldzhatin type);  
- F-Mo-U deposits in volcano-tectonic structures (Streltsovian type);  
- uranium deposits in crushed zones of leucogranite (Chikoyan type);  
- uranium deposits in carbonaceous cherty rocks (Ronneburgian type);  
- uranium-thorium-rare-earth, deposits associated with silico-alkaline metasomatism and subalkaline rocks.

All known deposits and most ore occurrences were produced during two major uranium ore formation epochs:

(i) Late Mesozoic with uranium deposits associated with volcano-tectonic structures composed of late Mesozoic basalt-rhyolite assemblages. The main stage of hydrothermal-metasomatic activity is dated at 135-140 Ma.  
(ii) Cenozoic with uranium deposits resulting from the Gimalaid collision. The most promising are uranium deposits from stratal and ground oxidation zones (sandstone roll type) in the cover complex and intermontane depressions. Numerous uranium occurrences in coal-bearing rocks, as well as those of exogenic-diagenetic origin (sandstone stratal type) were generated at the same epoch. The uranium-deposit formation epochs are associated with the earlier stages of the major geostructures in Mongolia.

Metallogenic forecast of the uranium potential of the Mongolian mineral resources is carried out by methods of metallogenic analysis. The latter, traditionally, consists in two major tasks: one - revealing the general regularities of mineral deposit distribution in connection with the development of the earth crust structures in space and time, another – at the scale of the region. Metallogenic units are derived taking into account the ages of the uranium mineralization and the location of the uranium deposits in space, and their connection with their geotectonic (geodynamic) setting responsible for formation of the geological
structures.

The major unit for regional metallogenic analysis is a uranium-ore province. As a result of the investigations made in Mongolia, the following uranium-ore provinces have been recognized: Mongol-Cis-Argun, Gobi-Tamtsag, Khentey-Dauria and North-Mongolia. Abundant uranium occurrences in these provinces are randomly distributed and grouped into uranium-ore areas, knots and zones. Uranium deposits and large ore occurrences were revealed in North-Choibalsan, Berkhen, East-Gobi and Sainshad regions. Besides, potential uranium ore zones worth to explore are Khangai, Khentei, Mongol-Altay, Aragol, Butelinur and Bayan-Khangor ones (Fig. 1).

A further uranium-forecast-oriented study may lead to recognizing other uranium deposit formations known to belong to similar geological settings in the adjacent areas of China, Kazakhstan and Russia. Thus, uranium deposit discoveries are possible in Precambrian complexes near structure-stratigraphical unconformity zones, in zones of regional faults (Elconian type); uranium deposits associated with zeolites in crushed zones of highly-radioactive Mesozoic granite (Gorny type), uranium-coal deposits in West Mongolia (Koldzhatian type). Noteworthy, the uranium-bearing sediments from the Big Lakes Basin (NW part of Mongolia) must be also reassessed because of the number of accumulated data and their improved knowledge. In addition, a high potential for the discovery of Vitim type uranium deposits exists in the terrigenous depressions with Cenozoic eruptive manifestation in Khentay and Darigang.

Special attention should be paid to the Gobi region which is similar in its geological pattern to the Central Kyzylkum uranium-ore province where ore-controlling stratal oxidation zones (sandstone roll type) are complicated with reduction foci (barrier between reduced and previously oxidized rocks). The Gobi province is incorporated in the Eurasia young plate zone where all along its 9000km extension from Iberian mountains to the Sunlyao depression there are over 100 uranium deposits which have
been discovered. This increases highly the potential of the region for hydrogenic (sandstone type) uranium mineralization (Mironov, 2006a).

Moreover, aero gammaspectrometric data together with rock sampling enabled compiling radiogeochemical maps, as well as detecting specialized rock complexes and their structures. In total, 54 volcano-tectonic complex, over 20 Mesozoic highly-radioactive granite massifs, a number of early Cretaceous depressions and areas of Cenozoic volcanism development are ranked among the most promising for the discovery of new uranium ore districts and deposits.

The quantitative data assessing the Mongolian mineral resources were first reported in the International Red Book in 1995 based on the materials of IAEA technical committee’s symposium and amounted to 83,000 tons of reasonably assured resources (RAR) and 11,000 tons of estimated additional resources (EAR-1) for the price less than $40 /kg (Norov, 2004), with the an assessment of a total resource potential for Mongolia amounting to 1,070,000 t U, which is seven times as much as Mongolian coal resource proportion of the total world coal resources.

Importance and prospectivity of exploring uranium mineralization in Mongolia are emphasized in the “Law on Mineral Resources” adopted in its new edition and put in force by Mongolian government. It refers to uranium deposits as mineral deposits of strategic significance. This is a great step of the state recognizing the actual value of its mineral resource base development and its potential economic effect.

Further uranium exploration in the Mongolian People’s Republic will certainly increase its mineral resources and ensure their better exploitation.

ACKNOWLEDGEMENTS:

To Nigel Cook, IAGOD Secretary General, and Reimar Seltman, GeRCAM Director, for kindly giving the opportunity to publish this paper.

REFERENCES:


Factors controlling the uranium mineralization in Um Ara granite, South Eastern Desert, Egypt

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ABSTRACT: The post tectonic younger granites (YG) of Egypt contain most of the discovered radioactive mineralization. The Um Ara granitic pluton is one of the promising sources of possible uranium mineralization especially along the contact with the Dokhan volcanic rocks. It is characterized by a disseminated type uranium mineralization slightly affected by alteration possesses. The present study aims to establish guide criteria for the development of the uranium resources in this granite. Detailed mapping and field observations as well as a spectrometric survey were acquired according to a 20x50m. grid pattern for the most important anomalous zones. Analyzing major oxides and trace elements for thirty three samples covering the granite. A metasomatic rather than crystal fractionation process has been proposed for the rare metal enrichment in the Um Ara granite. The rare metal mineralization results from upward movement of post-magmatic fluids which has leached the metals from the lower part of the pluton and concentrating them in the apical part.

KEYWORDS: granite, apical part, metasomatism, U-mineralization

1 GEOLOGIC BACKGROUND

The importance of the younger granites as uranium deposit host rocks extends to its role as the source of possible uranium mineralization at the contact between the basement complex and its sedimentary cover (Abdel Meguid, 1981b; Ibrahim, 2002). Uranium occurrences in Um Ara granitic pluton have been discovered by Abdel-Meguid (1981) and are restricted to the medium-grained variety of the pluton.

Um Ara granite has some part of its roof and northwards petrographic variations due to albitionization. The upper part of the pluton has a medium grain size, is extensively albitized and microclinitized, is enriched in uranium and hosts all the radioactive anomalies (Fig.1). Peculiar dendritic and rectangular yellowish, brownish and blood reddish stained patterns are well developed along the main cleavage planes of feldspars and biotite flakes, manifesting later meteoric Fe-Mn rich fluids. Moreover, fluorite and topaz indicate high temperature alteration.

2 PETROGRAPHY

The Um Ara granite comprises coarse equi-
complex history of their crystallization. The presence of large primary crystals of plagioclase associated with potash feldspar and quartz indicates non-ideal early hypersolvus texture. The northern apical parts of the pluton have finer grained crystals and are characterized by pronounced albitionization and microclinitization. The porphyritic texture of the medium-grained variety is typically trans-solvus: large relics of hypersolvus potash feldspar and quartz crystals are enclosed into a subsolvus aggregate of medium-grained albitized and microclinitized granite.

The most interesting accessory mineral in the Um Ara medium-grained leucogranites is perfectly euhedral uraninite cubes (Fig. 2) with its radiation damage haloes. Apatite, titanite, zircon and iron oxides are the main accessory minerals, monazite, pyrite and columbite were also recorded.

Figure 2. Euhedral crystals of uraninite with its radiation damaged rim.

3. SPECTROMETRY

Ground spectrometric measurements were conducted to cover the northern apical part of the medium-grained granite using a Gad-6 spectrometer, Sintrex Ltd, Canada, with gamma-ray sensor model (Gsp-4). Systematic measurements were performed along a grid pattern survey with a 50×20m spacing. The eUppm and eThppm maps were the subject of qualitative and quantitative interpretations.

The eU contour map (Fig. 3) show that the uranium anomalies are encountered as zones of different intensities ranging between 50 and >400 ppm eU. These anomalies are mostly controlled by NW-SE trends in the highly albitized and microclinitized part.

Figure 3. Equivalent uranium contour map in ppm with background topographic isoelevation lines for the northern U-mineralized albitized zone in Um Ara pluton south ED Egypt.

There is no significant relation between Th and U concentrations in the study area which may reflect a metasomatic U-enrichment in this part of the granite.

The association of the highest K-readings (4.5) with the highest U-anomalies (more than 400ppm) indicates the correlation of uranium with the microclinized albitized northern part of the medium-grained granite.

4. GEOCHEMISTRY

Thirty three samples representing Um-Ara granitic pluton have been selected for major and trace element analyze at the CRPG., Nancy, France by ICP-MS and at the NMA, Cairo by wet chemical analysis for major oxides and x-ray diffraction for the trace elements, Table (1) gives selected analyses. Most of the samples have adamellite to granite compositions (Fig. 4). An evolution trend corresponding to high potassium calc-alkaline (HKCA) magma fractionation with compositions varying from slightly metaluminous adamellite to slightly peraluminous granite. According to the alteration trends of Cuney et al (1989) albite enrichment with slight quartz depletion is indicated (dotted arrow in Fig.5). Such a trend may be related to episyenite like alteration or to a magmatic fractionation in relation with fluorine enrichment of the melts as observed in rare metal granites.

The U/Th ratio increases from 0.06 in the coarse grained granite (circles in Fig. 6) to 21.9
Table 1. Selected geochemical analyses for the Um Ara granites. Major oxides in wt%, trace elements in ppm.

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in the highly albite microcrined medium grained granite (crosses). The binary relation generally showing increasing U with stability of Th. Abrupt uranium enrichment is developed in the two granite types (dashed arrow). In the minor part of the medium granite Th is slightly enriched together with uranium (solid arrow). Such a behaviour result from a magmatic to late magmatic enrichment, with the involvement of F-rich magmatic fluids, as indicated by the occurrence of fluorite veining. The analyses of principal component of the geochemical data leads to the definition of four main factors representing 82.57% of the total variance of the system for the Um Ara granite.

**Factor 1:**

\[
F1 = 0.2 \text{TiO}_2 + 0.2 \text{MgO} + 0.16 \text{FeO}_t + 0.16 \text{Al}_2\text{O}_3 + 0.14 \text{P}_2\text{O}_5 + 0.13 \text{CaO} + 0.03 \text{Th} + 0.02 \text{U} - 0.2 \text{SiO}_2
\]
The contrary behavior of SiO₂ refers to the epi-syenitization, which starts early, may be under sub-solidus conditions (Cathelineau, 1986).

**Factor 2:**
\[
F2 = 0.33 \text{Na}_2\text{O} + 0.32 \text{CaO} + 0.31 \text{P}_2\text{O}_5 + 0.12 \text{SiO}_2 - (0.1\text{U} + 0.26 \text{FeO}_t + 0.33 \text{Th})
\]

Is correlated to albitization and secondary quartz formation and oxidation condition. Where the albitization was associated with radiation and iron dissolution. This factor may reflects the original impregnation of U in the magma and the negative role of soda excess on the U-fertility.

**Factor 3:**
\[
F3 = 0.49 \text{U} + 0.45 \text{K}_2\text{O} + 0.17 \text{CaO} + 0.12 \text{SiO}_2 + 0.11 \text{P}_2\text{O}_5 - (0.7 \text{FeO}_t + 0.32 \text{Na}_2\text{O} + 0.3 \text{Al}_2\text{O}_3 + 0.1 \text{Th})
\]

Shows a well correlation between U and microinitization, whilst the contrary positive correlation with CaO is attributed to the high fluorite content that mostly associated with secondary uranium enrichment. On the other hand, iron, soda, alumina and thorium were enriched in the melt.

**Factor 4:**
\[
F4 = 0.61 \text{U} + 0.5 \text{Th} + 0.4 \text{Na}_2\text{O} + 0.13 \text{P}_2\text{O}_5 + 0.1 \text{MgO} + 0.1 \text{FeO}_t - (0.18 \text{Al}_2\text{O}_3 + 0.4 \text{K}_2\text{O})
\]

Representing the late phase of U-enrichment that indicated by the highly positive loaded on Th, Na₂O, P₂O₅ and MgO. This enrichment was contemporaneous with the hydrothermal affected on the apical part of the medium-grained granite added thorium, soda and Mg.

5 CONCLUSIONS

The field observations as well as petrography, geochemistry and uranium & thorium distribution revealed that Um Ara granite is a uraniferous granite strongly enriched in uraninite. The mineralogical interpretation for the mineralized northern apical part of the medium grained granite is identical with the so called Rare Metal Granites.

The main part of the Um Ara pluton (coarse grained phase) presents a magmatic fractionation typical of High-K Calc-Alcaline (HKCA) granites. The medium to fine grained phase present a different trend with strong albite enrichment associated with a slight decrease in quartz as observed in F-rich magmatic systems of the Rare Metal Granites: fluorine enrichment of the residual melts leads to a shift of the granite eutectic composition towards the albite corner in the quartz-albite-K-feldspar triangle (Manning, 1981). The Um Ara granite however represent a unique case with strong a magmatic uranium enrichment late fractionated HKCA Rare Metal Granites during this process, other granites of this type presenting a more moderate uranium enrichment (Linnen & Cuney, 2005). Secondary uranium enrichment by late magmatic fluids migrating at the top of the granite plution below the impermeable Dokhan volcanic may represent a way to obtain this extreme uranium enrichment in late-magmatic conditions. Therefore, a late-magmatic rather than a pure crystal fractionation mechanism is proposed for the uranium enrichment in Um Ara granite with an upward movement of post-magmatic fluids from the lower part of the pluton and concentrating them in the studied apical part. The volume of this apical part of the Um Ara pluton should be checked through core drilling, to test if the low grade uranium mineralization may have a sufficient volume to envisage the development of an economic ore deposit as at Rössing in Namibia (Berning et al., 1976) where the average ore grade is only about 300 ppm.

REFERENCES:


Heavy mineral exploration for Uranium in Narigan area, Central Iran

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ABSTRACT: Previous exploration (geochemistry, geophysics, outcrop mapping) was carried out in the Narigan area the Central Iran Zone, Iran, at a scale of 1:100,000. This paper presents some of the data obtained from 1:20,000 scale follow-up heavy mineral mapping. Twenty-two bulk heavy mineral samples were collected. The samples were analysed for U-bearing and other heavy minerals such as xenotime, zircon, barite, monazite, titanite, allanite, epidote, pyrite, haematite, allanite and apatite. The results indicate the predominant radioelement-bearing mineral phase to be thorite. This anomaly pattern correlated well with U and Th anomalies, as does monazite and haematite. In contrast, zircon does not correlate well.

KEYWORDS: Heavy minerals, uranium, Narigan, Iran

1 INTRODUCTION

Iran’s uranium deposits occur mainly in the Central Iran zone. Several uranium deposits have been discovered in this zone. The Narigan area is one of the important uranium mineralized area in this zone.

The aim of our project is to develop a regional exploration strategy for uranium within igneous rocks of the Narigan area based on geology and heavy mineral sampling at the 1:20000 scale.

2 GEOLOGY

The oldest rock units within the area are pyroclastic series of the Precambrian (Saghand Formation) which has been intruded by a Narigan granite. The uranium-bearing sequences in this area are contained in the plutonic to volcanic rocks of so called-Narigan granites. These rocks have been affected by pervasive hematitic silicic alteration.

The uranium mineralization Is related to faults/lineaments and alterations halos. The uranium mineralization in this area is hydrothermal in origin (probably vein-type).

3 SAMPLING AND ANALYTICAL DETAILS

A grid-based sampling program was carried out based on the integrated results of previous geochemical mapping at a scale of 1:100,000, geophysical data, outcrop mapping and alteration mapping. Twenty-two, bulk (ca. 15 kg), heavy mineral samples were collected from the study area. The sample was split into three size fractions of less than 20 mesh. The samples were collected using normal methods (Boyle 1982) from 30-40 cm depth within the stream bed.

The 22 samples were analysed for U-bearing and other heavy minerals such as xenotime, zircon, barite, monazite, titanite, allanite, epidote, pyrite, haematite, allanite, thorite and apatite. The data processing shows good anomaly for these minerals in the studied area (except for xenotime and allanite).

4 RESULTS

Stream-sediment sampling of the area, which has originally shown anomalies with conventional methods, has produced anomalies using heavy mineral data. The mineralogical investigation revealed that these sediments contain considerable amounts of heavy minerals.
These data indicate that a great enhancement of U anomalies can be expected from the heavy mineral concentrates. In fact, U and Th anomalies may be lost in the sieving process (Figures 1 and 2). Thorite is the predominant U-bearing mineral in Narigan stream sediments which ranges up to 0.3 wt.% (Figure 3). Zircon shows remarkable variations in morphology, colour, chemistry and provenance. U-poor and U-rich varieties of zircon were discriminated containing UO$_2$ in the ranges of 0.2–4.0 wt.%, respectively (Figure 4). However, the zircon distribution does not correlate well with either U or Th anomaly patterns. Monazite (Figure 5), which ranges from 0.002 to 0.028 wt.%, correlates well with the U and Th anomaly patterns. Haematite, which reaches up to 52 wt.% (Figure 6) correlates well with the U and Th anomaly patterns. This furthers the observation that it can be used as a good pathfinder mineral for U mineralization in the area.

5 CONCLUSIONS

Previous exploration (geochemistry, geophysics, outcrop mapping) was carried out in the Narigan area the Central Iran Zone, Iran, at a scale of 1:100,000. Twenty-two bulk heavy
mineral samples were collected. The samples were analysed for U-bearing and other heavy minerals such as xenotime, zircon, barite, monazite, titanite, allanite, epidote, pyrite, haematite, allanite and apatite, thorite. The results indicate the predominant radioelement-bearing mineral phase to be thorite. This anomaly pattern correlated well with U and Th anomalies, as does monazite and haematite. In contrast, zircon does not correlate well.

REFERENCES

Boyle, R.W., 1982, Geochemical Prospecting for Thorium and Uranium Deposits, Elsevier, Amsterdam, 498p
ABSTRACT: The Long Lake polymetallic vein-type uranium occurrence is located in north-central New Brunswick, approximately 31 kilometers northeast of Plaster Rock. The uraniumiferous veins are hosted by late-to post-Acadian granites of the Lower Devonian North Pole Pluton and occur in hydrothermally altered and highly brecciated, northwesterly trending fractures. The uranium mineralization is commonly associated with chalcedony (jasperoid) veins, although there is a significant amount of uranium present in the highly altered granites surrounding these siliceous veins. Furthermore, there are economically significant amounts of other elements present, such as copper, lead, zinc, molybdenum, bismuth, tungsten, tin, indium, silver, and gold.

KEYWORDS: uranium, polymetallic vein, Long Lake, New Brunswick

1 REGIONAL GEOLOGY

The Lower Devonian North Pole pluton was emplaced at shallow depths, into polydeformed Cambro-Ordovician metasedimentary and plutonic rocks of the Miramichi Anticlinorium (Fig. 1). This anticlinorium encompasses the famous Bathurst Mining Camp of New Brunswick, but it has potential for undiscovered uranium (Hassan & McAllister 1992). The Miramichi Anticlinorium also contains several other occurrences that have some combination of copper, lead, zinc, tungsten, molybdenum, tin, antimony, silver, gold, and uranium (Ruitenbergh & Fyffe 1985).

The North Pole Pluton comprises the youngest granitic rocks in the Long Lake area. This pluton is syntectonic with respect to the Devonian Acadian Orogeny and thus it does not have deformation fabrics like the Ordovician plutons. The stratified rocks intruded by the North Pole Pluton have been thermally metamorphosed in a zone up to 2km wide around the contact, to an alkali feldspar-cordierite-andalusite-biotite-muscovite hornfels (Fyffe & Pronk 1985).

2 GEOLOGY OF THE NORTH POLE PLUTON

The North Pole Pluton consists of three, probably co-magmatic phases; biotite granite (oldest phase); biotite-muscovite granite; and quartz-feldspar porphyry granite (youngest phase). The oldest phase yielded a U-Pb monazite age of 417 ± 1 Ma, but the muscovite granite yielded younger K-Ar mineral ages ranging from 414-381 Ma (Whalen 1993). Existing petrochemical data for the North Pole Pluton suggest that it is a peraluminous, ‘S-type’ (to a lesser extent an evolved crustal ‘A-type’) granite. This indicates that the magmas were derived from partial melting of pre-existing sedimentary rocks. The North Pole Pluton is geochemically and texturally similar to the Pokiok Batholith of New Brunswick and the South Mountain Batholith of Nova Scotia, both of which host stibnite-bearing uraniumiferous quartz vein systems (Fyffe & Pronk 1985).

Two-mica granites are recognized by a number of geologists for their metallogenic specializations in U, Sn, Mo, Be, Li, and F mineralization, with the Hercynian granite of Massif Central, France being the best example of a uraniumiferous polymetallic vein deposit in two-mica granites (Cerny et al. 2005). Based on geochemistry, the uranium at Long Lake is likely derived predominantly from the two younger phases of the pluton (Hassan & McAllister 1992).

The altered and U-Sn-bearing rocks fall within the area of specialized granites on El
Bouseily & El Sokkary (1975) Rb-Sr-Ba ternary variation diagram that classifies granitic intrusions (Fig. 2), suggesting that both uranium and tin mineralization may favour altered rocks with chemical characteristics of specialized granites. However, the unaltered rocks of the North Pole Pluton fall within the area of normal granites, and hence cannot be consid-
ered as specialized granites.

3 PREVIOUS EXPLORATION

Exploration of the Long Lake area dates back to 1956 when the Anthonian Mining Corporation, followed by Cominco, began a nine-year effort to develop the prospect, consisting of geochemical, geophysical, and drilling surveys (33 holes totaling 4040m) in the Cheavers Lake region.

In 1963, three holes were drilled by Consolidated Mining and Smelting after conducting soil and electromagnetic surveys southwest and northeast of the Anthonian work. Canadian Occidental Petroleum’s involvement in the area began in 1971 (2 holes, totaling 305m), but was abandoned from 1974 to 1978, then reactivated in 1979 to 1982 (24 holes, totaling 3011m). Their three-year mapping, trenching, and drilling campaign yielded grades up to 3440 ppm U over 0.15m from drill core, and 8800 ppm U from float.

The area was staked again in 1983 by Kidd Creek Mines to evaluate tungsten and molybdenum anomalies delineated by a federal government silt survey. Finally in 1986, CEGB Exploration (Canada) Ltd. obtained a grade of 5420 ppm U from a boulder when they staked sixty claims over favorable geological and geochemical targets.

Uranium- and sulphide-bearing silica veins (mostly jasperoid and chalcedony) occur in at least four northwest-trending faults that intersect the North Pole Pluton. The mineralization and associated alteration are most commonly concentrated in fault breccias believed to be the result of the release of silica-rich hydrothermal fluids into fractures surrounding the fault zones. The fact that the trends of the breccia faults are parallel to the trends of the metamorphic foliation of the Cambro-Ordovician metasedimentary rocks (northwest to north-northwest), suggests that brecciation was produced by the action of hydrothermal fluids (Fyffe & Pronk 1985). Pyrite, chalcopyrite, sphalerite, galena, covellite, and molybdenite are the main sulfide minerals, along with small amounts of arsenopyrite, matildite, and native bismuth. Autunite-torbernite and cassiterite have been identified in highly mineralized float along the eastern shore of Long Lake.

Gasprarrini (1981) investigated the mineralization in float samples and identified uranium in discrete grains, in fracture fillings, and disseminated throughout the rock. Four phases of secondary uranium minerals where identified in a petrographic and electron microprobe study of two of the thin sections from medium-grained muscovite granite float, as follows:

I. Uranium-phosphorus-copper phase:
This mineral, identified as torbernite $\text{Cu}(\text{PO}_4)\text{UO}_2\cdot8-12\text{H}_2\text{O}$, is the most abundant uranium-bearing phase. It is distributed among the rock-forming minerals of the granite.

II. Uranium-phosphorus-iron-copper phase:
The mineral of this compound forms platy crystals and was identified as a mixture of iron oxide and torbernite.

III. Iron-phosphorus phase, minor uranium:
This unidentified mineral is very fine-grained, deep red under transmitted light, and is distributed in fractures and dispersed through the rock.

IV. Iron-uranium-phosphorus phase:
This unidentified mineral is less common than the above and is opaque under transmitted light.

The variation in uranium content with respect to hydrothermal alteration and mineralization within the various phases of the North Pole Pluton is illustrated in Figure 3. Hydrothermal alteration of the samples increases the uranium content considerably. This is apparent in the biotite-muscovite granites where a two-fold increase is noted, but is most pronounced in the quartz-feldspar porphyry. In addition, the uranium content in mildly altered rock is more highly concentrated than within intensely altered rocks (Fig. 3).
4 CONCLUSIONS

The Miramichi metallogenic domain is part of a uranium-bearing belt that extends from Europe to North America. The polymetallic vein-type uranium deposits in this belt are all similar in character in that they all occur in plutons and the mineralization is associated with re-activated faults intersecting highly evolved peraluminous two-mica granites. Uranium and other lithophile elements in this belt, such as Sn, W, and Mo, appear to be temporally associated with the main orogenic events, i.e., the Hercynian Orogeny in Europe and the Acadian Orogeny in North America.

Available geological, geochemical, and geophysical data from the granitic rocks of the North Pole Pluton indicate that the best target for uranium exploration in the area is the centre of Long Lake and along its eastern shore.

ACKNOWLEDGEMENTS

Thanks go out to the Geological Surveys Branch of the New Brunswick Department of Natural Resources who provided a research grant to UNB, as well as an NSERC Discovery grant to Dr. David Lentz (UNB).

REFERENCES


Fyffe LR, Pronk AG (1985) Bedrock and surficial geology, rock and till geochemistry in the Trousers Lake area, Victoria County, New Brunswick; New Brunswick Department of Natural Resources 20, pp. 74.


ABSTRACT: Uranium, tantalum niobium and zircon mineralization at Kanyika is hosted by an elongate, alkalic granitoid intrusion. Exploration by Globe Uranium in 2006 and 2007 identified four NNE-striking, sub-parallel mineralized zones. High-grade mineralization to 2,909ppm U3O8 is associated with narrow, discontinuous pegmatite vein swarms, whilst lower grade mineralization is controlled by disseminated uranpyrochlore throughout the alkalic granitoid intrusion. Uranpyrochlore contains the uranium, tantalum and niobium and is the main potential ore mineral, whilst zircon may represent a significant possible byproduct.

KEYWORDS: Alkalic, granitoid, uranium, pyrochlore, Malawi

1 INTRODUCTION

The Kanyika Project in Malawi has the potential for a significant uranium-tantalum-niobium-zircon deposit. The mineralization, hosted by an alkalic granitoid intrusion, is unusual because the uranium mineral is uranpyrochlore.

Globe Uranium has begun exploration at Kanyika in order to ascertain whether an economically viable uranium-tantalum-niobium-zircon deposit exists.

2 EXPLORATION HISTORY

2.1 UNDP airborne survey

The United Nations Development Program (UNDP) conducted a major airborne radiometric and magnetic survey over most of Malawi, at 1km line spacing, between 1984 and 1985. This survey led to the identification of a significant U and U-Th anomaly, measuring 3km by 1km, at Kanyika.

2.2 Government Exploration

A field program to investigate the Kanyika airborne radiometric anomaly was conducted by the Malawi Geological Survey in 1986 (Shouls 1987). A ground total-count radiometric survey was completed over an area of 2km by 0.7km. Areas of high radiometric response correlated to foliated nepheline syenite.

A total of 91 soil samples and 21 rock-chip samples were taken and analysed for Nb, Zn and Pb. Chemical analyses returned Zn and Pb results that were at or near background. However, Nb up to 1.20% in soils and 0.13% in rocks was returned, although there was a poor correlation with radiometrically anomalous zones. The analytical suite did not include U, Zr, Ta or REEs due to limitations of equipment available to the Survey at that time.

Mr M.M. Shouls, the author of the report concluded, “These results are not encouraging, but on the other hand, the lack of correlation between the radiometric results, the soils and the rocks indicates that some errors could have crept into the results. The balance of evidence at the moment is that this nepheline syenite gneiss is not economic, but checks should be run.”

2.3 Globe Uranium Exploration 2006

Globe Uranium Limited acquired the Kanyika Project in late 2005 and conducted a reconnaissance ground radiometric survey, soil and rock-chip sampling field program in mid-late 2006. An area of 3.6km in length and up to 2.7km wide was covered by total count ground radiometrics at 200m line spacing. A total count radiometric anomaly was defined as two distinct, 020°-striking, parallel zones over 2.5km strike length.
Geological mapping, soil sampling and rock-chip sampling was completed over the 2.5km strike length of the main ground radiometric anomaly at 100m by 50m sample spacing. Analytical results show a 2.5km long, coherent, +100ppm U₃O₈ soil anomaly, with a peak of 482ppm U₃O₈, and attendant strong Ta and Nb anomaly (Figure 1). High-grade rock-chip samples including 0.29% U₃O₈ and 0.26% U₃O₈ with coincident high-grade niobium and tantalum to 5.12% Nb and 0.52% were returned. No analyses for Zr were performed on these samples.

2.4 Globe Uranium Exploration 2007

At the time of writing, the Company had completed a detailed rock-chip sampling program and a substantial trenching program was underway. Results from the first 110 samples indicate four separate NNE-striking zones of U-Ta-Nb-Zr mineralization in the central and northern parts of the anomaly.

The Pangano Zone on the western side of the anomaly is in excess of 600m long, 20-35m in width and is open to the north and south where outcrop sampling was not possible due to soil cover. Peak values returned include 595ppm U₃O₈, 901ppm Ta₂O₅ 15,100ppm Nb₂O₅ and 23,097ppm ZrSiO₄ (zircon).

The Uzambazi Zone near the centre of the ridge is in excess of 300m long, 5-15m in width and is open to the north and south where the zone becomes covered by soil. Two well-mineralized samples just east of the southern portion of the Pangano Zone may represent a southern strike continuation of the Uzambazi Zone. Peak values from the Uzambazi Zone include 549ppm U₃O₈, 829ppm Ta₂O₅ 14,071ppm Nb₂O₅ and 10,735ppm ZrSiO₄.

The Chikoka Zone on the eastern flank of the ridge measures at least 500m long, 3-15m wide and is open to the north and south. Peak values from the Chikoka Zone include 290ppm U₃O₈, 255ppm Ta₂O₅, 5,746ppm Nb₂O₅ and 8,029ppm ZrSiO₄.

The Milenje Zone forms the northern part of the Kanyika anomaly and may link up to the Chikoka Zone in the south. At the time of writing, the results for 79 non-selective rock chip samples over the Milenje zones were still pending. However, selective rock-chip grab sampling at highly anomalous radiometric locations within the Milenje Zone in 2006 returned results of up to 2,909ppm U₃O₈, 6,317ppm Ta₂O₅ and 68,774ppm Nb₂O₅.

At the time of writing, the southern 800m of strike length of the Kanyika total count radiometric anomaly was yet to be thoroughly investigated.
3 REGIONAL GEOLOGY

The Kanyika area lies within the Malawi Provinces of the Mozambique Orogenic Belt (Kemp 1974). It is almost entirely underlain by Precambrian and Lower Palaeozoic Basement Complex, mostly gneissic metamorphic rocks. The majority of the rocks in the area are paragneisses originating from variable protoliths including pelites, sandstones and limestones. Several granitoid bodies of variable size have intruded the gneissic basement. As well, a few small concordant bodies of alkaline syenetic rocks, such as the body hosting Kanyika, occur in the area.

4 LOCAL GEOLOGY

4.1 Lithologies

The host rock is a fractionated alkaline granitoid. Compositions include diorite, monzodiorite, nepheline diorite and urtite (nepheline-rich rock) (Purvis 2007). Dominant minerals include sodic plagioclase, nepheline, K-feldspar, whilst minor/accessory minerals include cancrinite, carbonate, biotite, aegirine, magnetite, ilmenite, pyrochlore and zircon.

The country rock on the eastern side of the alkaline granitoid is gneiss of generally intermediate composition. Augen gneiss of intermediate to mafic composition occurs on the western side of the alkaline granitoid body.

4.2 Structure

The strongly NNE-elongate alkaline granitoid unit is dominated by a steep, well developed, pervasive NNE-striking foliation, S₁. Locally, tight, upright folds, F₁, of S₁ are observed which have an associated steep axial planar foliation, S₂. A sub-horizontal, NNE and SSW plunging intersection lineation, L₁, parallels the F₂ fold hinges. In many areas, a composite S₁/S₂ foliation is observed and is due to reactivation along the S₁ planes during the D₂ deformation phase.

The intermediate and augen gneisses to the east and west of the alkaline granitoid body are more strongly deformed and exhibit a distinct gneissosity. The implications are that the alkaline granitoid intruded the gneissic sequence relatively late-syn D₁ and hence has not undergone as intense deformation.

5 MINERALIZATION

Uranium, tantalum and niobium occur in uran-pyrochlore (U, Ca, Ce)₂(Nb, Ta)₂O₆(OH, F). The entire alkaline granitoid body contains various amounts of uranpyrochlore in disseminated form. Uranpyrochlore is relatively coarse grained, with grain sizes in the range 0.03 to 1.00mm across.

Higher-grade mineralization is generally associated with nepheline, zircon and uranpyrochlore-rich pegmatite veins and dykes up to 1m in width.

SEM analysis on uranpyrochlore indicates between 8.2 and 12.5 wt% UO₂ (Muhling 2007). Zircon grains returned results of near detection to 0.14 wt% UO₂.

6 CONCLUSION

Preliminary data relating to grade, geology, mineralogy and metallurgy indicate that the Kanyika prospect has good potential as a uranium, tantalum, niobium and zircon target. Significant grades of uranium, tantalum, niobium and zircon are present from surface. Mineralization is hosted in an alkaline granitoid body by medium-grained uranpyrochlore in disseminated form. High-grades are commonly associated with narrow discontinuous pegmatite veins and dykes.

Four mineralized zones have been identified, and form part of a mineralised system that remains open in most directions.

Mineralization at Kanyika is unusual in that it has significant uranium hosted in uranpyrochlore. Pyrochlore is a common ore mineral of niobium and to a lesser extent tantalum, but significant uranium production from it is not known.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contribution and assistance received from the Malawi Government in relation to work on the Kanyika Project.

REFERENCES


Muhling J (2007) SEM and WDS analysis of uranium minerals in four samples of rock from the Kanyika Project, central Malawi. Centre for Microscopy Characterisation and Analysis, University of Western Australia, pp12.

ABSTRACT: U-Pb zircon and monazite results are presented here from basement drill core samples immediately east of the basement-hosted Millennium uranium deposit. These results provide additional constraints on the regional stratigraphic correlation and thermotectonic interpretation of the eastern part of the sub-Athabasca basement, in particular within the Cree Extension area. U-Pb mineral ages coupled with U-Pb-Th chemical ages from uranium mineralization, respectively, suggest that the major overthrusting of the basement rocks (i.e. structural preparation) in the Cree extension area took place at circa 1790 Ma and that reactivation of this structure with associated fluid and heat flow at ca. 1350 Ma produced the Millennium U deposit.

KEYWORDS: U-Pb zircon/monazite geochronology, overthrusting, structural reactivation, Millennium unconformity-type uranium deposit

1 INTRODUCTION

New, high-quality U-Pb results from two basement drill core samples in the Cree Extension area are presented here for regional stratigraphic correlation and thermotectonic evolution of the eastern sub-Athabasca basement (Annesley et al. 1997, 2005). Drill core pieces of Archaean granitic gneiss sample CX-28 (at 760.25-760.50 m) and granitic pegmatite sample CX-30 (at 713.0-713.6m) were dated at the Jack Satterly Geochronology Laboratory at the University of Toronto by the U-Pb IDTIMS method. Both samples yielded both zircon and monazite for U and Pb.

2 CREE EXTENSION GEOLOGICAL SETTING

On the basis of several nearby drill holes, the granitic gneiss overthrusts Wollaston Group metasediments and Archaean tonalitic-trondhjemitic gneisses. Basement-hosted unconformity-type U mineralization occurs in a reactivated jog of this overthrust. The Millennium uranium deposit occurs approximately 35km north of the Key Lake mine and 45km southwest of the McArthur River uranium deposit and the mineralization has been dated at ca. 1350 Ma from drill hole CX-40, based on electron microprobe methods on uraninite.

The Archaean granitic gneiss in drill hole CX-28 varies from a fairly homogeneous rock, that is well foliated and weakly injected by thin granitic pegmatite veins, to a highly heterogeneous, in part migmatitic to agmatitic, granitic to granodioritic gneiss. It is flesh-pink to greenish grey to greyish white to mottled black, holocrystalline, essentially equigranular, fine-to medium-grained, hypidiomorphic, well foliated to weakly gneissic, very weakly retrograded, and fresh to weakly altered. The granitic gneiss is composed of quartz, K-feldspar, subordinate plagioclase, biotite, trace magnetite, and accessory minerals. The gneissic foliation is moderate to steeply inclined.

3 ANALYTICAL PROCEDURES

Zircon and monazite were separated from the rock samples by standard heavy liquid and magnetic separation techniques. All zircon fractions have had an air abrasion treatment (Krogh, 1982). Mineral dissolution and isolation of U and Pb from zircon and monazite generally follow the procedure of Krogh (1973), modified by using small anion exchange columns (0.05 ml of resin) that permit
usage of reduced acid reagent volumes. Pb and U were loaded together with silica gel onto outgassed rhenium filaments. The isotopic compositions of Pb and U were measured using a single collector with a Daly pulse counting detector in a solid source VG354 mass spectrometer. Data are corrected for a mass discrimination of 0.07 %/AMU and a dead time of 22.9 nsec. The thermal source mass discrimination correction is 0.1 %/AMU. Laboratory blanks for Pb and U are usually less than 1 and 0.1 pg, respectively. In this study, the total common Pb for the zircon and monazite analyses was low and attributed to laboratory Pb, thus no correction for initial common Pb was necessary. Error estimates were calculated by propagating known sources of analytical uncertainty for each analysis including ratio variability (within run), uncertainty in the fractionation correction, and uncertainties in the isotopic composition and amount of laboratory blank and initial Pb. Decay constants are those of Jaffey et al. (1971). Age calculations and concordia figures were derived using Isoplot/Ex (Ludwig, 2000) and Davis (1982). All age errors quoted in the text and error ellipses in the concordia diagrams are given at the 95 % confidence interval.

4 ARCHAEOAN GRANITIC GNEISS: U-Pb ISOTOPIC RESULTS

Most zircons are metamorphically rounded, cracked, hazy, colourless prismatic crystals. Some clear, pale brown fragments are also present, giving the least discordant data. Six, single-zircon analyses are variably discordant (0.8 % to 2.8 % discordant) with a small amount of scatter, correlating loosely with U concentration. A line calculated through all 6 data gives an upper intercept age of 2727±36 Ma and a lower intercept age of 1937±260 Ma (MSWD = 3.2). If only the four best data are used in the regression (Figure 1), the upper intercept age is 2731±25 Ma (MSWD = 0.043). An absolute minimum age estimate for the granite is given by the least discordant data with a 207Pb/206Pb age of 2705.4±4.3 Ma.

Monazite occurs as flat, shiny, yellow crystalline fragments that contain moderate concentrations of U (200-300 ppm) and high Th/U of 23-29. Three, single monazite analyses gave discordant (1.9 % to 6.6 %), colinear data (Figure 2) that have an upper intercept age of 1791.3 +8/-7 Ma (46 % probability of fit).

A line calculated through the zircon data and anchored at the time of monazite formation gives an upper intercept age of 2704±16 Ma, with a poor MSWD of 4.8. The projection of such a line is extensive, hence the near colinearity of the zircon data strongly suggests that the event that formed the monazite also induced Pb loss and morphological rounding of zircon grains. Thus, the best estimate for the granite crystallization age is given by the zircon data alone at 2731±25 Ma (96 % probability of fit).

5 HUDSONIAN GRANITIC PEGMATITE: U-Pb ISOTOPIC RESULTS

Zircons are pale yellow, euhedral, translucent, with aspect ratios of 2/1 (Figure 3), although many 3/1 and 4/1 prismatic grains are present.

U-Pb data for three single zircons partially overlap within their stated uncertainties and have Pb/206Pb ages of 1817.6±1.9 (0.6 % discordant), 1815.1±2.6 (0.5 % discordant), and 1811.6±3.4 Ma (0.5% discordant). Given that there is overlap among the error ellipses, the mean of the 3 data at 1815.9±6.7 Ma (MSWD=5.6; probability=0.4 %), can be interpreted as a minimum estimate of the age of the
zircons. The Th/U ratios are low (0.04-0.07) for magmatic zircon (which are typically ~0.2-1.5), and are more typical of zircon that have crystallized under metamorphic conditions. The slight discordance of the data may be attributable to Pb loss during the event at 1792.4 ± 1.2 Ma with recrystallization or new growth of monazite. Fitting a line through the zircon and monazite data gives a very approximate late Archaean age and there is a limited possibility that the zircons contain trace amounts of inherited (i.e. Archaean) material. However, if this was the case, it is unlikely that the points would cluster as they do, and variable Th/U ratios would be expected. Hence, the minimum age estimate of 1816 ±7 Ma is interpreted as the best approximation of the age of the zircons.

Translucent monazite grains (Figure 3), largely devoid of cracks and alteration, were analyzed. The data are plotted on the same diagram as the CX zircon data (Figure 4), where the 3 data plot with a younger 207Pb/206Pb age at 1792.4 ± 1.2 Ma, which is based on the mean

6 U-Pb CHEMICAL AGE DATING OF URANIUM MINERALIZATION

Five microprobe traverses of uraninite/pitchblende for U, Th, Pbo, and other elements, were undertaken for mineralized samples CX-40-1-386.7 and CX-40-1-390.3. All grains and veins show inhomogeneity related to fracturing, alteration, and possibly core-outer rim effects. Single-point ages were calculated by four different methods using the equation (Pb = U [0.99276 exp (λ1t) – 1 + 0.007196 exp (λ2t) – 1] + Th exp (λ3t – 1)) for the radioactive decay of U and Th. The first term of the equation is related to the decay of 238U to 206Pb, the second term to the decay of 235U to 207Pb, and the third term to the breakdown of 232Th to 208Pb. The largest proportion of Pb comes from the decay of 238U to 206Pb, and as noted by Bowles (1990), a simple approximation of the age is given by t (Ma) = Pb (wt %) x 100 (our Method 1). Empirical formulas by Ranchin (1968) and Bowles (1990) have been fitted to the radioactive decay of U and Th to Pb (Methods 2 and 3). Also, we have used the rigorous iteration method of Bowles (1990) to produce a best fit between the measured Pb and the calculated Pb from the equation for production of radiogenic Pb by the decay of U and Th. By this method, uraninites/pitchblendes with greater than 50 wt % U yielded ages of 1346 to 501 Ma. Sample CX-40-1-686.7, the massive ore, gives the oldest ages at 1350-1250 Ma with remobilization and/or new growth at 1200-900 Ma, and 750-550 Ma (Figure 5). Sample CX-40-1-690.3, the vein material, gives mostly younger ages at 1200-900 Ma and 700-500 Ma.

7 DISCUSSION AND CONCLUSIONS

U-Pb dating of Archaean granitic gneiss yields an upper intercept crystallization age of
2731.0 ± 25 Ma from 4 zircon points; similar in age to some Archean granitic gneisses in the western Wollaston Lake area and near Key Lake. Three monazites in this sample yielded an upper intercept age of 1791.3 ± 8/7 Ma (MSWD=5.6; probability=0.4%); interpreted as its minimum age of crystallization. The zircon ages fall within the bracket of 1818 to 1805 Ma, the age of peak thermal metamorphism for the Wollaston Domain, whereas the monazite ages do not. This suggests that granitic pegmatite intrusion in the McArthur River area was coeval with peak thermal metamorphism and then overprinted by a very strong Hudsonian event, related to ductile overthrusting at ca. 1790 Ma.

U-Th-Pb chemical dating of two different types of uraninite/pitchblende samples from the Cree Extension basement-hosted mineralization yielded age clusters of 1350-1250 Ma, 1200-900 Ma, and 750-550 Ma. The 1350-1250 Ma cluster correlates with the Stage 1 mineralization of Fayek & Kyser (1997). The 1200-900 Ma cluster correlates with the Stage 2 mineralization of Fayek & Kyser (1997); attributed to the far-field stresses of the Grenvillian Orogeny. The 750-550 Ma cluster is attributed to the far-field stresses from Rodinia breakup.

ACKNOWLEDGEMENTS

Funding was provided by the Saskatchewan Research Council and the Jack Satterly Geochronology Laboratory. Special thanks go to Michel Cuney in reviewing this contribution.

REFERENCES


OPEN SESSION

(GENERAL ECONOMIC GEOLOGY)

EDITED BY:

COLIN ANDREW

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Oxygen Isotope Compositions of Iron Oxides from High Grade (>63 wt% Fe) BIF-related Iron Deposits of the Pilbara Province, Western Australia

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ABSTRACT: The δ¹⁸O values of iron oxides (magnetite and haematite) were analysed from unmineralised BIF, hypogene carbonate-altered BIF (proto-ore), talc altered BIF and high-grade iron ore from the Paraburdoo, Channar and Mt Tom Price deposits and Ratty Springs prospect. Iron oxides from hypogene proto-ore and high-grade ore samples are strongly depleted in ¹⁸O relative to unmineralised BIF, with supergene and talc-altered ore samples having intermediate δ¹⁸O values between unmineralised BIF and high-grade ore. Samples with the lowest δ¹⁸O values occur proximal to fault zones and are less depleted in ¹⁸O towards the periphery of the ore body as a result of increased hypogene fluid flow and fluid:rock interaction within fault zones. The δ¹⁸O values of iron oxides provide a useful tool for discriminating between supergene and hypogene ores and act as a vector for the structures that controls mineralization.

KEYWORDS: Oxygen, Isotope, Iron, Oxide, Hypogene, Pilbara

1 INTRODUCTION

This paper reports results of an oxygen isotope investigation of the iron oxides from the Mt Tom Price, Paraburdoo and Channar high-grade iron ore deposits in the Pilbara Province, Western Australia. The δ¹⁸O values of iron oxides have been studied to determine: (1) the spatial distribution of the oxygen isotope composition of iron oxides within and between each deposit; (2) the relationship of oxygen isotope values to faults zones that control hypogene fluid flow and (3) the variation of oxygen isotope composition of oxide minerals during the paragenetic steps from unmineralized BIF to high-grade iron ore.

2 GEOLOGICAL SETTING OF THE MT TOM PRICE, PARABURDOO AND CHANNAR IRON ORE DEPOSITS

The Mt Tom Price deposit occurs as a southerly dipping sheet within the eastern fold closure of the Turner syncline with the majority of the Fe ore hosted within the Dales Gorge Member of the Brockman Iron Formation. Studies of the Mt Tom Price deposit (Barley et al., 1999; Taylor et al., 2001; Thorne et al., 2004; Thorne et al., 2005) identified three hypogene alteration zones between unmineralized BIF and high-grade iron ore (Fig. 1). Firstly, a distal magnetite-siderite-stilpnomelane zone; secondly, an intermediate haematite-magnetite-ankerite-talc-chlorite, and thirdly a proximal martite-microplaty haematite-magnetite-apatite alteration zone. These hypogene carbonate alteration zones are referred to as ‘proto-ore’ because they result in the crystallization of microplaty haematite, essential in the formation of high-grade martite-microplaty haematite ore (Thorne et al., 2004). Supergene weathering of the proto-ore, removes relict carbonate and apatite from the proto-ore. Pervasive talc alteration post-dates the proto-ore and locally forms pods of high-grade iron ore in the hangingwall of the Southern Batter Fault.

Supergene ores (i.e. Marra Mamba ore; Fig. 1) are formed solely by deep supergene enrichment of the precursor banded iron formations with no hypogene alteration (Taylor et al., 2001).

Mineralization at the Paraburdoo deposit is controlled by flat faults that now underlie both the 4W and 4E orebodies, and NW trending
dolerite dykes (Taylor et al., 2001). Mineralisation is equally distributed between the Dales Gorge and Joffre Members and consists of martite-microplaty ore, similar in style to the Mt Tom Price high-grade ore but with distinctly higher goethite content. A proximal haematite-ferroan dolomite-chlorite-pyrite alteration zone (proto-ore) occurs between unmineralised BIF and high-grade ore occurs at the 4W deposit (Fig. 1; Thorne et al., 2007 in press).

The Channar orebody is located on the southern limb of the Bellary Anticline with mineralisation controlled by northwest trending normal faults and dolerite dykes. Hosted within both the Dales Gorge and Joffre Members the high-grade ore is similar in texture to Paraburdoo ore but with noticeably more goethite (Fig. 1; Taylor et al., 2001). No proto-ore has been identified at the deposit.

3 SAMPLE SELECTION

A total of 49 samples were collected from diamond drill core and hand samples from the Mt Tom Price (n=36), Paraburdoo (n=9) and Channar (n=3) deposits and Ratty Springs prospect (n=1). Samples from unmineralized Dales Gorge and Joffre Member BIF, proto-ore, and high-grade iron ore from varying pit locations and depths within the deposit were sampled.

4 ANALYTICAL METHODS

The oxygen isotope composition ($^{16}$O, $^{17}$O, $^{18}$O) of the samples were measured at the Institute of Mineralogy and Geochemistry, University of Lausanne, Switzerland using a method similar to that described by Sharp (1990) and Rumble & Hoering (1994) and is described in more detail in Kasemann et al. (2001). Oxygen isotope compositions are given in the standard $\delta$-notation, expressed relative to VSMOW in per mil ($\%$). Replicate oxygen isotope analyses of the standards used (NBS-28 quartz (n=13) and UWG-2 garnet (n=7) have an accuracy of $\delta^{18}$O values better than 0.2$\%$ compared to accepted $\delta^{18}$O values for NBS-28 of 9.64$\%$ and UWG-2 of 5.8$\%$.

5 RESULTS AND INTERPRETATION

All the proto-ore, high-grade iron ore, talc-altered BIF and supergene ore samples are depleted in $^{18}$O relative to unmineralised BIF (Table 1). The $\delta^{18}$O values of iron oxides from hypogene proto-ore at the Paraburdoo deposit have a similar isotopic composition as the high-grade ore whereas Mt Tom Price proto-ore samples are similar or more depleted in $^{18}$O relative to unmineralized BIF. Haematite from talc-altered samples at the Mt Tom Price deposit has a similar isotopic composition as supergene ore. The $\delta^{18}$O value of high-grade iron ore is lowest at Channar (ave. -7.2$\%$), Paraburdoo (ave. -5.9$\%$) and Ratty Springs (ave. -5.6$\%$) display similar $\delta^{18}$O values, and the Mt Tom Price deposit (ave. -4.4$\%$) has the highest $\delta^{18}$O values.

<table>
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<tr>
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Figure 1. Paragenetic sequence of oxide minerals between unmineralised BIF and high-grade ore for various deposits in the Hamersley province (Thorne et al., 2007 in press).
6 CONCLUSION

The $\delta^{18}O$ values of proto-ore and high-grade ore from the studied deposits are much lower (~9 ‰) relative to unmineralized BIF. This depletion in $^{18}O$ occurs predominantly during the initial carbonate alteration with subsequent carbonate removal and supergene overprint having little effect on the isotopic composition of the iron oxides.

The depletion of $^{18}O$ in iron oxides is strongly controlled by fault zones at the Mt Tom Price Deposit (Fig. 2), with the most depleted samples close to fault zones and less depleted samples, with respect to unmineralized BIF further from fault zones. This is interpreted as the result of higher fluid flow and isotopic exchange close to faults, with the faults serving as fluid conduits. $\delta^{18}O$ values of iron oxides from high grade ore increase away from the faults and approach values similar to those in the host rock. The $\delta^{18}O$ values of iron oxides thus provide a useful vector towards the structures controlling the mineralization.

As supergene weathering of hypogene samples does not appear to considerably change the $\delta^{18}O$ values of iron oxides, this potentially may be a useful tool to discriminate between hypogene and supergene ore samples, a task that is not always easily done.

ACKNOWLEDGEMENTS

All field work was supported by Pilbara Iron with special thanks to Raul Bitencourt, Pat MacKenzie, Matt Ramsden, Joffre Buswell and Wayne Zarb. This project is funded by an ARC linkage grant, Rio Tinto and the University of Western Australia.

REFERENCES


Figure 2. The $\delta^{18}O$ values of iron oxides from Mt Tom Price, 14000E (Thorne et al., 2007; in press)


ABSTRACT: Models for the genesis of giant microplaty haematite ores derived from banded iron formation (BIF) hitherto have not resolved the relative importance of deep- versus shallowly derived fluids. Reaction path modeling for Western Australian Hamersley Province ores (Mt Whaleback and Mt Tom Price) indicates that reaction of BIF with heated meteoric fluids (200 to 250°C) can explain the predominant 18O-depleted isotopic signals of these ores and the commonly observed zonation from magnetite-carbonate-silica BIF to haematite-quartz altered BIF to haematite rich ore. Silica-absent iron oxide-carbonate rocks found in footwalls of some deposits (Mt Tom Price, Kivoy Rog, Quadrilátero Ferrífero) require silica loss prior to oxidation - surface-derived fluids cannot produce this change. Ongoing research is testing whether or not this geochemical ground preparation by reduced basinal fluid is crucial for subsequent oxidation reactions and ore genesis.

KEYWORDS: iron ore, fluid infiltration, oxygen isotopes, hydrothermal geochemistry

1 INTRODUCTION

Major iron ore provinces of the world, mostly hosted in Neo-Archaean or Palaeoproterozoic banded iron formations (BIFs), contain several ore deposit styles ranging from young (Mesozoic to Recent) clastic, pisolithic and crustiform types (commonly rich in goethite) through to relatively uncommon but giant (> 0.5 billion tonnes) microplaty haematite ores. Although the younger varieties appear to relate to low temperature supergene processes and subsequent surficial reworking, the older microplaty haematite deposits appear to have formed at higher temperatures (100 to 400°C) by silica loss and oxidation, leaving a residue of hematized magnetite (martite), microcrystalline or ‘microplaty’ haematite, and partly collapsed porosity from the silica loss (Powell et al. 1999; Taylor et al. 2001; Webb et al. 2003; Riosiere & Rios 2004). Older models for low temperature supergene enrichment followed by metamorphism (e.g. Morris 1980) have largely been discounted for this ore type (e.g. Barley et al. 1999; Powell et al. 1999; Brown et al. 2004; Dalstra & Guedes 2004). Although most recent workers agree on the hypogene origin of the giant microplaty haematite deposits, uncertainty remains regarding whether the fluid(s) responsible for ore genesis were deep-seated (and carbonate-equilibrated, e.g. Taylor et al. 2001; Dalstra & Guedes 2004) or essentially heated near-surface waters (Webb et al. 2003; McLellan et al. 2004), or both (e.g. Powell et al. 1999; Webb et al. 2004). Resolution of these issues would assist explorers if it could be demonstrated that silica-depleted magnetite siderite or haematite-carbonate protores observed in some deposits were essential for subsequent ore genesis, particularly if such protores were developed in specific structural sites.

To address the problem we have gathered a large database of stable isotope, geochemical and mineralogical data from BIFs, altered BIFs (those containing haematite and quartz or magnetite and siderite), microplaty haematite ores and some Tertiary to Recent goethite-dominant ores and ‘hardcap’ laterites from the Hamersley Province in Western Australia, surrounding two of the world’s largest microplaty haematite deposits, Mt Whaleback and Mt Tom Price. We use reaction path modeling of oxygen isotopes
and mineralogical and geochemical changes to assess the various models for silica loss and oxidation leading to genesis of these premier iron ores.

Similar to other Precambrian iron ore districts, the geological evolution of the Hamersley Province involved an earlier phase of metamorphism and folding (c. 2.3 to 2.2 Ga) followed by one or more fault-related hydrothermal phases resulting in ore genesis (2.2 to 2.0 Ga). Most metamorphic and hydrothermal events that affected the West Australian, Brazilian and South African BIFs were Palaeoproterozoic.

2 STABLE ISOTOPE RESULTS

136 mineral separates of oxides and quartz were analysed for oxygen isotopes, and a further set of carbonates (a few of which are presented here) were analysed for carbon and oxygen isotopes. Samples were selected from drill core, road cuts, field outcrops and mines, in particular in and around Mt Whaleback and Mt Tom Price and from the Geological Survey of Western Australia core facility. Figure 1 shows the results which are divided as follows: a) unaltered BIF preserving magnetite and quartz in addition to combinations of haematite, siderite, stilpnomelane and riebeckite, typically found > 1 km away from the microplaty haematite deposits, b) altered, oxidized BIF forming a km-scale halo around the deposits in which carbonate has been removed, magnetite has been converted to haematite, and silica remains, c) altered BIF in which silica has been removed and either magnetite and siderite are preserved, or are converted to haematite and ankerite, typically on the edges of the major microplaty haematite mine, d) microplaty haematite ores, e) goethite-martite ores, most commonly forming as caps on microplaty haematite ores, near modern or older Phanerozoic weathering surfaces, and f) Recent to Tertiary lateritic rocks, commonly pisolithic, forming on modern weathering surfaces. The isotope data, along with fluid inclusion data (Hagemann et al., 1999; Oliver et al. 1999; Brown et al. 2004; Dalstra & Guedes 2004), indicate a) a major component of meteoric fluid was involved in the formation of all deposit types, b) the microplaty ores formed at higher temperatures than the goethite-rich ores and younger “hardcaps”, and c) temperatures of formation of the microplaty ores were in the range 100-250°C, but in some locations appears to be preceded by the formation of higher temperature magnetite-rich ores (e.g. Mt Tom Price, also Quadrilátero Ferrífero, Rosiere & Rios, 2004; Kivoy Rog, Dalstra & Guedes 2004).

Quartz from fresh and altered BIFs shows little difference in $\delta^{18}O$ ratios, indicating it did not exchange efficiently with the same low $^{18}O$ fluid that affected iron oxides – there is no evidence that quartz achieved isotopic equilibrium with any post-metamorphic fluid. Any altered rocks retaining magnetite do not show substantial $^{18}O$ depletions of the magnetite, from which Taylor et al. (2001) proposed that these rocks had lost silica by interaction with a relatively reduced (magnetite-stable) fluid derived from depth. In marked contrast with primary BIF haematite and magnetite, haematite from the ore bodies shows $\delta^{18}O$ ratios as low as -11‰, requiring either an extremely $^{18}O$-depleted (as low as -16‰) supergene meteoric fluid source, or a heated meteoric (100 to 250°C) fluid source (Fig. 2). The latter is consistent with oxygen isotope geothermometry on haematite-ankerite pairs at Mt Tom Price (66 to 270°C for 6 pairs, 4 pairs in the range 115 to 145°C) and ore-related fluid inclusion data (Hagemann 1999; Brown et al., 2004).

The large range of $\delta^{18}O$ ratios for the ores could be explained by stable isotope disequilibrium between haematite, fluid and gangue minerals but is more likely to be due to variations in the composition of the incoming fluid as it passes through different rock packages with different amounts of equilibration prior to ore genesis, as suggested by the $\delta^{18}O$ ratios of altered BIFs, intermediate between those of unaltered BIF and ores (Fig. 1). The most depleted
would most likely ensure oxygen isotope equilibration between haematite and ore fluid as assumed in our calculations of ore fluid composition (Figs 2, 3).

To test the potential role of deep-seated fluids stripping silica prior to oxidation, we modelled isothermal and down-temperature flow of fluid equilibrated with dolostone at 350 to 250°C with BIF at 250 to 100°C, based on the conceptual ore genesis scenario presented by Taylor et al. (2001). All models failed to produce δ18O depletions in the BIFs, with moderate to high fluid fluxes producing small δ18O enrichments, which may not easily be detected in the data. These results do not permit resolution of the potential isotopic contribution of the deep seated fluids to ore genesis.

3 GEOCHEMICAL REACTION PATH MODELS

Using the Gibbs minimization package HCh combined with the Unitherm database available via Geoscience Australia (see http://www.ga.gov.au/rural/projects/geofluids.jsp and Cleverley & Oliver, 2005), we applied a scenario of isothermal reaction of different amounts of heated (250°C) fluid with BIF, using a simple meteoric fluid composition with 0.3M NaCl equivalent, a 2:1 molar ratio of Na to Ca, and fO2 set at atmospheric. A representative unaltered BIF was taken from the modal mineralogy of Webb et al. (2003). We have not yet modeled (at the time of writing) up-temperature flow of meteoric fluid nor down-temperature flow of fluid equilibrated with dolostone. However this preliminary model produced an array of assemblages in which oxidation of magnetite to haematite occurs at lower fluid/rock ratio than removal of silica, mimicking the spatial distribution of assemblages in the field, from magnetite-quartz±carbonate BIF to haematite-quartz altered BIF and then silica-absent haematite ore as reported by Webb et al. (2003) for Mt Whaleback (Fig. 4).

Production of tale as a by-product silicate provides some confirmation that our model assumptions are reasonable as tale is associated with ore at both deposits (Taylor et al. 2001; Webb et al. 2003). The model does not replicate the reduced magnetite-siderite assemblage observed in the Mt Tom Price footwall (and some other deposits), consistent with the premise deduced from the oxygen isotopes that indicates another fluid was responsible for this as-

values may reflect the ambient meteoric fluid composition, higher values reflecting a greater amount of equilibration with the host rock package.

Using the silica solubility data of Fournier & Potter (1982), and assuming that silica was stripped from at least a 1km path length (the open cut at Mt Whaleback is 5km long), the amount of silica dissolved from the deposits at 200°C and 1 kbar requires a fluid flux on the order of 6 x 10⁷ moles H₂O cm⁻². This high flux

Figure 2. Calculated composition of fluid in equilibrium with BIF and ores of the Hamersley Province (contact authors for fractionations used). Temperatures are derived from fluid inclusions and mineral pair oxygen isotope geothermometry (1), with the exception of the Tertiary to Recent martite-goethite (mar-gt) ores which are assumed to be supergene. Calculated fluid required to explain the Mt Whaleback and Tom Price haematite ores by low temperature (incl. supergene) processes would have required extremely 18O-depleted fluids (2).
semblage (Taylor et al. 2001).

4 CONCLUSIONS

Stable isotope and geochemical models of reaction paths leading to the derivation of microplaty haematite iron ores from BIF indicate that the predominant isotopic and geochemical signal of the ores was produced by reaction of BIF with voluminous, oxidized, probably meteoric fluid at about 200°C. Silica-poor carbonate-present alteration in the footwalls of some deposits does not show distinctive isotopic signals and requires involvement of a reduced, silica undersaturated fluid. Ongoing modeling is testing whether such footwall alteration is crucial for all deposits of this type, despite its apparent absence in some giant deposits.

ACKNOWLEDGEMENTS

Ian Cartwright, Jodie Miller, and Zach Sharp provided isotope analyses, Jerry Dickens, Adam Webb and Mat Brown contributed in the field. The research was supported by the Australian Research Council, Predictive Mineral Discovery CRC, BHP Billiton and Rio Tinto iron ore companies – particular thanks to Peter Waters, Janos Ronaszeki and Hilke Dalstra.

REFERENCES

Barley ME, Pickard AL, Hagemann SG, Folkert SL (1999) Hydrothermal origin for the 2 billion year old Mount Tom Price giant iron ore deposit, Hamersley Province, Western Australia. Min Dep 34: 784-789


Morris RC (1980) A textural and mineralogical study of the relationship of iron ore to banded iron-formation in the Hamersley Iron Province of Western Australia. Econ Geol 75: 184-209


Iron oxide paragenesis, quartz vein chronology and hydrothermal fluid evolution at the giant North Range Carajás iron deposits in Brazil

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ABSTRACT: In the North Range hydrothermal iron deposits of Carajás, Brazil hydrothermally altered JPs and iron ores exhibit a range in alteration and iron oxide paragenesis from least to most altered stages. Primary-pseudosecondary fluid inclusions were trapped at 190 to 350°C and 0.3 to 1.2 kbars, respectively, have low- to high-salinity and the presence of cations such as Ca, Mg, Fe, Na, suggest that complex aqueous fluids penetrated the deposit during distinct paragenetic stages. The δ¹⁸O variations in hydrothermal jaspilites, iron oxides of the various alteration stages, and quartz indicate an evolution from fluids rich in ¹⁸O to those depleted in it.

KEYWORDS: fluid inclusions, oxygen isotopes, iron ore, Carajás

1 INTRODUCTION

Hydrothermal iron ore deposits are located in the Carajás Province, and hosted in the Archaean metavolcanic-sedimentary Grão Pará Group, Itacaiúnas Supergroup. Jaspilites (JP) host discontinuous, high-grade iron ore bodies (>65% Fe), which are under- and overlain by mafic rocks. The North Range Carajás iron deposits currently contain the N4 and N5 active open pits, with production in 2004 of about 80 Mt of iron.

The iron ore bodies postdate Archaean metamorphism and all fold and shear events documented in the Carajás Province. The ore bodies developed in distinct high permeability zones within the regional, kilometre-scale hinge zone of the antiformal Carajás Fold (Rosière et al. 2006). Later, post-metamorphic, mineralising fluids infiltrated at relatively shallow crustal-level (Lobato et al. 2005a, b).

This contribution provides: (a) a paragenesis for the different iron oxide species, (b) a detailed hydrothermal vein and breccia chronology, (c) preliminary microthermometric results on fluid inclusions trapped in quartz veins and breccias, and (d) oxygen isotope results on quartz and oxides. These data are used to constrain the hydrothermal evolution at the North Range Carajás iron deposits.

2 IRON OXIDE AND QUARTZ VEIN CLASSIFICATIONS

Detailed petrography, SEM analyses and images of hydrothermally altered JPs and iron ores were used to establish the following par-
agenesis for the iron oxides (cf. Lobato et al. 2007; Figueiredo e Silva 2004), from the least to the most altered stages: (i) Microcrystalline haematite (MiH); (ii) Magnetite (Mgt – kenomagnetite (Kmgt) (iii) Martite (Mt); (iv) Micro-platy or -lamellar haematite (MpH), (v) Anhedral-AnH haematite, and (vi) Euhedral and/or tabular- EH-TH haematites.

Table 1 – Summary of the relative timing, fluid inclusion assemblages and microthermometric data of fluid inclusions trapped in V1 to V5 vein types.

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<th>Microthermometry data (°C)</th>
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<td>H$_2$O-CaCl$_2$-MgCl$_2$-FeCl$_2$</td>
<td>$-54 &lt; T_e &lt; -32$; $-0.4 &lt; T_{m_{ic}} &lt; -0.3$; $253 &lt; T_{h_{tot}} &lt; 294$</td>
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<td>V1 P2</td>
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<td>V4 P1</td>
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<td>P/PS1 S2</td>
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<td>$-6.4 &lt; T_{m_{ic}} &lt; -0.1$</td>
</tr>
<tr>
<td>V5 P/PS2</td>
<td>H$_2$O-CaCl$_2$-FeCl$_2$-MgCl$_2$</td>
<td>$-60 &lt; T_e &lt; -50$; $-12.7 &lt; T_{m_{ic}} &lt; -7.1$ &amp; $23.7$; $250 &lt; T_{h_{tot}} &lt; 308$</td>
</tr>
</tbody>
</table>

Detailed fluid inclusion petrography identified distinct fluid inclusion assemblages (Table 1) for the different quartz vein types. In all vein types primary, pseudosecondary and secondary fluid inclusions were mapped and microthermometrically analysed. Primary and pseudosecondary inclusions are mostly liquid-rich (10 to 20 vol.% vapour) and occur as clusters or internal trails. The shapes are oval to irregular and the sizes range from <5 to 35 microns.

4 MICROTHERMOMETRIC RESULTS

Preliminary microthermometric results for primary fluid inclusion types trapped in the five quartz vein types are presented in Table 1. The hydrothermal fluids are dominated by aqueous solutions with variable amount of cations such as Na$^+$, Ca$^{2+}$, Mg$^{2+}$ and Fe$^{2+}$ and salinities varying from 0.7 to 29.3 eq wt% CaCl$_2$. The trapping temperatures and pressures range from 190 to 350°C and 0.3 to 1.2 kbars, respectively for the different vein types.

5 OXYGEN ISOTOPES

Oxygen isotope compositions (given as $\delta^{18}$O values) were analysed using a CO$_2$-laser line at the Institute of Mineralogy and Geochemistry, University of Lausanne. A total of 39 samples were analysed that contained all types of iron oxides (MiH to EH-TH and Mgt), and vein quartz from hydrothermally altered JPs and ores (Fig. 2). The latter are associated with vein types 3, 4 and 5. Ten whole-rock hydrothermalised (Mgt±Mt±MpH) JP samples were also analysed.

The results are displayed in Fig. 2. The $\delta^{18}$O values range from the least altered JPs (+15.2‰) to the latest EH-TH oxides in the iron ores (−9.5‰). Note that magnetite, which is the first hydrothermal oxide to develop after MiH, has intermediate $\delta^{18}$O values between JPs and the different types of haematites (Fig. 2). As pointed out by Zheng (1991), the O isotope
Fractionation between haematite and magnetite reflects differences in crystal structures and Fe-O bond characteristics.

For quartz, $\delta^{18}O$ varies from $+18.8\%$ in V3 type to $+10.1\%$ in V5 type veins.

6 PALAEOHYDROTHERMAL EVOLUTION

The first evidence for hydrothermal fluids that infiltrated the JPs is vein type 1, which contains Ca-Mg-Fe-rich fluid inclusions with very low salinities (0.7 to 0.8 eq wt% CaCl$_2$), and trapping temperatures of 253 to 294°C. Quartz $\delta^{18}O$ values could not be obtained, since this phase only occurs finely intergrown with jasper in the JP bands.

The next stage of hydrothermal fluid infiltration is characterised by vein type 2, which contains high salinity Na-Fe-Mg-rich and Ca-rich fluid inclusions (up to 19.2 eq wt% CaCl$_2$) with $T_{\text{hid}}$ of 190 to 288°C.

Vein type V3 is characterised by high salinity Na-Mg-rich fluid inclusions with trapping temperatures of 240 to 277°C, and low salinity, Ca-Fe-rich inclusions.

Brecciated vein type V4 has Ca-rich, high salinity FIs, trapped at 220 to 324°C, and low salinity Na-K-Mg fluid inclusions trapped at 235 to 283°C. Secondary FIs are low salinity Mg-Fe-rich with trapping temperatures of 230 to 285°C.

Brecciated V5 vein type contains Ca-Fe-rich high salinity (up to 29.3 eq wt% CaCl$_2$) fluid inclusions with $T_{\text{hid}}$ of 206 to 308°C.

As depicted in Fig. 2, each oxide type displays a unique range in $\delta^{18}O$ values, from higher (MiH & altered JPs) to lower (EH-TH) values, suggesting a trend in $\delta^{18}O$ depletion of the fluid with time. Based on the average trapping temperature of 300°C and the haematite-water (Zheng 1991) equation, the calculated $\delta^{18}O$ value of the fluid falls within the $+8$ to $-1\%$ range.

7 CONCLUSIONS

Vein types V1 to V5 (see Fig. 3) are related to the iron mineralization at Carajás and trapped complex aqueous fluids between 190 to 350°C and 0.3 to 1.2 kbars.

This is clearly shown by the occurrence of primary-pseudosecondary, low- to high-salinity fluid inclusions and the presence of cations such as Ca, Mg, Fe, Na in these veins.

Fluid compositions typical for magmatic-metamorphic (+5 to +10‰) and meteoric fluids (down to $-1\%$) are compatible with the range of $\delta^{18}O_{\text{fluid}}$ values (Taylor, 1979). We propose that the iron mineralization resulted from inter-

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**Figure 2** – Diagram showing measured (stippled rectangles & square; median values) $\delta^{18}O$ values for hydrothermally altered JPs, oxide types and quartz from vein types V2, V3 and V5. Calculated $\delta^{18}O$ values for the fluid is displayed, based on the haematite-water (Zheng 1991) equation (grey field, squares enclosing triangles; median values). Microcrystalline haematite (MiH); Magnetite (Mgt); Martite (Mt); Micro-platy or lamellar haematite (MpH), Anhedral haematite (AnH); Tabular haematite (TH).
action of a magmatic hydrothermal fluid with the jaspilites.

The higher $^{18}$O$_{\text{fluid}}$ values correspond to the earlier-stage haematite types, whereas the lower values to the more advanced anhedral and tabular haematites. Since $^{18}$O is depleted in haematite relative to magnetite (Zheng 1991), lower $^{18}$O/$^{16}$O ratios would be expected where euhedral-tabular haematites are typically precipitated. These zones may also represent the zones with the highest fluid/rock ratios. It is therefore reasonable to interpret that the decreasing isotopic values (Fig. 2) reflect variations in fluid/rock ratios during iron ore mineralization, under relatively shallow crustal conditions (Lobato et al., 2007).

Figure 3 – Schematic diagram showing relative timing of vein types V1, V2, V3, V4 & V5 relatively to hydrothermally altered Jasper and ore components.

ACKNOWLEDGEMENTS

We wish to thank Companhia Vale do Rio Doce for providing logistical, technical and financial support. Thanks are also due to UFMG, UWA and UNIL. We greatly acknowledge the Grants received from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and scholarships from Coordenadoria de Apoio ao Pessoal de Nível Superior (CAPES).

REFERENCES

Figueiredo e Silva RC (2004) Caracterização petrográfica e geoquímica de jaspilitos e minérios de ferro,
Mineralizing fluid evolution and REE patterns for the hydrothermal Carajás iron ores, Brazil, and for selected Hamersley iron deposits, Australia

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ABSTRACT: In the Carajás Northern Ridge hydrothermal iron ore deposits, different types of oxides are present, microcrystalline haematite being the most primitive, while euhedral-tabular haematite the late-stage hydrothermal phase. Relative to jaspilites, some rare earth elements (REE) patterns in ore samples show general increase in ΣREE, light-REE enrichment, a near-horizontal configuration and Eu anomalies that ranges from positive to negative. Ore samples from selected Hamersley deposits show similar features, with less pronounced enrichment in LREE. The shifts in the REE patterns are directly related to the mineralogical evolution. The overall higher REE contents of the Carajás compared to the Hamersley ore samples suggest different mineralizing fluid sources.

KEYWORDS: iron ore, Carajás, iron oxides types, rare earth elements, Hamersley

1 INTRODUCTION

Structurally controlled (Rosière et al., 2006), hydrothermal iron ore deposits (Lobato et al. 2005a, b) are located in the Carajás Province of Brazil, hosted in the Archaean metavolcano-sedimentary Grão Pará Group, Itacaiúnas Supergroup. Jaspsilites (JP) host discontinuous, high-grade, soft and hard iron ore bodies (>65% Fe), which are under- and overlain by basaltic rocks (Zucchetti et al. 2007). The N4 and N5 active open pits produced in 2004 about 80 Mt of iron.

Different iron oxides in JPs and iron ores give place to various rock associations, which reflect the intensity of hydrothermal alteration. Distinctive geochemical changes, experienced during alteration attending iron mineralization, are spectacularly displayed by rare earth elements-REE data (Figueiredo e Silva 2004), and help constrain fluid source and evolution. The Carajás REE results are compared with the Tom Price, Paraburdoo and Brockman BS2 iron deposits, Hamersley, Australia.

2 PETROGRAPHIC STUDIES

Samples from drill holes (down to 300 m) were selected from the N1, N4 and N5 deposits of Carajás. These encompass haematitised JPs and hard iron ores (Figueiredo e Silva 2004), which are banded and/or brecciated, and variably porous. Jaspsilites contain iron oxides, jasper, chert-quartz, whereas iron oxides dominate iron ores; carbonate and sulphide veinlets are subordinate.

For the Carajás Northern Range deposits, a mineralogical sequence for the iron oxides has been established: MiH → Mgt → Mt → MpH → AnH → EH-TH (Figueiredo e Silva 2004).

Microcrystalline haematite (MiH) – the earliest oxide, which is overgrown by magnetite (Mgt) porphyroblasts. It is typical for the jaspilite layers but stable even in the more advanced hydrothermal alteration stages.

Martitised magnetite (Mt) – has kenomagnetite (Kmg) relics, and is commonly surrounded by haloes of recrystallised jasper, resulting in fine-grained, haematite-free granoblastic quartz.

Micro-platy or lamellar haematite (MpH) – commonly partially fills vugs, or is associated with quartz and carbonate veins.

Anhedral haematite (AnH) – results either from progressive martitization, forming abundant lenticular, mosaic agglomerates, or from MiH recrystallization, mainly where in contact with euhedral and/or tabular (EH-TH) haema-
tite veins. The latest-stage oxides EH-TH haematites occur in discordant veins and veinlets. Usually comb-textured, they further cement open spaces or vugs. Growth lamellae are common in EH, and locally also occur in AnH, TH, rarely in MpH. These features indicate shallow, epithermal crustal conditions (Lobato et al. 2005a, b).

Banded, brecciated and porous ore samples from the Mt. Tom Price, Paraburdoo and Brockman deposits show the following noteworthy characteristics:

(i) Mt. Tom Price: Eight samples. AnH dominates the majority of samples, in which MpH partially occupies vacancies. Kmg relics are present in one sample, both in Mt and in MpH. Where MpH (±AnH) dominates, it may be comb textured.

(ii) Paraburdoo: Seven samples. One sample is Mt rich with MpH, the other dominated by AnH massive bands + MpH veins and vugs.

(iii) Brockman BS2: Four samples. One rich in Mt bands + MpH vugs, and the other is dominated by MpH, which is coarser grained close to the vugs.

The petrographic study clearly shows that Mt aggregates may evolve to form AnH and/or MpH. However, MpH is more common in vugs and veins.

All Carajás samples are devoid of weathered products, whereas some Hamersley samples contain goethite, suggesting weathering overprint. The petrographic study reveals a close similarity in the mineralogical and textural characteristics of the Carajás and Hamersley iron ores.

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Figure 1. Chondrite-normalised REE diagrams. (A) N4W and N5E jaspilites. (B) Different types of iron ores containing oxides described in the text (most Carajás data from Figueiredo e Silva 2004). Carb: carbonate (C) BIF from the North Deposit, Dales Gorge (data in Alibert & McCulloch 1993). (D) Different types of iron ores from deposits of the Hamersley basin.
3 RARE EARTH ELEMENTS - REE

The REE patterns of the Carajás JPs (Fig. 1A) depict low ΣREE contents, light REE enrichment, and positive europium anomalies (Eu/Eu* > 1), similarly to Archaean BIF worldwide (e.g., Klein & Ladeira 2002).

Various REE populations of hematitised jaspilites and ores are identified (Fig. 1B).

(i) N1 (horizontal) and N4E (hatched lines; Fig. 1B) ore samples exhibit LREE enrichment and, like JPs, positive Eu anomaly. This resemblance may be explained by the fact that these ores have oxides similar to those of hematitised JPs (Mt-rich, MpH, MiH). The similarity is also born out by the low heavy REE signature below chondrite.

(ii) LREE-enriched N4E ore samples with negative Eu anomaly (wide crosses, Fig. 1B) are MpH-rich, with Mt ± MiH. This association is interpreted as the intermediate hydrothermal mineralization stage.

(iii) One group of NSE ores (vertical lines, Fig. 1B) displays the highest ΣREE, mainly LREE. They are composed essentially of later-stage haematites, AnH-EH-TH and MpH.

(iv) Another N5E group (dense grey, Fig. 1B) has near-horizontal REE patterns, with relative LREE and HREE enrichment.

The patterns of Hamersley BIF deposits (Fig. 1C) depict low ΣREE contents (samples ND85/79(207)BIF14 & 15 from Alibert & McCulloch 1993). While the positive Eu anomaly of the Archaean Carajás JPs is pronounced, it is discrete in the Palaeoproterozoic Hamersley BIFs.

Patterns of banded and brecciated ore samples from the Mt. Tom Price, Paraburdoo and Brockman (Fig. 1D) iron ore deposits allow the following interpretation:

(i) All samples exhibit REE enrichment, especially LREE. The HREE have a near-horizontal pattern.

(ii) Tom Price samples exhibit the highest ΣREE contents. This is the only deposit where most of the ore samples contain AnH (at the expense of Mt), and also MpH and Mt.

4 DISCUSSIONS AND CONCLUSIONS

The hydrothermal iron mineralization at Carajás was associated with: (i) early formation of Mgt; (ii) jasper recrystallisation to quartz with its cleansing with expulsion of MiH (V1 quartz vein type of Figueiredo e Silva et al. 2007); (iii) progressive leaching of chert, jasper, or quartz, leaving MiH and innumerable vacant spaces; (iv) partial space filling by MpH; and (v) continued, more efficient space filling by EH and TH.

Leaching of SiO₂ and quartz in BIF is principally a function of temperature, in the 150-250°C range (Taylor et al. 2001), certainly the case in Carajás (Lobato et al. 2005a, b). The evidence suggests that martitization is somewhat contemporaneous to chert recrystallisation and to the onset of SiO₂ leaching of jaspilites.

As pointed out by Lobato et al. (2005a, b), the Carajás porous, high-grade soft ore, rich in MpH and AnH, must have derived from interaction with this relatively hot SiO₂-leaching fluid. On the other hand, the hard ore probably developed due to closer fluid-rock equilibrium conditions allowing the precipitation of the EH-TH that cements the soft-haematite ore, typically at NSE.

Early-stage SiO₂ leaching may have resulted in a relative general REE augmentation during the incipient hydrothermal phase. However, the significant REE enrichment in ores, with associated changes in the shapes of the REE patterns, must have resulted from interaction with the mineralizing, hydrothermal fluid.

The first significant shift in LREE occurs in the Mt(±Mgt)-rich Carajás samples. This can be explained by the distribution coefficients KD of magnetite, which favours the fixation of LREE (Li 2000). As a result, MpH formation and the advance of martitization to form AnH may have favoured the relative increase of HREE in the residual fluid. This lead to the near-horizontal REE patterns associated with the later stages of mineralisation, of ores dominated by AnH-EH-TH and MpH (± MiH in relic SiO₂-leached jaspilite fragments). A general REE enrichment with near-horizontal HREE patterns are also present in ores from the Mt. Tom Price Deposit, containing AnH and MpH (Fig. 1D).

As fluid-rock interaction advanced, more oxidising conditions prevailed, and new haematite types developed. The remaining Eu²⁺ was no longer incorporated into the rocks, resulting in REE patterns with a weakly negative Eu anomaly in high-grade ores samples (Fig. 1B).

At Carajás, the development of Mgt(±Mt) as the incipient-alteration oxide suggests that the early-stage hydrothermal fluid had an fO₂, in disequilibrium with the original oxide MiH (Lobato et al. 2005a, b). The ore samples maintained an Eu positive anomaly (Fig. 1B),
similar to JPs (Fig. 1A), probably equilibrated with a fluid capable of retaining Eu$^{2+}$.

The LREE enrichment in Hamersley (La = max. 30x chondrite, especially Mt. Tom Price) and most of the Carajás (La = 40x chondrite) ore samples is similar. However, the N5E samples (vertical lines, Fig. 1B) represent an exceptional group, dominated by AnH-EH-TH + MpH and lacking MiH, with La close to 70x chondrite. Indeed, to date N5E is a distinctive deposit within the entire district, hosting mostly hard haematite ore. Its units are interpreted to have been the loci of the highest fluid:rock ratios (Lobato et al. 2005, Rosière et al. 2006). The N5E REE geochemical features may thus be used as a powerful exploration tool.

Mt. Tom Price ore samples from the Centre Pit and Southern Ridge deposits are typically more folded and harder. Also, they come from different proximities to the Southern Batter Fault (e.g., Hagemann et al. 1999). The δ$^{18}$O study of iron oxides shows that areas of higher fluid flow near faults have the greatest isotopic interchange (Thorne et al. 2007). Such higher fluid-rock ratios are also reflected by the REE evolution, since the Mt. Tom Price samples exhibit the highest ΣREE contents (rich in AnH).

The overall higher REE contents of the Carajás compared to the Hamersley ore samples suggest that different fluid sources may have been involved in the deposit origins. For Carajás, a magmatic fluid source has been postulated (Lobato et al. 2005; Figueiredo e Silva et al. 2007), whereas Hagemann et al. (1999) indicate that basinal brines were involved in the origin of the Mt. Tom Price deposit.

ACKNOWLEDGEMENTS

We thank Comp. Vale do Rio Doce-CVRD for providing technical and financial support. Thanks are also due to UFMG and UWA. This research was in great part financed by Financ. de Estudos e Proj. (FINEP) & Dept. Nac. de Pesq. Mineral (DNPM), with Agência Desenv. Tecnol. da Indústria Mineral Brasil. (ADIMB). We acknowledge grants received from the Conselho Nac. Desenv. Cient. e Tecnológico (CNPq) and scholarships from Coorden. Apoio Pes. Nivel Superior (CAPES).

REFERENCES


Hydrothermal alteration of basalts that host the giant Northern Range Carajás iron deposits, Brazil

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ABSTRACT: Archaean basalts enclosing the Northern Range Carajás iron deposits show petrographic and geochemical changes caused by the hydrothermal iron mineralizing event. The basalts were subdivided into three hydrothermal alteration types: least, intermediate and highly altered. The intermediate and highly altered rocks show intense mineralogical and geochemical changes compared to the former. The basalts display trace elements (e.g., Nb and Th) behaviour that is consistent with an arc-related setting and continental crustal contamination.

KEYWORDS: Archaean; Carajás; Basalts; Iron ore; Hydrothermal alteration

1 INTRODUCTION

The Carajás Mineral Province comprises Archaean metavolcano-sedimentary sequences that are grouped together into the Itacaiúnas Supergroup. The iron deposits are hosted by the metavolcano-sedimentary rocks of the Grão Pará Group, which comprises the Parauapebas, Carajás and Igarapé Cigarra Formations. The Parauapebas Formation consists mainly of basalts and basaltic volcaniclastic rocks, intercalated with rhyolitic lavas and tuffs. This unit is overlain by jaspilites of the Carajás Formation that host high-grade iron ore bodies (>65% Fe) with minor intercalated mafic volcanic rocks. Iron ores are banded, massive and brecciated, and are associated with haematite (±martite) (Lobato et al. 2006, 2007). The Igarapé Cigarra Formation comprises basaltic lavas and volcaniclastic rocks. Sedimentary clastic rocks overline the sequence. The rhyolites of the lower unit exhibit SHRIMP U-Pb zircon age of 2760 ±7 Ma (Trendall et al. 1998).

The Northern Range iron deposits are enclosed by basaltic rocks. These are massive and vesicular flows, and minor volcaniclastic intercalations, with gabbrros, dolerite dykes and rare intercalations of chert and pelitic rocks. Basalts display features indicative of seawater hydrothermal alteration, and were subsequently metamorphosed at the greenschist facies (e.g., Zucchetti et al. 2006). As a result of the hydrothermal iron mineralizing event (Lobato et al. 2006), the mafic rocks were then chlorititised and hematitised at the contacts with the iron ores at the N4 and N5 deposits.

This work has subdivided the basaltic rocks into three alteration types based on their mineral phases and chemical composition: (i) Least, (ii) Intermediate (not discussed here), and (iii) Highly altered.

The present contribution presents the geochemical signature and tectonic setting for the basaltic rocks, and the first data on the effects of their chlorite-haematite hydrothermal alteration related to the iron mineralization.

2 LEAST-ALTERED BASALTS

The least altered basalts preserve porphyritic, variolitic, intergranular and ophitic textures. They contain phenocrysts of plagioclase, augite and hornblende relics and pseudomorphs after olivine, together with fine-grained titanomagnetite, set in a fine-grained groundmass of devitrified glass. Although primary igneous minerals and textures are preserved, all samples contain evidence for low temperature seawater alteration and regional greenschist facies metamorphism. Olivine is completely replaced...
by chlorite and rare carbonate. The groundmass is composed of plagioclase laths, altered to chlorite, white mica and albite. The plagioclase interstitial material is composed of chlorite, white mica, titanite, iron oxide granules and carbonate. Amygdales are common in volcanic and volcanoclastic rocks, displaying chalcedony infilling from the Archaean seawater alteration, and subordinate carbonate and epidote.

2.1 Whole-rock geochemistry

Results from representative geochemical analyses of three least altered basalts are listed in Table 1. In present-day submarine basalts, new minerals form by replacement of pre-existing magmatic phases during seafloor alteration, resulting in changes in the primary chemical composition (Teagle & Alt 2004). In the present study, only the behaviour of trace and rare earth elements (REE) are evaluated. The commonly immobile elements Hf, Nb, Ti, Zr, and heavy-HREE display the highest correlation coefficients ($R^2 > 0.85$ with the origin set at zero, cf. MacLean 1990) in the least altered basalts, indicating the immobility of these elements (Fig. 1). On the other hand, the scattered distribution of Th and Ta vs. Zr (not shown) points to their mobile behaviour. The chondrite-normalised REE diagram shows steep light REE (LREE) enrichment, flat HREE pattern, and negative Eu anomaly (not shown).

A multi-element plot normalised to N-MORB (not shown) displays Nb-negative anomaly (not shown). The Th-enrichment (Fig. 2) indicates that the basaltic rocks enclosing the jaspilites-iron ores at Carajás experienced continental crust contamination (Pearce 1982).

3 CHLORITE-HAEMATITE ALTERATION

Massive flows close to the hard iron ore, amygdaloidal flows and volcanoclastic rocks all show high chlorite and haematite contents, which are the most important hydrothermal alteration minerals. The most intensely altered rocks have been transformed in chloritites and haematite chloritites. Despite the hydrothermal alteration, some rocks partially preserve primary features, such as variolitic texture. Chlorite replaces mafic minerals, plagioclase and the groundmass. Both chlorite and haematite occur in veins and amygdales. In the most hydrothermally altered samples, haematite also re-

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Major oxides in wt.% and trace elements in ppm. Iron is expressed as Fe$_2$O$_3$. 

Table 1. Geochemical data for 6 representative analyses of least altered (LA) and highly altered (HA) basalts from the Grão Pará Group, Carajás.

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3.1 Mineral chemistry

Chlorite from chloritites and haematite chloritites were analysed with an electron microprobe, and classified using the Bailey’s (1980) classification scheme. Chlorites of the highly altered basalts are clinochlore (Mg-rich) and chamosite (Fe-rich), irrespective of whether crystals are located in amygdales, veins, or replacing primary minerals and groundmass.

Chlorites display variations in the Fe (2.28-5.96 pfu) and Mg (2.86-6.48 pfu) concentrations, depending on whether hydrothermal haematite is stable. Chlorite-dominant altered rocks, practically haematite free, display chlorites with the highest Fe/Fe+Mg ratios (~0.6).

On the other hand, chlorites of the haematite chloritites display the lowest Fe/Fe+Mg ratios (0.28-0.49). Chlorite crystals of the haematite-free, highly altered chloritites are more iron rich than those bearing haematite.

It is clear from the mineral analyses that the composition of hydrothermal chlorites is not influenced by the country rocks chemical composition. Experimental work by Bryndzia & Scott (1987) has shown that the Mg/Mg+Fe ratios increase with increasing f(O2) and f(S2). Thus, in oxidising conditions, like those of the iron ore mineralization at Carajás (Lobato et al. 2007; Figueiredo e Silva et al. 2007), chlorite tends to become Mg-rich, whereas Fe is incorporated in haematite (cf. Beaufort et al. 2005).

3.2 Whole-rock geochemistry

Whole-rock geochemistry data for representative samples of highly altered basalts are provided in Table 1, and their results are discussed in comparison with the least altered basalts.

While Fe2O3T is highly enriched, MgO was only moderately added. The Al2O3 contents are slightly enriched, and SiO2 is depleted with increasing alteration. Calcium, Na2O, and K2O are strongly depleted, and almost completely leached in the most altered samples. The Hf, Nb, Ti and HREE vs. Zr plots follow the linear trends of the least altered basalts (Fig. 1). These linear trends indicate that the slight higher values are due to net mass gains and losses of the mobile elements in the altered rocks.

Chondrite-normalised REE diagrams show profiles that are parallel to those of the least altered basalts (not shown). It is suggested that the changes in the proportions of the REE were caused also by net mass changes in the mobile major elements, thus producing only vertical shifts in the profiles.

Despite the pervasive nature of chlorite-haematite transformation, the highly altered rocks retained the chemical characteristics of volcanic-arc basalts, with a calc-alkaline affinity, and crustal contamination indicated for the least altered basalts (Fig. 2). Crustal contamination was pointed out also by other authors based on εNd values (e.g., Olszewsky et al. 1989; Lobato et al. 2006).

4 CONCLUSIONS

evolutionary history for the Archaean basaltic rocks enclosing the iron ore deposits of
Carajás. This investigation shows that their trace element geochemistry is characteristic of arc-related settings, and that they experienced continental crust contamination.

The original, crustal contaminated basaltic rocks underwent seawater hydrothermal alteration, which caused selective chemical modifications, a feature clearly shown by the major suite of elements of the least altered basalts. Subsequently, these basalts were submitted to regional greenschist facies metamorphism. Later, chlorite-haematite hydrothermal alteration related to the iron mineralising event mobilised all major elements. However, high-field-strength elements and REE retained their geochemical signature.

ACKNOWLEDGEMENTS

We wish to thank Companhia Vale do Rio Doce for providing logistical, technical and financial support. This research was in great part financed by Financiadora de Estudos e Projetos (FINEP) & Departamento Nacional de Pesquisa Mineral (DNPM), with Agência para o Desenvolvimento Tecnológico da Indústria Mineral Brasileira (ADIMB). We greatly acknowledge the Grants received from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). MZ acknowledges also the Geological Survey od Brazil for logistical support.

REFERENCES


Teagle DAH, Alt FC (2004) Hydrothermal Alteration of Basalts beneath the Bent Hill Massive Sulfide Deposit, Middle Valley, Juan de Fuca Ridge. Economic Geology 99: 561-584


Talc mineralization and genesis of soft haematite ore: the Gongo Soco deposit, Minas Gerais

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ABSTRACT: Talcose bodies are scattered within the soft haematite of the Gongo Soco ore deposit as haematite–talc schist. Bulk-rock analyses indicate that the haematite–talc schist has F contents ranging from 0.05 to 1.01 wt%, as well as a constant Fe:S ratio. Sulphur values vary from 0.006 to 0.038 wt% and possibly represent sulphate S from fluid inclusions trapped in specular haematite. It is proposed that the haematite–talc schist resulted from Mg–F metasomatism of itabirite within shear zones by a chemically homogenous fluid (constant Fe:S ratio). This fluid evolved from the leaching of dolomitic itabirite that then resulted in the formation of soft haematite ore.

KEYWORDS: talc, Mg–F metasomatism, soft haematite ore, Gongo Soco, Minas Gerais

1 INTRODUCTION

Supergene leaching of carbonate and quartz from itabirite is considered by many authors to be an important haematite ore-forming process in the Quadrilátero Ferrífero of Minas Gerais, Brazil (e.g. Dorr 1964; Eichler 1967; Spier et al. 2003). This concept has been challenged by a few authors (e.g. Guimarães 1953; Cabral et al. 2003), who assert that leaching of gangue minerals to form soft haematite ore could have been accomplished by hypogene hydrothermal fluids. An impairment of such a hypogene hydrothermal model is the absence of hypogene alteration other than haematitization. The Gongo Soco mine in Minas Gerais is a rare example of a soft haematite deposit in which talc mineralisation occurs within the soft haematite orebody. We present here data indicating that the talcose rock is enriched in F and probably represents Mg–F metasomatism on itabirite.

2 GONGO SOC0 HAEMATITE DEPOSIT

Gongo Soco is a high-grade (~60% Fe), soft haematite deposit currently being mined by Companhia Vale do Rio Doce (CVRD) at a capacity rate of 8.4Mtpa. The deposit occurs within the itabirite unit of the Itabira Iron Formation of Harder & Chamberlin (1915), later designated as the Itabira Group (e.g. Dorr 1969). The Itabira Group has a minimum Pb–Pb age of 2.4 Ga (Babinski et al. 1995). It consists of two formations: the Cauê Itabirite (also known as Cauê Formation), a metamorphosed, laminated iron formation which grades upwards into dolomitic rocks of the Gandarela Formation.

At Gongo Soco, metamorphism attained greenschist conditions within the cummingtonite zone (Pires 1995). The itabirite unit at Gongo Soco is between 300 and 400m thick. The soft haematite orebody is about 1300m long and is slightly discordant to the strike of the itabirite. The western end is close to the footwall of the host formation, and approaches the hanging wall at the eastern end (Fig. 1).

Fresh wall-rock itabirite is composed of quartzose, talc–dolomite–sericite-bearing bands that alternate with laminae and bands of iron oxides, i.e. specular haematite and porphyroclasts of magnetite (Cabral et al. 2003). A tectonic foliation given by the planar arrangement of haematite crystals is pervasive in the wall-rock itabirite and soft haematite ore. According to Rosière et al. (2001), this haematite fabric is
related to the ~0.6 Ga Pan-African-Brasiliano orogeny.

3 TALC MINERALIZATION

Talc mineralization amounting to ~12Mt occurs within the soft haematite orebody and along the contact with friable wall-rock itabirite as tightly folded haematite–talc schist composed of alternating talcose and haematitic bands (Figs. 1, 2). Haematite crystals, ranging in length from 10 to 50 µm, define an axial planar foliation that transposes bands of granoblastic and lepidoblastic haematite at fold hinges. Such a foliation-forming specular haematite is analogous to the pervasive haematite foliation developed in the soft haematite ore and wall-rock itabirite.

Figure 1. Simplified map of the Gongo Soco open cast; geology by O. G. Rocha Filho.
3.1 Bulk-rock chemical data

Bulk-rock chemical analyses were performed at Activation Laboratories Ltd., Ancaster, Canada. Analytical methods used were INAA for Fe, ICP-OES for Ca, Mg, Mn and S, ISE (ion selective electrode) for F and PGNAA (prompt gamma activation analysis) for B.

Results for eight samples indicate compositional ranges from 2.8 to 13.7 wt% Mg and from 6.3 to 43.0 wt% Fe. Manganese contents vary from a few hundred ppm to 3.5 wt%. Sulphur values are low, from 0.006 to 0.038 wt%,(perhaps better to quote in ppm or ppb?? given the low concentration) but are significant because they are positively correlated with total Fe (Fig. 3). Fluorine is present in amounts ranging from 0.05 to 1.01 wt%. The latter coincides with the highest Ca value and suggests the existence of fluorite. Except for one sample (6 ppm B), B abundances are below the detection limit of 2 ppm.

3.2 Mineral chemistry

Electron-microprobe analyses were carried out at Université Laval, Quebec, Canada, with a Cameca SX100.

Talc is the dominant F-bearing mineral, with contents as high as 0.6 wt% F. Talc also contains minor Fe (2.0–3.5 wt% FeO) and Al (0.1–1.4 wt% Al₂O₃).

4 DISCUSSION

Figure 3 shows a remarkable positive linear correlation between total Fe and S. Total Fe and S were determined by different methods, i.e. INAA and ICP-OES, respectively, hence chemical and instrumental interferences are unlikely. However, the acid digestion ICP technique employed is reported to yield sulphide S because S associated with barite is not dissolved. Since no sulphide minerals have been microscopically observed in the haematite–talc schist, it is permissible to assume that the S values reflect sulphate S from fluid inclusions hosted in specular haematite. Crush-leach analyses have revealed that specular haematite from various localities in the Quadrilátero Ferrífero has fluid inclusions with considerable sulphate contents (Lüders et al. 2005). It is suggested that the bulk-rock S values represent sulphate S from fluids trapped in specular haematite. Consequently, the constant Fe:S ratio should be derived from a chemically homogeneous fluid. This interpretation is corroborated by a narrow range of Na:K ratios in fluid inclusions in quartz and haematite from itabirite-truncating, haematitic veins (Lüders et al. 2005).

Dolomitic itabirite was the probable protolith of the Gongo Soco soft haematite ore. The ore is characterised by alternating laminae of specular haematite and bands of a porous, Mn–Al–P–Si-bearing matrix of ferruginous material, which is possibly the result of leaching of dolomite–quartz-rich bands (Cabral et al.)
2003). The leaching process would have engendered a Mg–F-enriched fluid capable of reacting with unaltered itabirite in shear zones to form F-bearing talc and, subordinately, haematite. Progressive deformation, facilitated by ductile talc, would have produced the same mylonitic fabric of specular haematite found in the haematite ore. As oxidation conditions were buffered by haematite, formation of talc was favoured instead of minnesotaite.

Bulk-rock F contents are noteworthy. Metamorphic rocks of evaporitic origin commonly have F-bearing minerals (e.g. Cook & Ashley 1992). Unmineralized itabirite elsewhere in the Quadrilátero Ferrífero contains F-bearing silicates, i.e. talc and amphiboles, as well as Na–K mineral assemblages in dolomitic bands (Pires 1995). In addition, halogen ratios of fluid inclusions in quartz and haematite from haematitic veins are consistent with a fluid diluted after having dissolved and re-precipitated halite (Lüders et al. 2005).

5 CONCLUSION

Fluorine-rich talcose schist occurs within the soft haematite orebody at Gongo Soco. It is proposed that Mg–F metasomatism generated the haematite–talc schist. A chemically homogenous fluid (constant Fe:S ratio) evolved from the leaching of gangue minerals from dolomitic itabirite, which was converted to soft haematite ore. The fluid reacted with itabirite in shear zones to form haematite–talc schist enriched in F.

ACKNOWLEDGEMENTS

CVRD is thanked for providing access and permission to sample. Mr Alex M. Borges (Gongo Soco mine staff) kindly digitised the map of Figure 1. Prof. G. Beaudoin made available analytical facilities at Université Laval. The data presented here were obtained during a DIVEX scholarship to ARC.

REFERENCES


Dorr JVN (1964) Supergene iron ores of Minas Gerais, Brazil. Econ Geol 59: 1203–1240

Dorr JVN (1969) Physiographic, stratigraphic and structural development of the Quadrilátero Ferrífero, Minas Gerais, Brazil. US Geol Surv Prof Pap 641-A


Guimarães D (1953) Notas à margem da crítica. Instituto de Tecnologia Industrial, Estado de Minas Gerais, Belo Horizonte, Avulso 16


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"Digging Deeper" C.J. Andrew et al (editors)
The world’s largest Zn-Pb-Ag deposit: A re-evaluation of Broken Hill (Australia)

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ABSTRACT: The world’s largest Zn-Pb-Ag deposit formed in a Palaeoproterozoic continental shallow water lacustrine rift environment wherein invasion of high Fe-Ti tholeitic mafic melt established large geothermal systems constrained by pelite aquifer caps. The tops of cycles of upward coarsening sediment sequences and mafic and felsic rocks underwent premetamorphic hydrothermal alteration and precipitation of large volumes of non-sulphide zinc and lead minerals. Eruption of felsic volcanics and coeval granite intrusions increased fluid pressure was followed fluid leakage and iron formation precipitation and breaching of the principal aquifer cap. Sediment replacement was followed by six events of subaqueous hydrothermal precipitation coeval with clastic sedimentation in the medial rift. Some fluid spilled over into a horst and the geothermal system closed with the precipitation of an iron formation. Ore fluids and contained metals were of mixed magmatic, crustal, evaporitic and possibly lacustrine origin and had a low sulphur content. Coeval multiphase high grade metamorphism and deformation has retextured, remobilised and reconcentrated parts of the Broken Hill sulphide masses and weathering and erosion removed at least 80 Mt of a system that originally contained 400 Mt of sulphide rocks.

KEYWORDS: Broken Hill, zinc, lead, silver, replacement, structure

1 INTRODUCTION

The Palaeoproterozoic Broken Hill Zn-Pb-Ag deposit occurs in the Willyama Supergroup of the deformed high to low metamorphic grade Curnamona Craton of New South Wales. Lithologies are dominated by metasediments and meta-igneous rocks aged ~1710 to 1640 Ma, the Willyama Supergroup is overlain by Neoproterozoic clastic, glacial and carbonate rocks (Stevens 1999). At Broken Hill, the Willyama Supergroup underwent multiphase coeval deformation and granulite facies metamorphism in the Olarian Orogeny at ~1600 Ma with D1 characterised by layer parallel S1 silimanite, D2 characterised by axial plane S2 in isoclinal folds and D3 characterised by open folds (Page & Laing 1992). In the Broken Hill mines area, D4 is displayed by open disharmonic folds with axial plane quartz-garnet veins or cracking. Argon loss at 1200-1300 Ma can not be related to a deformation event (Harrison & McDougall 1981), intrusion of mafic dykes and plugs was at ~830 Ma and in the De- lamerian Orogeny (~505-460 Ma), the area underwent coeval low grade metamorphism, two episodes of folding and reactivation of D3 shear zones (Corbett & Phillips 1981).

Despite the intense multiphase deformation and metamorphism, original sedimentary features such as bedding, cross bedding, graded bedding, concretions and pull-apart structures are evident and, combined with bedding-schistosity relationships and schistosity overprinting relationships, a coherent stratigraphy and structure at Broken Hill has been established and validated (Willis et al. 1983).

Sedimentological studies in proximity to sulphide rocks (Haydon & McConachy 1987, Plimer 2006) have delineated a marker pelite horizon (4.6 Pelite). A prominent laminated quartz-manganano almandine marker horizon occurs in the 4.6 Pelite. New work shows that the footwall sequence to the Broken Hill orebodies comprises fans of upward coarsening sequences wherein the psammite top is capped by massive pelite. The psammite tops contain abundant blue quartz, gahnite, manganano al-
mandine and sulphides and, in some places contain economic (Potosi Mine) and uneconomic (Tin Street, Burke Street, Crystal Lane) mineralization (Plimer 2006). The Broken Hill orebodies occur stratigraphically above the thinnest segment of the 4.6 Pelite. Contrary to the views of Plimer (1979, 1984), it is suggested that the Broken Hill orebody formed in a shallow water lacustrine sequence rather than a deep water marine rift. Immediately above the thinnest portion of the 4.6 Pelite are metasediments flooded with blue quartz, gahnite, pyrrhotite, sphalerite and manganese almandine (C Lode). Less mobile trace elements of C Lode are indistinguishable from Willyama Supergroup metasediments thereby indicating that pre-metamorphic replacement of metasediments. Overlying massive sulphide horizons contain no metasediment immobile trace element signature and the top of the Broken Hill mine sequence contains a prominent banded iron formation (Stanton, 1976).

Meta-igneous rocks at Broken Hill comprise amphibolite (dated at ~ 1685 Ma) and metagranite (~1685 Ma). The Broken Hill orebody has been dated at ~1685 Ma. Amphibolite is a high Fe –T tholeiite, contains rare ophitic and amygdaloidal textures, contains up to 25% FeO and the FeO content increases in proximity to sulphide rocks. Fe-rich amphibolite close to sulphide rocks contains almandine garnet, grades into leucocratic foliated felsic gneiss and contains common transgressive quartz-gahnite-pyrrhotite-sphalerite assemblages. It is argued that mafic melts intruded wet sediments, established geothermal systems and underwent pre-metamorphic hydrothermal alteration (Plimer 2006). Felsic rocks comprise metagranite which, in proximity to sulphide rocks, is peraluminous. Stevens & Barron (2002) showed that a felsic gneiss facies equivalent to the Broken Hill orebody contains sediment rip-up clasts, mass flow cobbles, amygdules or lithophysae, eutaxitic textures, euhedral feldspar phenocrysts, bipyramidal embayed quartz phenocrysts and calc-silicate ellipsoids. They interpret these rocks as felsic metavolcanics. Other felsic rocks in proximity to sulphide rocks are psammitic metasedimentary rocks (Haydon & McConachy 1987).

It has been suggested that the Willyama Supergroup formed in a Palaeoproterozoic rift (Willis et al. 1983) with heat to drive geothermal systems from thin crust and bi-modal new igneous rocks (Plimer 1984). However, because it has now been recognised that these igneous rocks are both intrusive and extrusive, models for the formation of the Broken Hill orebody must be amended.

The presence of Palaeoproterozoic two mica granite clasts in overlying Neoproterozoic tillite suggests uplift and erosion of at least 12 km of Willyama Supergroup rocks. Uplift took place during the Olarian and Delamerian Orogenies, erosion may have taken place during the Permian glaciation and cover by the terrestrial and shallow marine Permian–Cretaceous Great Artesian Basin covered the area until uplift and intense Cretaceous-Tertiary tropical weathering. Remnants of a Cretaceous peneplain remain. About 80Mt of the Broken Hill orebody has been removed by weathering and erosion, probably in post-Cretaceous times and the gossan and secondary minerals to the Broken Hill orebody are superimposed by assemblages formed in post Pliocene aridity. The Broken Hill orebody is transgressed by numerous fault zones, commonly filled by carbonate. These late stage brittle deformation structures are probably associated with the numerous generations of Phanerozoic uplift.

2 THE BROKEN HILL OREBODY

The Broken Hill Zn-Ag-Pb deposit in western N.S.W., Australia, is one of the largest base metal deposits in the world. The deposit comprises six separate chemically, mineralogically and spatially distinct sulphide rock masses comprising (from stratigraphic base to top): C Lode (11 Mt 3% Pb, 5% Zn, 20 g/t Ag), B Lode (46 Mt 5% Pb, 17% Zn, 40 g/t Ag), Upper, Lower, Western and South Eastern A Lode (53 Mt, 4% Pb, 10% Zn, 40 g/t Ag), Upper and Lower No 1 Lens (10 Mt, 8% Pb, 20% Zn, 50 g/t Ag), 2 Lens (85 Mt 14% Pb, 11% Zn, 100 g/t Ag) and 3 Lens (79 Mt 14% Pb, 14% Zn, 250 g/t Ag). New orebodies (e.g. Potosi, Potosi Extended) occur deeper in the stratigraphy and a facies equivalent of the main Broken Hill orebody is currently being developed (Western Mineralization). Since discovery in 1883, some 200 Mt ore has been mined at Broken Hill. The deposit is associated with a number of unusual rock types (quartz-gahnite rock, garnet quartzite, garnetite, plumbian orthoclase pegmatite).

The long history of deformation and metamorphism at Broken Hill has greatly modified the morphology, metal content and grain size of the orebodies (Plimer 1984). The greatest...
thickness and metal content of sulphide rocks occur in D2 and D3 fold hinges and at the intersection of cross cutting D3 and D4 folds. Quartz-sulphide veins, massive sulphide veins and sulphide breccias occur in S2 and S3, bedding parallel sulphide masses may be S1 and sulphides are transposed into D2, D3 and Delamerian shear zones. Where sulphides are concentrated in dilatant structures or transposed, the Ag:Zn and Pb:Zn ratios increase, the metal content increases and sulphide masses are commonly brecciated with bleached clasts of wall rocks. Sulphides at Broken Hill have an average grain size of 2mm. However, at the sulphide-silicate rock interface, microbreccias and sulphide schists are common and very coarse-grained pegmatoidal sulphide masses occur within metal rich orebodies, especially the galena-rich orebodies (No 2 and No 3 Lenses).

There is a wealth of mineralogical and mineral chemical data on Broken Hill sulphide rocks (Plimer 1984). The Broken Hill sulphide rocks are mineralogically unusual when compared with other massive sulphide rocks. Primary pyrite is absent, there are no primary sulphate phases such as barite and there are numerous S-poor base metal minerals such as plumbian orthoclase, native lead, galnite, zincian ilmenite, zincian silicates, celsian, hyalophane and barien biotite (Plimer 1984). Abundant fluorite, fluorapatite and calcite occur in No 2 Lens and the other sulphide masses have variable but high quantities of Fe, Ca and Mn. Any Mg minerals associated with the Broken Hill orebody are rare and sporadic. Smelter returns show that primary galena and sphalerite are enriched in Cl, Br and I (Toho Zinc, pers. comm). The S-poor nature of Broken Hill sulphide and associated rocks, the lack of sulphate horizons and the lack of a Mg-rich alteration assemblage led Plimer (2006) to concluded that sea water was a minor component of the ore fluids.

Isotopic studies, summarised in Stevens (2000) shows S isotopic data of sulphides (~0‰), Pb and Sr isotope data of sulphide, carbonate and silicate ores and B isotope data of associated tourmalinates (~ -20‰) suggesting a magmatic (S, Pb), crustal (Sr) and evaporitic (B) origin for ore fluids. More recent C and O data from carbonate rich sulphide rocks suggests reduction of biological carbon to carbonate (this study). By contrast, carbonate-filled fault zones that transgress the sulphide rocks contain biological C and S and derive these components from stratigraphically higher beds in the overturned sequence (this study).

Although the greatest concentration of sulphide rocks occurs as the six main Broken Hill orebodies, considerable quantities of base metals occur as galnite, plumbian orthoclase and disseminate sulphides in the psammite tops of upward coarsening metasediment beds in the Willyama Supergroup. It is probable that the total contained metal in psammite tops at Broken Hill is greater than the total metal content of the Broken Hill sulphide orebodies.

3 CONCLUSIONS

It is argued that the Broken Hill ore deposit formed in a continental rift dominated by freshwater lake akin to Lake Baikal. Sedimentation cycles were controlled by events of bimodal volcanism and associated high geothermal gradient resulting in a regional correlation between sulphide rocks and a high palaeogeo-thermal gradient. Most sedimentation took place in a medial rift with the six major sulphide orebodies formed in a graben and the Western/Eastern Mineralization formed on a horst.

The energy for hydrothermal systems derived from a thin crust, the flooding of the lower crust by high Fe-Ti basalts that partially melted the lower crust and the cooling of bimodal igneous rocks. Large volumes of granite may have been a long-lived source of heat. Basalt sills intruded wet porous permeable reactive feldspathic sediments resulting in stratal flow of hydrothermal fluids, replacement and the breaching of the thinnest section of an aquifer cap at the site of greatest sulphide rock deposition. Much of Broken Hill was non-sulphide zinc and lead deposited as footwall replacement in porous permeable reactive feldspathic rocks and subaqueous metal sulphide precipitates retained their S-undersaturated characteristics. Fluid rock interaction resulted in the formation of pre-metamorphic alteration dominated by gains in Fe, Zn, Mn and K (S, F, P) at the expense of Na and Ca. A cycle of geothermal activity from low T oxidised (4.6 Pelite iron formation) to higher T reduced (orebodies) to low T oxidised (banded iron formation of Stanton, 1976) characterises the Broken Hill Group as do significant facies changes with mineralization and sulphides present at the top of upward coarsening sediment cycles.

Components for the Broken Hill sulphide
rocks derived from the mantle, lower crustal rocks and clastic sediments, evaporites and volcanics of the Willyama Supergroup. Ore fluids precipitated masses of unusual composition, the Broken Hill ore deposit is depleted in S and enriched in halogens and P compared with other massive sulphide deposits and is a high tonnage-high grade deposit comprising at least six horizons of characteristic geochemistry and mineralogy.

During the Olarian and Delamerian Orogenies, the Broken Hill orebody was retextured, transposed into cataclastic masses and hydrothermally redeposited in quartz and sulphide veins enriched in Pb, Ag, Sb and As. Dilatant zones such as fold hinges, axial planes and dropers contain substantial tonnages of higher-grade ore and the Mn-rich sulphide rocks reacted with the aluminous wall rocks to form a garnet envelope. Sulphide-silicate competency differences controlled local structure and textures and during retrogression, dewatering established an alteration zone coincidental with sheared sulphides and the Main Lode Shear. Retexturing and remobilisation may have taken place in the Palaeozoic.

Weathering of the Broken Hill orebody could have taken place in the Neoproterozoic and Permian glaciations. Exhumation, weathering and erosion took place in Cretaceous-Tertiary tropical conditions forming secondary minerals recording a biological isotope signature. Post-Pliocene weathering records more arid conditions and a cosmogenic influence on weathering.

ACKNOWLEDGEMENTS

Ideas have evolved from decades of work at Broken Hill as a mine geologist, researcher and explorer. Students such as Rachael Brick, Liann Deyssing, Mike Feldman, David Groombridge, Kate Kitchen, Innocent Munyantwali, Annette Patchett, Tim Sproal and Richard Tully have helped to focus ideas as have Broken Hill geologists such as Paul Ashley, Pascal Blampain, John Collier, Iain Groves, Wolfgang Leyh, Paul Spry, Geoff Scott, Barney Stevens, Graham Teale and Ian Willis. Ideas have been tested on the hundreds of savagely critical and experienced geologists who have had the pleasure of my company on numerous Broken Hill field trips I have led.

REFERENCES


ABSTRACT: The giant epithermal Ag-Hg deposit of Imiter (Morocco) is investigated to test a possible transfer of chalcophile elements from the mantle to superficial crustal levels during Pan-African times. The accretion of the Anti-Atlas belt at the West African continent is characterized by a four stage succession of events, that is, extension, subduction, moderate collision and extension. The strongest metallogenic activity which is dominated by base- and precious metal deposit formation, occurs during the late extensional stage at the Precambrian-Cambrian transition. In the Imiter Ag-Hg deposit, the origin of metals and ligands, deduced from S, fluid inclusions, He, and Re/Os data obtained on sulphide phases and gangue minerals, had a dominantly mantle source.

KEYWORDS: Epithermal deposit, mantle source, Neoproterozoic, Anti-Atlas, Morocco

1 THE IMITER AG-HG DEPOSIT (MOROCCO)

The Imiter deposit is located on the northern side of the Saghro massif, which constitutes, with the other Proterozoic inliers (Ifni, Kerdous, Akka, Bou Azzer, Sirwa and Ougnat) the Anti-Atlas orogenic belt of Morocco (Fig. 1) bordering over more than 700km from the Atlantic Ocean to Algeria on the northern side of the western African Craton (“WAC”) (Ennih & Liegeois 2001; Gasquet et al., 2005). Magmatic activity extends from the Palæoproterozoic to the Neoproterozoic and corresponds to two successive periods of crustal accretion during the Eburnean (Birimian) and Pan-African orogenies. The widespread early Palæozoic cover makes the geology of Anti-Atlas a reference for the Precambrian/Cambrian boundary. Imiter is a world-class silver deposit with currently identified resources of 10 000 tonnes (t) metal. It was formerly interpreted through a black-shale remobilization model (Leistel & Qadrouci 1991) but is now considered as a case of Neoproterozoic epithermal mineralization (Levresse 2001; Cheilletz et al. 2002). Imiter Ag-Hg deposit is precisely dated at 550 Ma (zircon ion-probe U-Pb dating from associated rhyolites; Levresse 2001; Cheilletz et al. 2002) coeval with regional extensional tectonic activity characterizing the P/K transition.

The Imiter Ag-Hg deposit is hosted by black shales (BS) and volcanics (VS) of Middle and late Neoproterozoic age, respectively, and unconformably overlain by a Palæozoic sedimentary succession. The silver mineralization is genetically related to felsic volcanic rocks (domes and dykes) dated at 550 ± 3Ma (Levresse, 2001). This epithermal event post-dates a discrete base metal episode associated with granodiorite intrusions dated at 572 ± 5Ma (ion-probe U–Pb dating on zircon; Levresse 2001). Wall-rock alteration associated with the epithermal silver event was minimized by the neutrality of the hydrothermal fluids. The silver mineralization is structurally controlled by the Imiter fault zone which experienced two successive tectonic regimes (Levresse 2001). The earlier and predominant regime led to the development of normal faults trending N80°E; the second sinistral strike-slip regime led to reactivation of the normal faults, inducing an anas-
tomosed geometry. The epithermal silver event is divided into two successive stages characterized by two different gangue minerals, quartz and dolomite, in extensional veins, hydraulic breccias and quartz/dolomite laminations. Chronology based on the gangue vein mineral strongly depend of the country rocks (volcanite versus black shale) and very local fluid-rock interaction. Impressive deca-kilogram Ag-Hg° plates occur in the extensive fault zones and brecciated areas. Mercury content in Ag-amalgam increases from the quartz- to dolomite stage and ranges from 10 to 30% and from 20 to 40% respectively. Mineralogical textures in both stages are complex (association, replacement). Sulphides are the earliest phases. These are, in decreasing abundance, pyrite-arsenopyrite, sphalerite, galena and chalcopyrite. Sulphides occur mostly as aggregates or as xenomorphic. They are strongly corroded by native silver, sulphides and sulphosalts. Silver sulphosalts everywhere precipitated in association with or as replacement of sulphides. Imiterite is most common as needles in dolomitic geodes, associated with cinnabar and argentite. Oxydation is scarce and locally limited to the upper levels of the deposit.

2 MANTLE SOURCE FOR METALS AND LIGANS

The origin of the metals and ligands (sulphides) was deduced from S, He, and Re/Os isotopic data obtained on sulphide phases and gangue minerals and microthermometric and crush-leach analysis of fluid inclusions from gangue minerals.

2.1 Osmium isotopic evidences

Osmium isotopic ratios have been measured for the first time in Ag° and Ag–sulphosalts. These data and those obtained on other sulphide phases directly associated with the Ag mineralization show measured $^{187}$Os/$^{188}$Os ratios indicating a dominantly mantle source for the associated Os.

2.2 He and Ne isotopic evidences

Helium isotope analyses of sulphides and gangue minerals Q1 and Q2 (hosted in both VS and BS) yield similar results, with $^3$He/$^4$He ratios ranging from 0.76 to 2.64Ra. These data and the absence of $^{20}$Ne in the analyzed fluid inclusions suggest a mantle origin for the fluids associated with the epithermal silver event.

2.3 Sulphur isotopic evidences

Sulphur isotope analyses show the existence of two distinct isotopic reservoirs, one in pyrite from the surrounding black shale country rocks and the other in pyrites associated with a synchronous rhyolitic dome. The $\delta^{34}$S_CDT values of the base metals (Q1) mineralization event are similar than the rhyolitic dome values. The $\delta^{34}$S_CDT values of the silver mineralization (Q2) event range are extended (9‰ of variation) and are interpreted as resulting from preferential degassing of SO$_2$ in ascending fluids, as well as mixing between the magmatic isotopic reservoir and a country rock reservoir. The fluids...
interaction with the country rock reservoir increased in the late dolomite stage (variation extended from the black shales to the volcanic dome reservoir).

2.4 Fluid microthermometry

In Th versus Tmi plot Q1 (hosted in black shales and/or volcanic sequence) present an isosaline cooling path. Q2, hosted in the volcanic sequence, present a comparable evolution than Q1. Q2 and dolomite hosted in black shales present a negative correlation between Th and salinity. The inclusions in Q2 and dolomite present the same Th variation (ca. 220 to 150°C), with higher salinity fluids in dolomite, -20 to -5°C and -40 to -15°C respectively, which are interpreted as evidences of the presence of Ca and Ca-Mg complexes in Dolomite. The low salinity of the fluids in the mineralized vein hosted in the volcanic sequence pleads in favor of silver transport as a bisulphide complex (AgHS). The Th-Tmi negative correlation and the Ca-Mg evidence in Q2 hosted in BS highlight the importance of the water/rock interaction and a possible two fluids mixing.

2.5 Raman spectrometry

The gas phase analyzed in fluid inclusions in both Q1 and Q2 events present comparable composition, mostly CH₄ and N₂ with less H₂S and CO₂.

2.6 Ion content evidences

Halogen concentrations for different quartz and dolomite generations show an evolution suggesting the involvement of ancient seawater with at least another evolved fluid of primary unknown origin, but that can be also interpreted as a very evolved seawater that interacted with the regional rocks, probably by albitionization of plagioclases. Further studies must be performed to ascertain this kind of evolution.

Helium and Osmium isotopic data clearly indicate that the main source of the elements (ligands and metals) of the Q1-Q2 and dolomite events come from a mantelic source. The sulphur isotopes and the fluid inclusion analyses highlight the importance of the water/rock interaction with the black shales. The fluid inclusion analyses suggest the presence of effervescence and a possible mixing of fluids which are responsible for the metal precipitation.

3 DISCUSSION: IMITER AS A PRECAMBRIAN ANALOGUE TO MODERN EPITHERMAL DEPOSITS

In the Anti Atlas, the Neoproterozoic period is characterized by the transition to a passive continental margin coupled with extensional tectonics and the development of marine basins. During this period, magmatism and metallogenic activity have a long common history (Levresse et al. 2001). The post-collisional features, related extensive high-K calcalkaline magmatism, and marine basin development, together indicate a high heat flow contribution due to continental underplating and/or mantle upwelling. This geodynamic control is particularly fruitful for the development of superficial hydrothermal mineralization such as epithermal or base-metal porphyry deposits (Cheilletz et al. 2002). Moreover, huge metal transfers suggest the existence of vertical conduits able to mobilize the deepest parts of the lithosphere.

In the Ag-Hg Imiter deposit case, the source of metals, ligands and gas have mantle-like and pro parte infracrustal signature. Halogen data suggest that mixing between fluids can be a major control on the precipitation of minerals.

ACKNOWLEDGEMENTS

This study was supported by several scientific cooperation grants to A.C. and D.G. from the Reminex-SMI Managem Group (Morocco) and the Ministry of Industry (France), # 98 2 24 00 30 and 00 224 0002. O. Ennaciri, is thanked for assistance during field work. Technical assistance from E. Deloule, M. Champenois, D. Mangin and C. Rollion-Bard (sulphur isotope ion probe analyses), B. Marty, L. Zimmermann (Ne/He), and L. Reisberg, C. Zimmermann (Re/Os, Sr/Nd) is gratefully acknowledged.

REFERENCES


Why There is So Much Gold in Nevada

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ABSTRACT: In responding to questionnaires, exploration geologists and managers generally acknowledge that a major attraction (along with several other factors) to exploring for gold in Nevada is its favourable geology. What makes Nevada geology so favourable? A reasonable answer, given the close association in time and space between magmatic events and gold deposits (and several other mineral resources), is a rich geologic history punctuated by igneous activity, particularly during the Jurassic, Cretaceous, and Tertiary periods. Other geological features that may well be important include Palaeozoic stratigraphy and both Palaeozoic and Mesozoic episodes of compressional tectonics, which produced lithologic and structural pathways for groundwater flow; chemical and mineralogical compositions of host rocks, which may have contributed to ore deposition through wall-rock alteration; chemical compositions and tectonic settings of the magmas; and timing of crustal extension.

KEYWORDS: gold, metallogeny, epithermal, porphyry, polymetallic, replacement, skarn, Carlin, Nevada

1 GOLD FROM NEVADA

In recent years, Nevada (USA) has accounted for approximately 9% of total annual global gold production (Price et al. 2006). Since 1859, Nevada has produced approximately 5300 tonnes, 3% of total global gold production. Remarkably, over 85% of that production has occurred since the Carlin mine opened in 1965.

Recently, Davis & Tingley (2005) summarized information on over 900 precious metal deposits in Nevada in a database and associated map (Davis et al. 2006) and tabulated gold endowment (defined as past production plus known resources) for major deposits. Production has been from a wide range of deposit types, including Carlin-type deposits, epithermal and related hot-spring deposits, and polymetallic replacement and skarn deposits.

The Carlin-type deposits dominate (Table 1), and the Carlin trend itself has produced over 2000 tonnes of gold.

2 CARLIN-TYPE DEPOSITS

Whereas connections to igneous activity are readily apparent for most of the epithermal, hot-spring, polymetallic replacement, and skarn deposits in Nevada, controversies regarding the origin of Carlin-type deposits remain (e.g. Thompson et al. 2002; Muntean et al. 2004; Cline et al. 2005; Rhoden et al. 2005). Carlin-type deposits are typically replacement bodies in silty carbonate rocks. Gold occurs primarily in solid solution or as submicron-sized grains in arsenic-rich pyrite or marcasite, and hydrothermal alteration generally includes decarbonatization. Most deposits contain anomalous silver, sulphur, arsenic, and antimony, but base metals are rarely enriched. Sulphidization of detrital or diagenetic iron is a possible mechanism for ore deposition in some deposits (Hofstra et al. 1991). The orebodies are commonly stratigraphically and locally structurally controlled. The dominant host rocks for Carlin-type deposits in Nevada are Palaeozoic sedimentary rocks that have undergone repeated episodes of thrusting and at least one major episode of crustal extension.

The most compelling evidence for an igneous-related origin for Carlin-type deposits...
is the age of the deposits relative to local igneous events. Henry & Boden (1998) and Ressel & Henry (2006) have demonstrated a close link between voluminous Eocene magmatism and ore formation along the Carlin trend, and Eocene thermal events are now recognized in each of the trends with Carlin-type deposits (Hickey et al. 2003; Cline et al. 2005). Eocene intrusive rocks are locally mineralized, although they infrequently account for large tonnages of ore. Mapped crosscutting relationships are combined with radiometric dates of mineralized and unmineralized igneous rocks to indicate that gold mineralization is broadly (within one million years) coincident with magmatism in the Carlin trend, at Jerritt Canyon, in the Cortez-Pipeline area, and at Northumberland.

Table 1. Endowment of major gold deposits in Nevada (modified from Davis & Tingley 2005 and Muntean 2006, including deposits with greater than 31 tonnes of gold).

<table>
<thead>
<tr>
<th>Deposit Types</th>
<th>Endowment (tonnes Au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carlin</td>
<td>5900</td>
</tr>
<tr>
<td>(Carlin trend, Battle Mountain-</td>
<td></td>
</tr>
<tr>
<td>Eureka trend, Getchell trend,</td>
<td></td>
</tr>
<tr>
<td>Independence Mountains)</td>
<td></td>
</tr>
<tr>
<td>Epithermal &amp; hot spring</td>
<td>1300</td>
</tr>
<tr>
<td>(Round Mountain, Florida</td>
<td></td>
</tr>
<tr>
<td>Canyon, Comstock Lode, Goldfield,</td>
<td></td>
</tr>
<tr>
<td>Mida, Aurora, Tonopah, Sleeper, Rawhide)</td>
<td></td>
</tr>
<tr>
<td>Polymetallic replacement</td>
<td>700</td>
</tr>
<tr>
<td>&amp; skarn</td>
<td></td>
</tr>
<tr>
<td>(Battle Mountain complex,</td>
<td></td>
</tr>
<tr>
<td>Pioche, early production From Eureka)</td>
<td></td>
</tr>
</tbody>
</table>

Direct isotopic dating of Carlin-type deposits has been difficult, because of low concentrations of K, U, Rb, Re, and Sm in arsenic-rich pyrite, quartz, orpiment, stibnite, kaolinite, and most other minerals that precipitated with gold or that are paragenetically related to gold. One remarkable exception is galkhaite, (Cs,Tl,Rb)(Hg,Cu,Zn)$_6$(As,Sb)$_4$S$_{12}$, which has been dated at Getchell and on the Carlin trend (Arehart et al. 2003) to be coincident with local Eocene magmatism. Less direct measures of the age of Carlin-type deposits, including apatite fission-track and U/Th-He techniques, are consistent with Eocene ages for gold mineralization (Chakurian et al. 2003; Cline et al. 2005).

The coincidence of initial extension and Eocene magmatism may have contributed to developing the large hydrothermal systems (Hofstra et al. 1999), needed to produce the deposits scattered along the 60km-long Carlin trend and other trends of Carlin-type deposits in Nevada. Crustal shortening dominated the regional tectonics throughout the Mesozoic. Thrusting had ceased, and crustal extension, a precursor of widespread basin-and-range extension, began about the same time as Eocene magmatism. There is no clear evidence that Carlin-type deposits formed during emplacement of the regionally abundant Jurassic and Cretaceous plutons, and there does not appear to be any significant Carlin-type mineralization associated with Miocene intrusions and volcanic rocks that occur locally in and near the Carlin-type deposits.

The origin of the gold in Carlin-type deposits, whether coming directly from magmas or leached from large volumes of the crust into which intrusions were emplaced, has not been determined. With some local exceptions (e.g. at the Rodeo deposit on the Carlin trend; Emsbo 2000), most Paleozoic host rocks for these deposits do not appear to have been anomalously enriched in gold prior to Carlin-style mineralization (Hsu et al. 1995).

3 POLYMETALLIC REPLACEMENT AND SKARN DEPOSITS

Gold-rich polymetallic replacement and skarn deposits, locally associated with porphyry copper systems, are abundant in Nevada (Sherlock et al. 1996). Jurassic and Cretaceous magmatism in Nevada occurred primarily in a continental arc tectonic setting with the subduction zone to the west and simultaneous thrusting, largely from the west to the east. Some porphyry-copper deposits are associated with Mesozoic intrusions, notably Yerington (Jurassic, with little gold associated with the copper ore but some in peripheral skarns) and Robinson/Ely (Cretaceous, with substantial gold byproduct from the porphyry-copper ore and in adjacent skarn and replacement deposits).

Eocene magmatism is responsible for the
porphyry copper-gold and replacement deposits of the Battle Mountain district (with a gold endowment of 597 tonnes; Davis & Tingley 2005), the replacement deposits in the McCoy district, and the porphyry-copper and skarn deposits at Bingham, Utah. Although sediment-hosted gold deposits do occur on the fringes of some of the porphyry systems, no direct link has been established between the chloride-rich hydrothermal fluids of porphyry systems and the low-salinity fluids of Carlin-type deposits. Nonetheless, the Eocene igneous rocks exposed in the Carlin trend are largely silicic to intermediate calc-alkaline rocks (Ressel & Henry 2006) that are chemically and mineralogically similar to magmas associated with porphyry-copper deposits.

4 EPITHERMAL & HOT SPRING DEPOSITS

Magmatism, Carlin-type mineralization, epithermal vein mineralization, and local porphyry-style mineralization migrated southward across northern and central Nevada during Eocene time (Henry & Ressel 2000). Dominantly younger, Oligocene and Miocene volcanic rocks are hosts to many epithermal deposits (e.g. Round Mountain, Goldfield, Midas, Sleeper, Mule Canyon, Comstock; Sherlock et al. 1996), and some low-grade mineralization appears to be associated with fault-controlled hot springs (e.g. Florida Canyon; Hastings et al. 1988). Gold endowment of the Round Mountain deposit (417 tonnes; Davis & Tingley 2005) rivals that of other major types of deposits in Nevada.

5 CONCLUSIONS

Nevada is unusually enriched in gold. Gold was deposited in different types of deposits at different times. Although Eocene Carlin-type deposits dominate the known resources, Jurassic, Cretaceous, and Eocene porphyry systems and Miocene epithermal systems are significant contributors to total gold endowment. Deposits formed during both extensional and compressional tectonism. Most Carlin-type deposits occur in areas underlain by Proterozoic crust, but many epithermal deposits occur above younger terrains. Although iron mineralogy and structural preparation probably played a role in localizing Carlin-type deposits in Palaeozoic sedimentary rocks, the coincidence of mineralization in space and time with Eocene intrusions clearly links these types of deposits to igneous activity.

6 ACKNOWLEDGEMENTS

We thank David Lentz, Albert Hofstra, and Colin Andrew for their suggestions to expand this abstract, and we thank Jean Cline, Chris Henry, Mike Ressell, Greg Arehart, and Tommy Thompson for numerous discussions that helped to focus our concepts.

REFERENCES


Chakurian AM, Arehart GG, Donelick RA, Zhang X, Reiners PW (2003) Timing constraints of gold mineralization along the Carlin trend using apatite fission-track, \(^{40}\)Ar/\(^{39}\)Ar, and apatite (U-Th)/He. Econ Geol 98: 1159-1171


Davis DA, Tingley JV, Muntean JL (2006) Gold and silver resources in Nevada. Nevada Bureau of Mines and Geology Map 149: 1:1,000,000 scale


The thermal footprint of Carlin-type Au-deposits – defining the far-field extent of hydrothermal flow using low-temperature thermochronology

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ABSTRACT: The thermal footprint of hydrothermal fluid flow should extend distally further than most geochemical tracers and has the potential to be an effective far-field indicator of hydrothermal activity. Low temperature thermochronometers such as apatite fission-track (AFT) and (U-Th)/He in zircon (ZHe) provide a means to map out such thermal footprints. Gold deposits of the northern Carlin trend in Nevada are the product of shallow (<1-2 km), low temperature (<180-240°C), Eocene (~42-37 Ma) hydrothermal activity. Samples along and across the trend preserve evidence for partial to complete thermal resetting of AFT ages coinciding with the timing of mineralization. ZHe ages do not appear to be significantly reset by any Eocene thermal event. ZHe has a higher closure temperature than AFT and combining the two data sets together suggests that, on the timescale of hydrothermal activity (10^4-10^6 yrs), maximum temperatures attained by rocks along the Carlin trend was ~200-150°C; sufficient to totally reset AFT ages but not ZHe. Thermal resetting was a product of both direct advective heat transfer and thermal conduction out from zones of fluid flow. The conductive component of heat transfer results in a greater volume of rock affected by the thermal energy of a hydrothermal system than that recorded by geochemical alteration alone.

KEYWORDS: thermochronology, apatite fission-track, thermal footprint, fluid flow, thermal resetting, Carlin Au-deposits

1 INTRODUCTION

New mineral occurrences at the earth’s surface are rare, particularly in well explored terrains. The main challenge for mineral exploration now, and for the foreseeable future, is the discovery of deposits under pre- and post-mineralization cover. Being able to do this requires an ability to detect the far-field expression of mineralization; the further out this can be done, the greater the likelihood of successfully finding new deposits.

2 FAR-FIELD GEOCHEMICAL ALTERATION

Detecting the relative proximity to hydrothermal mineral deposits has traditionally relied on mapping relative patterns of geochemical metasomatism (major element, trace element & isotope) and hydration induced by the infiltrating hydrothermal fluid (e.g., Lowel & Guilbert 1970; Taylor 1974; Hoeve 1984; Reed 1997; Stenger et al. 1998; Arehart & Donelick 2006). The vertical and lateral limit of the resulting mineralogical alteration is constrained by a number of factors;

- a requirement for direct interaction between the host rocks and the infiltrating hydrothermal fluid;
- the magnitude of the fluid flux and associated fluid / rock ratios;
- the extent of disequilibrium between the host rock and the hydrothermal fluid (i.e., thermodynamic potential for host rock reaction).

Additionally, given that metasomatic reactions involve intercrystalline material transfer,
alteration may be kinetically retarded in low temperature hydrothermal systems.

Hydrothermal mineral deposits are commonly surrounded by distinct depletion or enrichment halos of $^2$H, $^{18}$O or $^{13}$C isotopes that extend far beyond zones of obvious mineralogical alteration (e.g., Taylor 1974; Stenger et al. 1998). The size of such halos reflects the preferential partitioning of these elements into the hydrothermal fluid relative to most metals (Bickle & McKenzie 1987) and represent one of the most far reaching geochemical expressions of a hydrothermal system. A difficulty in interpreting such isotope halos is establishing a clear temporal relationship to mineralization. In regions proximal to ore, patterns of isotopic exchange can be timed relative to the paragenetic sequence of mineralogical alteration. In more distal environments it can be difficult to separate out the effect of pre- and post-mineralization processes. This can be a critical problem as fluid flow commonly occurs more than once along structures controlling permeability in the crust.

3 FAR-FIELD THERMAL FOOTPRINTS

Although geochemical alteration is the most visible expression of a hydrothermal mineralizing system, the advection of heat is also a major component of hydrothermal fluid flow. Heat is transported by the infiltrating fluid at a rate greater than all but the most incompatible of geochemical tracers (e.g., He, H) (Bickle & McKenzie 1987). Therefore, transient heating associated with hydrothermal flow is quite likely to be one of the most distally developed expressions of a hydrothermal mineral deposit. Because heat is not only advected by the fluid itself, but also diffuses rapidly outward from the path of fluid flow, the volume of rock affected by the thermal energy of a hydrothermal system will be significantly larger than that recorded by geochemical alteration.

The thermal resetting of low-temperature mineral thermochronometers (e.g., fission-track and (U-Th)/He techniques) provides a means to demarcate thermal halos associated with hydrothermal flow. The resetting of thermochronometers is solely a function heat transfer; without the need for material transfer from other mineral grains or the hydrothermal fluid. Thermochronology also has the major advantage of providing an age for thermal resetting, enabling pre-, syn- and post-mineralization thermal events to be distinguished. Integrating age data from a range of thermochronometers with different closure temperatures provides an estimate of the maximum temperatures attained at any one location. The spatial and temporal distribution of such temperature maxima place constraints on the size, geometry, longevity and intensity of hydrothermal flow; information critical to identifying vectors toward ore.

4 THERMAL FOOTPRINTS ALONG THE NORTHERN CARLIN TREND, NEVADA

The world-class Carlin-type Au-deposits of the northern Carlin trend in Nevada are the product of relatively shallow hydrothermal activity in the middle to late Eocene at ~42-37 Ma. Maximum temperatures of the mineralizing hydrothermal system have been constrained to be <180-240°C (Cline et al. 2005).

An apatite fission-track (AFT) study of pre-mineralization rocks along and across the Carlin trend was undertaken to assess the size and extent of any thermal anomaly that accompanied mineralization. On the $10^4$-$10^6$ yr timescales that hydrothermal systems are likely to be active, the AFT thermochronometer will be significantly reset at $> ~160-100$°C and will be completely reset over a temperature range of $>~200-120$°C for most common fluoro-apatite compositions (Ketcham 2005). The zircon (U-Th)/He thermochronometer (ZHe) was also applied to a small number of samples. This system has a higher closure temperature than AFT. At timescales of $10^4$-$10^6$ yrs it will begin to reset at $~200-150$°C and will be completely reset at $~270-200$°C (Reiners & Brandon 2006).

4.1 AFT data

AFT ages of samples from the region encompassing the northern Carlin trend area fall into two main clusters. (1) An older, ~120-70 Ma, cluster of samples that for the most part are distal to areas of known Au-mineralization (>10 km). (2) A younger cluster of largely ~60-20 Ma ages centered over the northern Carlin trend. These data define a more pervasive core zone of 20-50 Ma AFT ages surrounded by a zone of mixed ages between 30 and 100 Ma that extends up to ~6km out from mineralized areas.

Thermal modeling of the older cluster of AFT ages indicates that those samples last cooled from $>100$°C to $<50$°C during the Sevier orogeny at $>60$ Ma, with one major pe-
period of cooling at ~100-70 Ma. This thermal history represents the regional background onto which the Carlin hydrothermal system was superimposed. The range of modeled Eocene temperatures for these older age samples suggests that the current erosional surface is no more than 1-2km below that present in the Eocene at the time of mineralization.

Thermal modeling of the AFT data suggests the cluster of younger AFT ages is largely a product of one or more episodes of transient reheating and rapid cooling between ~45 and 30 Ma. The spatial and temporal overlap of the young AFT ages with Au-mineralization in the northern Carlin trend is suggestive of a direct genetic relationship to the hydrothermal system responsible for mineralization. This proposed relationship is supported by the spatially heterogeneous nature of AFT resetting at the scale of the northern Carlin trend. This is most clearly observed in and around the Jurassic (158 Ma) Goldstrike and Little Boulder granodiorite stocks. Although largely unmineralized in its interior, the margins of the Goldstrike stock can be altered and auriferous. Samples of the mineralized stock yield AFT cooling histories involving an episode of rapid cooling from >100°C to <50°C at ~40 Ma. Samples of weakly altered, but unmineralized, 158 Ma lamprophyric dykes on the Betze pit immediately north of the Goldstrike stock exhibit essentially the same cooling history. Samples from the unmineralized and unaltered Little Boulder stock yield cooling histories characterized by a period of rapid cooling from >100°C to <40°C at ~80-60 Ma. The AFT data are inconsistent with any significant Eocene reheating on (maximum reheating of <~135-85°C at timescales of 10^4-10^6 yr). Samples from the weakly altered to unaltered core of the Goldstrike stock yield thermal histories consistent with an initial cooling below 120-100°C at ~80-60 Ma followed by partial resetting to <~160-85°C on timescales of 10^4-10^6 yr at ~40 Ma.

4.2 ZHe data

ZHe ages from samples of the unmineralized core of the Goldstrike stock, its mineralized northern edge and from a weakly altered lamprophyre in Betze pit are all ~70 Ma. This is interpreted as a regional cooling age reflecting Sevier age exhumation with little or no subsequent resetting by the Eocene hydrothermal event recorded in the AFT data. The latter observation suggests maximum temperatures reached by the ZHe samples during the Eocene event was not much greater than ~200-150°C for timescales of 10^4-10^6 yrs respectively; sufficient to completely reset apatite fission-tracks.

4.3 Interpretation of thermal data

The AFT and ZHe data together suggest that the northern Carlin trend underwent the following thermal history:

1. Regional exhumation from ~6-8km (~200°C) to <1-2km (<50°C) as part of the Cretaceous Sevier orogeny at ~70 Ma.
3. On 10^4-10^6 yr timescales mineralized areas were heated to no greater than ~150-200°C; sufficient to reset AFT, but not ZHe ages.
4. There was a zone of relatively pervasive upwelling of hot hydrothermal fluids along the core of the northern Carlin trend and this was flanked to a distance of up to 6km by more heterogeneous (fracture-controlled?) fluid flow. The lower permeability (intrinsic and fracture-controlled) of the Goldstrike and Little Boulder stocks restricted fluid flow through these units, leading to no, or only partial, resetting of AFT ages.
5. The thermal resetting of apparently geochemically unaltered samples indicates that thermal resetting was not only a direct product of advective heat transfer by hydrothermal fluids, but also by thermal diffusion out from zones of fluid flow.

Numerical modeling suggests that on the timescale of modern geothermal systems (up to 300ky), diffusion of heat alone is able to completely reset AFT ages 0.5-3km out from zones of upwelling 180-240°C Carlin-type ore fluids. This provides constraints on the maximum spacing of fluid conduits needed to pervasively reset AFT ages.

5 DISCUSSION AND CONCLUSION

The heterogeneous nature of thermal resetting combined with its overall spatial and temporal overlap with Carlin-type Au-mineralization is consistent with the former being a product of the mineralizing hydrothermal event. Thermal resetting of AFT ages extends laterally up to ~6 km out from individual Au-deposits along the northern Carlin trend and provides an effective means for delineating the far-field expression of the hydrothermal system.
responsible for Carlin-type Au-mineralization. Because the conductive element of heat transfer results in a greater volume of rock affected by the thermal energy of a hydrothermal system than that recorded by geochemical alteration alone, thermal footprints may be the most far-reaching expression of hydrothermal fluid flow.

ACKNOWLEDGEMENTS

We would like to acknowledge and thank the mine and exploration staff from Barrick Gold Corporation and Newmont Mining Corporation for their logistical support over the life of this study. This research was jointly funded by AngloGold North America, Barrick Gold Corp., Newmont Mining Corp., Geoinformatics Exploration Inc., Teck Cominco Ltd. and the Natural Sciences and Engineering Research Council of Canada.

REFERENCES


An overview of metallogenic relations of South China and adjacent areas of mainland SE Asia: Implications for mineral exploration

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ABSTRACT: The South China Region is rich in mineral resources and has a wide diversity of deposit types. The region has undergone multiple tectonic and magmatic events and related metallogenic processes throughout the earth’s history. These tectonic and metallogenic processes were responsible for the formation of the diverse styles of base and precious metal deposits (VHMS, SEDEX, MVT, porphyry, epithermal and skarn deposits) in South China, making it one of the resource-rich regions in the world. The adjacent mainland SE Asia Region also is rich in mineral resources and has a variety of deposit types and styles from VHMS deposits (\textit{e.g.}, Bawdwin, Myanmar), MVT deposits (\textit{e.g.}, Theinong Mine, Myanmar), orogenic gold deposits (world-class pre-War Raub Australian gold Mine, Malaysia) to sedimentary-rock hosted gold deposit (Sepon, Lao PDR), porphyry related skarn copper-gold deposit (Phu Kham, Lao and Puthep, Thailand), low-sulphidation epithermal gold deposit (Chatree, Thailand), and high-sulphidation copper deposit (Monywa, Myanmar). Further research are required not only to understand the genesis of the individual ore deposits or districts, but also to constrain the age of magmatic-volcanic events and mineralization to establish the time-space relations for mineralization in the entire region and to apply these results for better targeting the greenfield potentials and prospective ground for the explorers.

KEYWORDS: Metallogeny, base metals, gold, South China, Southeast Asia.

1 INTRODUCTION

The People’s Republic of China and adjacent mainland SE Asia is a resource-rich region in the world and has a long history of metal and non-metal mining. The region has a diverse deposit types and mineralization styles. This paper provides an overview of the metallogeny and mineral potential of base and precious metal deposits in the area and discusses the future direction in ore genesis research and mineral exploration in the region.

2 DEPOSIT TYPES

\textit{Lead-zinc:} Five different styles of Pb-Zn+Ag mineralization occur in South China: (1) VHMS deposits (\textit{e.g.}, Carboniferous Laochang and Dapingzhang deposits in Yunnan, and the Triassic Gacun VHMS deposit in Sichuan); (2) SEDEX deposits (\textit{e.g.}, Cenozoic Jinding deposit in Yunnan); (3) MVT deposits (\textit{e.g.}, Sinian-aged Daliangzi and Tianbaoshan deposits in Sichuan); (4) Lead-zinc skarn deposits (\textit{e.g.}, Jurassic Huangshaping deposit in Hunan), and; (5) Lead-zinc with precious metals in veins and porphyry deposits (\textit{e.g.}, Tertiary Beiya deposit in Yunnan) (Khin Zaw et al. 2002, 2007). A number of late Palaeozoic to Early Mesozoic VHMS deposits developed in the Sanjiang Fold Belt at the western part of the South China Region (\textit{e.g.}, Laochang and Gacun) (Hou et al. 2007). Significant Devonian to Carboniferous and Cenozoic stratabound base metal mineralization also occurs in South China (\textit{e.g.}, Fankou, Dabaoshan and Jinding deposits).

These late Palaeozoic stratabound deposits have features in common with the SEDEX class (Gu et al. 2007). They have been often overprinted by skarn systems associated with Yanjiangian magmatism (\textit{e.g.}, Chengmenshan,
Dongguashan and Qixiashan deposits). The VHMS and MVT deposits are also found in adjacent mainland SE Asia (e.g., the Cambrian Bawdwin deposit and the Ordovician Theingon deposit in Myanmar).

**Copper:** The South China region has the largest porphyry copper deposit in China (i.e., the Dexing deposit in Jiangxi Province) and is an important deposit type in South China because of the other emerging porphyry Cu-Mo-Au systems, such as the Yulong and Gangdese deposits in Tibet and the Beiya deposits in Yunnan. Au-(Ag-Mo)-rich porphyry-related Cu-Fe skarn deposits are present along the Lower to Middle Yangtze River metallogenic belt. Available contained metal tonnage data for the different deposit types show that porphyry copper and skarn deposits are the major source of Cu in South China (61% and 19%) accounting for at least 28 Mt contained Cu metal (Khin Zaw et al., 2007). Porphyry-related Cu–Fe–Au skarn systems are also found in contiguous mainland SE Asia (e.g., the Puthep Cu–Fe skarn and the Phu Thap Fah Au skarn in Thailand and the Phu Kham Cu–Au deposit in Lao PDR).

**Gold-silver:** The South China Region is rich in precious metal resources. At least three primary Au-Ag only deposit types are present: (1) Carlin-like gold deposits; (2) epithermal vein and breccia gold deposits; and; (3) orogenic gold deposits. Precious metals are also extracted from skarn, porphyry copper, SEDEX and VHMS deposits in South China. The Carlin-like gold deposits are hosted predominantly by Palaeozoic to Mesozoic-aged siliciclastic and carbonate lithologies. They are present in a region at the junction of Yunnan, Guizhou, and Guangxi Provinces called the ‘Southern Golden Triangle’, and are also present in NW Sichuan, Gansu and Shaanxi, in an area known as the ‘Northern Golden Triangle’ of China. The Southern Golden Triangle deposits lie within the Youjiang margin sag-basin or rift basin along the southwest margin of the South China Craton (SCC), whereas the Northern Golden Triangle deposits are present within the Songpan-Garze accretionary wedge terrain, along the northwestern margins of the SCC. They are similar to Carlin-type deposits in USA and are mostly epigenetic hydrothermal μm-scale-disseminated gold deposits with associated As, Hg, Sb ± TI ore minerals (Peters et al. 2007). Carlin-like deposits are also found in adjoining parts of the SE Asian region (e.g., Sepon gold deposit, Laos). Many porphyry-related gold skarn deposits also occur along the Lower to Middle Yangtze River metallogenic belt in South China (Chen et al. 2007). These deposits are related to Indosinian (Triassic) and Yanshanian (Jurassic to Cretaceous) magmatism associated with collision of the SCC and North China Craton (NCC) and westward subduction of the Palaeo-Pacific Plate. The South China Fold Belt, covering Fujian and Zhejiang Provinces along the southeastern margin of the Yangtze terrane, is characterised by well-developed Yanshanian intrusive to subvolcanic rocks associated with porphyry to epithermal style copper-gold mineralization and mesothermal vein deposits. The most important example is the Zijinshan district in Fujian Province. It is currently the only high-sulphidation epithermal system in mainland South China. Epithermal to mesothermal vein-type deposits are also found in Zhejiang Province (e.g., Zhilingtou). Epithermal style gold deposits also occur in nearby mainland SE Asia (e.g., low-sulphidation epithermal Chatree deposit in Thailand and high-sulphidation Monywa deposit in Myanmar).

Many orogenic gold deposits lie along the NW-trending Ailaoshan mega-shear belt in SW China; these deposits account for more than 500 t Au (Hou et al. 2007). They are mostly hosted in ophiolitic mafic-ultramafic rocks and minor sandstone and crystalline limestone. These deposits were most likely formed due to strong shearing and nappe development during the Himalayan Orogeny (Hou et al. 2007). Orogenic gold deposits are also found in Guangxi and Guangdong Provinces (e.g., Hetai goldfield). Unique world-class granitoid-hosted orogenic gold deposits occur along the boundary between the SCC and NCC in Shandong Province but their tectonic environment remains unclear. These deposits are the major gold producers in China with ore reserves exceeding 900 t Au. Orogenic gold deposits are also fairly widespread in the contiguous SE Asian region (e.g., Modi Taung and Payaungtaung deposits in Myanmar; and world-class pre-War Raub Australian deposit in Malaysia).

**Other metals:** Occurrences of Pt-Pd-Ni-Cu-Co are found in Permian-aged Emeishan continental flood basalt (ECFB) in South China (Jinbaoshan and Baimazhai in Yunnan Province and Yangliuping in Sichuan Province). Major skarn-vein-greisen type W-Sn-Bi-Be-sulphide deposits are also found in the Himalayan Orogeny (Hou et al., 2007). Porphyry-related Cu–Fe–Au skarn systems are also found in contiguous SE Asian region (e.g., low-sulphidation epithermal Chatree deposit in Thailand and high-sulphidation Monywa deposit in Myanmar).

Many orogenic gold deposits lie along the NW-trending Ailaoshan mega-shear belt in SW China; these deposits account for more than 500 t Au (Hou et al. 2007). They are mostly hosted in ophiolitic mafic-ultramafic rocks and minor sandstone and crystalline limestone. These deposits were most likely formed due to strong shearing and nappe development during the Himalayan Orogeny (Hou et al. 2007). Orogenic gold deposits are also found in Guangxi and Guangdong Provinces (e.g., Hetai goldfield). Unique world-class granitoid-hosted orogenic gold deposits occur along the boundary between the SCC and NCC in Shandong Province but their tectonic environment remains unclear. These deposits are the major gold producers in China with ore reserves exceeding 900 t Au. Orogenic gold deposits are also fairly widespread in the contiguous SE Asian region (e.g., Modi Taung and Payaungtaung deposits in Myanmar; and world-class pre-War Raub Australian deposit in Malaysia).
deposits associated with Yanshanian magmatism also occurs in South China (e.g., the Shizhuyuan and Xihuashan deposits). The South China region has important world-class stratabound base metal-tin deposits (e.g., the Dachang deposit in Guangxi). Large antimony deposits are also found in South China. Similar W-Sn and antimony deposits are also found in adjacent SE Asia region.

3 DISCUSSION AND CONCLUSIONS

Many different deposit types and mineralisation styles occur in the South China region: VHMS, SEDEX, MVT, skarn, porphyry, epithermal, orogenic and vein deposits. However, further research on the potential and prospectivity of the IOCG mineralization in South China and mainland SE Asia remains to be investigated. Metamorphosed Proterozoic sedimentary rocks along the Red River Fault in South Yunnan contain iron-oxide-copper occurrences, and they are similar to those found along the same zone at the Fe-Cu-Au-REE Sin Quyen deposit in Vietnam. Mesozoic and Cenozoic sandstone-hosted stratabound copper deposits are distributed in South China (e.g., Kirkham et al. 1994; Cox et al. 2003) but their nature, origin and potential are poorly explored. It is difficult to adequately classify all of the South China mineral deposits using currently available ore deposit models because some deposits show hybrid natures between various typical deposit types, and the many deposits were formed by multiple episodic mineralization and overprinting processes. The depth of ore formation and age of mineralization are also not well-constrained for many of the deposit types. Further research is required not only to understand the genesis of the individual ore deposits or districts, but also to constrain the age of magmatic-volcanic events and mineralization to establish the time-space relations for mineralization in the region.

The adjacent SE Asia Region also has a great diversity of metallic and non-metallic mineral deposits and recent discovery and delineation of major gold and copper deposits (e.g., Sepon, Phu Kham, Chatree, and Puthep) in the region has attracted interest from international mining and exploration Companies. Despite political doldrums, the region is emerging as one of the exploration challenges remaining in the world.

The mainland SE Asia Region is characterised by an assembly of major crustal terranes of Gondwana affinities involving Shan-Thai, Indochina and west Myanmar terranes. These crustal terranes host major mineralised Fold Belts (e.g., Palaeozoic to Cenozoic Loei Fold-Belt in Thailand and Laos, Palaeozoic Troungson Fold Belt in Laos and Vietnam and Cenozoic Monywa-Wuntho belt in Myanmar). The intense tectonic collision of Indian and Asian continents during the Cenozoic resulted in indentation, rotation and reorganisation of the terranes (e.g., Tapponnier et al. 1982; Lee & Lawver 1995; Barley et al. 2003) and tectono-thermal overprinting of the fold belts in South China and SE Asia (Khin Zaw et al. 1999). Hall (1996, 2002) reconstructed the movement of various crustal elements for the last 50 Ma in the SE Asia Region and Barley et al. (2002) related the magmatism and ore deposit formation and the timing of plate reorganisation in the region. Garwin et al. (2005) recently provide a comprehensive overview of the geotectonic setting and gold-copper deposit styles of the Cenozoic magmatic arcs in western Pacific and part of mainland SE Asia and the metallogenic development in the last 50 Ma. However, the tectonic and metallogenic evolution of mainland SE Asia during pre-Cenozoic era remain poorly understood due to lack of high-precision geochronology and detailed geochemical and isotopic data. Further works are required to understand the geodynamic setting, nature of plate orientation and interaction, metallogeny, tectonic history, evolution of the mineralised Fold Belts, and uplift and block faulting relating to the preservation of ore deposits prior to 50 Ma. These studies will provide key criteria and important guidelines for exploration of world-class mineral deposits in the region and will help explorers better targeting the greenfield potential and prospective ground which are critical to the future discoveries in this fertile region.

Such studies should involve regional tectonic and metallogenic synthesis and deposit characterisation across country borders by extensive field work and laboratory studies using modern analytical facilities and could be performed by a group of passionate geoscientists both from academia and industry including geologists from the countries of origin. Extensive funding from major donors and funding agencies such as Australian Research Council, UNDP, IUGS, UNESCO, World Bank, Asian Development Bank and a consortium of major international mining Companies is fundamen-
tally important and required. One example is a current on-going Utas Centre of Excellence in Ore Deposits research project on “Geochronology, Metallogenesis and Deposit Styles in the Loi Fold Belt of Thailand and Laos PDR” funded by the Australian Research Council and three industry partners, Kingsgate Consolidated Limited, Oxiiana Limited and Pan Australian Resource NL. This project aimed to better constrain the age, style and origin of deposits in the context of regional tectonic and magmatic cycles and is providing improved conceptual and genetic models and defining new exploration criteria vital to future discoveries of world class copper-gold resources in this region.

ACKNOWLEDGEMENTS

The authors have greatly benefited from discussions with Chinese colleagues in particular Professors Lianxing Gu, Yanjing Chen, Xinbiao Lu, Pie Ni, Taofa Zhou, Xiaming Qu, Dr. Zhaoshan Chang and Dr. Guojian Xu and staff members of Centre of Excellence in Ore Deposits (CODES), University of Tasmania.

REFERENCES


Geochemistry of the Mesozoic Intrusive Rocks in the Tongling Cu-Au-Fe district, South Anhui Province, China

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ABSTRACT: The Tongling region is an important copper-gold-iron mining district in China. The formation of the metal deposits has close genetic relations with Mesozoic intrusions. The petrology, element and isotopic geochemistry of the Mesozoic intrusive rocks in the Tongling region were systematically investigated and are summarized here. These intrusive rocks are mainly of high-K calc-alkaline series and shoshonitic series, most likely related to fractional crystallization. The element geochemistry and Sm-Nd and Rb-Sr isotopes indicate that the sources of the intrusive rocks in the Tongling region are mixtures of more than two compositional end members. The sequence of intrusions is: pyroxene diorite and monzodiorite → quartz diorite and monzodiorite → granodiorite → quartz monzonite. Mixing of mantle and crustal materials might have been the main mechanism through which the Tongling intrusive rocks (SiO₂ > 55 wt%) were produced.

KEYWORDS: high-K calc-alkaline, Mesozoic intrusive rock, magmatic mixing, Tongling region, China

1 INTRODUCTION

The Tongling region of Anhui Province is an important ore district of the famous Lower and Middle Yangtze metallogenic belt in China, and also representative of skarn deposits in China (e.g., Chang et al. 1991; Pan & Dong 1999). Many researchers have noted that the metal deposits are closely related to the Mesozoic intrusive rocks in the region (Zhou & Li 2000; Wang et al. 2003). Our investigation concentrates on the petrology and geochemistry of intrusions related to Cu-Au-Fe ore deposits (e.g., Tongguanshan, Shizishan, Fenghuangshan and Xinqiao ore fields). The geochemical characteristics of the intrusive rocks in the Tongling region are summarized here based on systematic analysis of major and trace elements together with data collected from the literature.

2 REGIONAL GEOLOGICAL SETTING

The Tongling region in east-central China is situated along the northern margin of the Yangtze craton (Fig. 1). Cambrian to middle Triassic sedimentation developed on stable Precambrian basement, forming a thick sedimentary sequence, which became the country rock for the later Cu, Au, and Fe deposits related to the collision event of the Yangtze and Sino-Korean platforms in the middle Triassic (Li et al. 1993). During the Yanshanian period (Jurassic/Cretaceous), this region became active again within an intraplate deformational stage and magmatism. The Indosinian-Yanshanian movements produced NE trending folds, faults and depressions. Intensive intermediate felsic magmatism and associated hydrothermal activity formed multiple metal mineralizations.

3 PETROLOGICAL CHARACTERISTICS

The Yanshanian magmatic event (J-K) is extensive and produced 76 intrusions in the Tongling region along the lower Yangtze River. These intrusions are mostly located within the Yangtze magmatic metallogenic belt controlled by the E-W trending Tongling – Nangling deep
fault (Fig. 1), where a series of multiple metal deposits have been discovered, such as primary Cu-Au-Fe deposits of the Tongguanshan, Shizishan, Xinqiao and Fenghuangshan ore fields.

The Tongling intrusive rock types have mainly four rock associations: (i) Pyroxene diorite- pyroxene monzodiorite associations; (ii) Quartz diorite-quartz monzodiorite associations, which are the most important magmatic rocks in Tongling region primarily related to Cu-Fe deposits; (iii) Granodiorite associations, which are closely related to polymetallic deposits; (iv) Quartz monzonite-monzonite associations, which are closely related to gold deposits.

The intrusive relationships indicate that pyroxene diorite is earlier than quartz diorite. Granodiorite with quartz diorite enclaves lies in the interior of the Fenghuangshan intrusion, while quartz diorite lies at the edge of the intrusion, suggesting that the emplacement of quartz diorite was earlier than that of granodiorite. Isotopic dating results also support the field observation (Wang et al. 2004; Xu et al. 2005).

The sequence of intrusions in the Tongling region is: pyroxene diorite and monzodiorite(143Ma) → quartz diorite and monzodiorite(137Ma) → granodiorite(133Ma) → quartz monzonite(130Ma).

4 RESULTS AND DISCUSSION

4.1 Major elements

The contents of SiO$_2$ of the Tongling intrusive rocks vary from 47.6% to 76.5 wt%. The total alkali contents vary from 4.5 to 8.8 wt%, with K$_2$O contents ranging from 1.3% to 4.7%. Most samples of the Tongling intrusive rocks belong to high-K calc-alkaline series, a few samples to shoshonitic series, only one sample falls between high-K calc-alkaline and middle-K calc-alkaline series (Fig. 2).

In Harker diagrams, several features are prominent: (i) High Al$_2$O$_3$ (>15.0 wt%) and rich in Na (Na$_2$O/K$_2$O>1.0), with the exception of several samples; (ii) Negative linear correlations between SiO$_2$ contents (from 48 to 77 wt%) and those of TiO$_2$, MgO, CaO, TFeO and P$_2$O$_5$; (iii) No linear correlation between SiO$_2$ and trace elements of Sr and Co.

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Figure 1. Geological sketch map of the Tongling metallogenic district, East China: 1 Granite, 2 Granodiorite, 3 Diorite, 4 Silurian, 5 Devonian, 6 Carboniferous-Permian, 7 Triassic, 8 Fault, 9 Geological boundary, 10 Tongling-Nanling deep fault, 11 the Cu-Au-Fe ore deposit.

Figure 2. The SiO$_2$ v.s. K$_2$O diagram of different intrusions from the Tongling metallogenic province (data are analyzed by XRF in the Physical-Chemical Center of USTC, Open Lab of CAS)
The diagrams indicate that the magmas evolved from mafic- to intermediate-acid through fractional crystallization. The diagrams of K$_2$O, Na$_2$O versus SiO$_2$ have three trends: (i) Positive correlation with SiO$_2$ (samples with <55 wt% SiO$_2$); (ii) K$_2$O negatively correlated with SiO$_2$, while Na$_2$O is positively correlated (SiO$_2$ content varies from 55 to 65 wt%); (iii) When the, K$_2$O is positively correlated with SiO$_2$, while Na$_2$O is negatively correlated with SiO$_2$ (SiO$_2$ >65 wt%). These characteristics suggest magma mixing of at least two end members. This is consistent with previous results on xenoliths from the intermediate-acid intrusive rocks, which implied mixing between mantle-derived and crust-derived magmas (Wu et al. 2003).

4.2 REE and trace elements

The total REE concentrations of the Tongling intrusive rocks range from 63 to 387 ppm with a mean value of 154ppm. The LREE/HREE ratios vary from 8.6 to 13.9, with an average of 10.5, whereas the ratios of (La/Yb)$_N$ change from 7.9 to 31.2 (mean 12.5). The chondrite normalized REE patterns have a negative slope without obvious Eu anomalies (Fig. 3a). As a whole, the total REE concentrations gradually increase from basic rocks to intermediate-acidic rocks, which probably reflects magma mixing processes.

The chondrite normalized diagrams (Fig. 3b) show consistent patterns for LILE, with positive K, Rb anomalies, depletions in Nb, Ta and Ti, and a large range of Sr, similar to that of the continental crust. By contrast, the transitional metal elements (Fig. 3c) show similar patterns to MORB, with depletions in Cr, Ni and positive Ti, Co.

4.3 Isotopic evidence

The Nd, Sr isotopic compositions Tongling intrusive rocks show a large range [($)^{87}$Sr/$^{86}$Sr$]=-0.7061$-$0.7105$, $\varepsilon_{Nd}(t)=-7$-$-17$. The $\varepsilon_{Nd}(t)$ values are negatively correlated with $^{87}$Sr/$^{86}$Sr(t). This cannot be explained by partial
melting of a homogeneous source region, but rather supports mixture of more than two compositional end-members, probably mixtures of mantle and crustal sources. In a $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ diagram, the correlation trend extends along the mantle array (Fig. 4). Therefore, the Dongling and Kongling basement cannot be a major component in the genesis of the intrusive rocks in the Tongling region.

5 CONCLUSIONS

(i) The intrusions in the Tongling region are mainly high-K calc-alkaline and shoshonitic series with the intrusive sequence of pyroxene diorite and monzodiorite → quartz diorite and monzodiorite → granodiorite → quartz monzonite;

(ii) Chemical and isotopic data support the fact that the intrusions are mixtures of more than two compositional sources.

ACKNOWLEDGEMENTS

This study is supported by Chinese Ministry of Science and Technology (2006CB403505). Prof. Chang Yinfo is highly appreciated for instruction.

REFERENCES


Renewable energy technologies for the 21st century: The Iberian Pyrite Belt as a possible supplier of indium

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ABSTRACT: In the realm of the 21st century, mankind is forcibly turning to renewable energy sources, namely using PV technologies. To do this effectively it is imperative to understand the raw material limitations related to the mass production of these technologies as the manufacturing process is highly dependant on a constant supply of rather expensive, high-tech raw materials, e.g. Indium. The limitations imposed by raw materials supply is a catalyst for further mineral exploration in order to feed the hungry high-tech metal industries supplying, in turn, expanding renewable energy industries. One world class metallogenic province that merits investigation for its anomalous indium and other high-tech elements is the Iberian pyrite Belt, where the occurrence of Indium in the well documented Neves Corvo deposit. It follows that the other, marginal and now inoperative, deposits could also host accessory In and should therefore be investigated.

KEYWORDS: Renewable energies, photovoltaic cells, Iberian Pyrite Belt, indium

1 INTRODUCTION

High costs and environmental issues related to fossil fuels use are forcibly turning the industrial society towards renewable energy technologies. To do this effectively it is imperative to understand the raw material limitations related to the mass production of these technologies (Andersson, 2000; Sanden, 2003).

A radical transformation of the energy system in the 21st century will require a large-scale diffusion of a range of renewable energy technologies, which will necessarily include photovoltaic technologies. Thin-film solar photovoltaic (PV) have been suggested as possible major components of a more sustainable energy system. However, as with other renewable energy technologies, the energy source may indeed be renewable but the equipment to collect it is not. Therefore, scenarios of raw material demand have to be predicted, considering eventual massive diffusion of renewable energy technologies occurring as a response to increasing fossil fuel prices and/or environmental restrictions on their use. The availability of a range of high-tech elements (In, Ge, Se, Té, in particular), incorporated in thin-film PV, therefore needs to be assessed.

According to Andersson (2000) and Sanden, (2003), the material limitations are particularly strong for indium (In) and tellurium, employed in thin-film photovoltaic (PV) cells, so that the search for sources of these high-tech elements will likely constitute a rewarding investment. Considering the present energy crisis and forecasted fossil fuel price hikes, an updated evaluation of the possible scenarios for high-tech element demands is fundamental. Of these elements, indium is already very valuable, with prices hovering in the USD 1000/kg mark, as the demand for flat-screen displays is booming. Its use in photovoltaic cells will further expand its markets.

The study of mineral deposits and ores hosting high-tech elements is essential in establishing what kind of supply exists to fulfill the expected increasing demand. It is likely that demand may outstrip supply. In this case, the consequential resource scarcity constitutes an unique opportunity for mining companies and local communities, who could benefit from the discovery of new deposits that are rich in the required high-tech elements or from the re-evaluation of known base-metal deposits for their high-tech elements content, eventually turning sub-economic base-metal deposits into
profitable mines if high-tech elements can be produced as a co- or by-product.

2 THE PORTUGUESE SCENARIO

Portugal has few fossil energy resources. The strong dependence on imports of oil, coal and gas, which are the basis of the energy consumption structure, is much higher than the European Union average. On the other hand, Portugal is one of the EU countries, which makes more use of its available renewable energy resources (mainly biomass and hydropower), as part of its energy mix.

The former E4 Programme (Energy Efficiency and Endogenous Energies) launched in 2001, established goals concerning the exploitation of renewable energy sources for power (and thermal) generation, which were consistent with the EU Directive on renewable electricity (2001/77/CE), under which Portugal has to aim to deliver 39% (including large hydro) of its gross electricity consumption by 2010. The current energy policy framework is in line with the E4 Programme and, for some renewable energy sources, the Portuguese government has set even more ambitious targets for 2010, namely: wind power: 3750 MW (currently ~300 MW) and photovoltaics: 150 MWp (currently ~2 MW).

Currently, the government has clearly identified the deficit and will support the construction of a €58 million, 11-megawatt solar power plant, to be made up of 52,000 photovoltaic modules, plant near Serpa. This plant will cover a 60-hectare southern-facing hillside and will produce enough electricity for 8,000 homes. However, despite its immense size, its contribution towards the energy targets set is clearly insufficient. One can, therefore, imagine the demand of high-tech metals that will be induced by the implementation of such ambitious targets.

3 THE IBERIAN PYRITE BELT

To meet demands, new sources of high-tech metals have to discovered and brought into
production relatively quickly and efficiently.

One metallogenic province in southern Portugal merits detailed study as it may contain significant concentrations of these high-tech metals, namely the Iberian Pyrite Belt (IPB) (Fig. 1). Due to its unique geological nature and mining legacy, it is a particularly well-suited target for assessing the concentrations, mode of occurrence and paragenesis of high-tech elements.

Foremost in the scope of the VMS deposits typical of the IPB should be the identification and characterisation of ores anomalous in high-tech elements, from Aljustrel-type deposits and associated remobilised vein deposits, located within the Iberian Pyrite Belt, a metallogenic province long known for its massive sulphide base metal resources and which is a strong candidate as a supplier of high-tech elements. Aljustrel-type deposits include, in addition to Aljustrel itself, the Lousal, Lagoa Salgada and Salgadinho deposits. Remobilized vein deposits include Barrigão and Ferrarias. The identification and characterisation of ores anomalous in high-tech elements would allow for the reassessment of what are presently considered sub-economic deposits, potentially kick-starting a new stage in the long mining history of this province. The focus should be on indium because it has already been identified and recovered from one of the producing mines of the IPB, the Neves Corvo mine. However, other high-tech elements which are commonly associated with indium in massive sulphide deposits should also be studied, namely selenium and tellurium. These studies should encompass the distribution and content of the high-tech elements taking into consideration the crystal chemistry of different ore minerals, thus leading to the identification of carrier minerals. The studies of the distribution of high-tech elements are fundamental to assess the potential for their recovery. Additionally, the position of the carrier minerals in the paragenetic sequence will be determined, thus allowing disclosure of possible mechanisms leading to the deposition of high-tech elements within the framework of the volcanogenic massive sulphide metallogenic model and subsequent remobilization processes. Such a model can contribute towards the establishment of exploration strategies leading to further discoveries.

4 INDIUM IN NEVES CORVO

In the Iberian Pyrite Belt it is well known that at the copper-rich Neves Corvo deposit, significant concentrations of some high-tech elements occur. Gaspar (2002) provides a compilation of mineralogical and chemical data on ore minerals, mostly gathered from an EU Brite-Euram II project. This compilation shows that important amounts of In occur in chalcoprite, sphalerite, tetrahedrite, tennantite, cassiterite, stannite-kesterite, mawsonite and stannoidite, especially in sphalerite and tennantite from MC3 (bornite-bearing massive copper sulphide) ore, but also in tin sulphide phases from MH (Cu-rich massive sulphides with Zn, Hg, Ag, As, Sb and Sn) and MS (massive sulphides with high Cu and Sn) ores. Significant amounts of Se and Te were also identified during the same study.

Additionally, Serranti et al. (2002) investigated the issue of high-tech elements distribution in different ore minerals from the Neves Corvo deposit and determined possible thermodynamic conditions for the precipitation of the major mineral phases. The geochemical trends advanced in an earlier crystal chemical approach to polymetallic sulphides (Figueiredo & Basto, 1988) were confirmed by these studies.

In terms of ore grades, Benzaazoua et al. (2003) calculated that MS and MC ore types from Neves Corvo contain approximately 1.5% stannite, which corresponds to a grade of approximately 200 ppm In, and estimated that even tailings can contain approximately 20 ppm In.

5 CLOSING COMMENTS

The pressing need to come up with new production sources of high-tech metals for the PV industry implies a critical evaluation of the above mentioned literature pertaining to Neves Corvo and whether the same results can be extrapolated to other deposits within the Iberian Pyrite Belt and also whether they contain anomalous concentrations of high-tech elements. Stratiform, polymetallic massive sulphide deposits (e.g.: Lousal, Salgadinho, Lagoa Salgada, Aljustrel) and the vein deposits formed by their remobilization (e.g.: Barrigão, Ferrarias) occur in the Iberian Pyrite Belt and are genetically related to the Neves Corvo deposit (Carvalho et al. 1999). Both deposit types are therefore favourable targets to extrapolate and complement the Neves Corvo findings. The identification of ores displaying anomalous contents of high-tech elements and their crystal chemical characterization is essential to evalu-
ate the potential for the metallurgical recovery of high-tech elements that could meet the foretold future deficit of those elements.

REFERENCES


The Rock Geochemistry Database of Finland – a new tool for large scale exploration and crustal studies

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ABSTRACT: The Rock Geochemical Database of Finland contains chemical data for 6544 bed-rock samples throughout Finland. Stratified sampling strategy was used to ensure that all major lithologies are well represented in the database. Major and trace elements were analysed by XRF, ICP-MS, ICP-AES and GFAAS techniques. Precision and analytical drift were estimated using 375 duplicate sample pairs. The lowest reliable concentration was determined for each element using the precision estimates. In addition to the chemical concentrations, the database contains the geographic location and several geological attributes for each sample.

KEYWORDS: Geochemistry, volcanic rocks, plutonic rocks, sedimentary rocks, Finland

1 INTRODUCTION

The Precambrian bedrock of Finland is among the best-mapped Precambrian areas in the world. Despite many published geochemical studies of bedrock in selected geographic areas from around Finland, no consistent geochemical database covering the whole of Finland has been available. The Geological Survey of Finland undertook a major project in the 1990's with the objective to obtain high quality and comparable geochemical data for bedrock from throughout Finland.

After a pilot study in 1989 (Lahtinen 1996), field sampling of bedrock started in 1990 and continued to 1995. Chemical analysis of the rock samples commenced between 1992 and 2001. Hence, the publication of the Rock Geochemical Database of Finland in 2007 (Rasilainen et al. 2007) was the culmination of over a decade long effort.

2 SAMPLING AND CHEMICAL ANALYSIS

2.1 Sampling

Stratified sampling strategy was used to ensure that the lithological variation seen on geological maps is reflected by the sampling density. Stratified sampling has the advantage that the diversity of rock types is well represented within the data set, but as a disadvantage, the number of samples for any rock type does not represent the actual area covered by the rock type.

The sampling density varied from one sample per 30km² in areas of complex lithology to one sample per 120km² in areas dominated by one homogeneous rock type. The sampling sites were pre-selected using 1:100 000 bedrock maps where available; 1:400 000 bedrock maps were used in areas lacking more detailed information. Both the scale of available bedrock maps and the existence of outcrops had an effect on the sampling density.

A field duplicate sample was taken for approximately every seventeenth site to provide information about the heterogeneity of the rock materials. For these same locations, a laboratory duplicate sample was produced to estimate the precision of the analytical methods.

The sampling was done by a portable mini-drill equipped with a diamond bit and water-cooling system. At each outcrop, four to six 15-20cm long (2.5cm diameter) drill cores were taken from a small area representing a distinct
homogeneous lithologic unit.

For each sampling site, the rock types and their age relationships, petrographic, textural and structural features were recorded on an observation form. The forms were scanned and linked with the data in the database. The geographic coordinates and several geological attributes for each sample are included in the database.

2.2 Chemical analysis

Rock samples were crushed to <5 mm grain size with a jaw crusher. Separate portions of the crushed material were pulverized in a ring mill to <60 µm grain size using a carbon steel bowl and a tungsten carbide bowl. Altogether, 6544 samples were processed and a laboratory duplicate sample was prepared for 375 samples.

The carbon steel pulverised portions of each sample were analysed by ICP-MS, ICP-AES and GFAAS. XRF, carbon and fluorine analyses were performed using the tungsten carbide pulverised sample portions. The concentrations of 53 elements are included in the database and many of these have been analysed using both total and partial leach methods (Figure 1).

3 QUALITY OF ANALYTICAL DATA

The laboratory duplicate sample pairs were used to estimate the precision of the concentration data reported by the laboratory and to establish the lowest reliable concentration for each element. They were also used to investigate analytical drift.

3.1 Precision and lowest reliable concentration

The precision was estimated from the spread of the concentration data derived from the laboratory duplicate sample pairs. Estimated this way, the precision includes the reproducibility error of the analytical method as well as errors due to sample preparation and sample heterogeneity.

An estimate of the error term for each laboratory duplicate sample pair is defined as:

\[ e_i = \frac{1}{\sqrt{2}} (C_{N,i} - C_{Z,i}) \]

was used to estimate the spread of the error terms. This non-parametric estimator minimises the effects of extreme values and is defined as:

\[ M . M A D(e) = \frac{1}{0.6745} \frac{\text{Median}\{e_i - \text{Median}(e_i)\}}{\text{Median}(C_i)} \]

where the term (1/0.6745) is included to ensure that the median absolute error term is a consistent estimator of the standard deviation of e, if the distribution of e is normal. The non-parametric coefficient of variation is defined as:

\[ CoV = \frac{M . M A D}{\text{Median}(C_i)} \times 100\% \]

where \( \overline{C_i} \) is the average of the concentrations in a laboratory duplicate sample pair. Precision is then defined as: \( P_{1-x} = t_{n-1,x} \times CoV \), where x is the probability of error, n is the number of sample pairs and t is the coefficient of Student's t-distribution. The precision was estimated at 95% confidence level.

The estimated precision values for any element and analytical method are usually poor at the lowest concentrations and gradually become better with increasing concentration. This emphasizes the need to define a limit above which the concentration data can be considered quantitatively reliable. For the Rock Geochemical Database data, the chemical laboratory of the Geological Survey of Finland made an exception to their normal procedure and reported all measured concentration values regardless of the detection limit. This made it possible to use the actual measurement values to determine a real-
istic threshold for reliable concentrations. The laboratory duplicate sample pair data was ordered according to increasing mean value concentration in the sample pair and the precision was then calculated for a moving window through the data. The lowest reliable concentration was defined as the minimum concentration value in the moving window when the precision calculated for the window (at the 95% confidence level) becomes better than or equal to 50% (Fig. 2). The precision was then estimated for concentrations above the lowest reliable concentration.

The precision for the major elements is generally better than 5% and when the lowest concentration ranges are excluded, the median precision for all of the trace elements is 13.5%. For concentrations just above the lowest reliable concentration, the median precision for the trace elements is 26%.

3.2 Analytical drift

Analytical drift causes a systematic change with time in the concentration values of an element, measured repeatedly from the same sample with the same method. For the Rock Geochemical Database of Finland, samples from geographically different regions were analysed at different times between 1992 and 2001, which makes the consideration of drift important when performing comparisons between samples in the database. The drift was evaluated using the relative error of the laboratory duplicate sample pairs (Fig. 3). Most of the drift is included as a component in the estimated precision value. However, the changes in the level of drift with time are gradual, which makes it practically impossible to separate the drift component from the precision estimates. Elements, for which the drift component dominates the precision, are noted in the database User's Guide.

4 DISCUSSION

4.1 Usability of the data

The lowest reliable concentration and precision were determined using analysis of paired normal and laboratory duplicate samples. The approach was designed to provide a more realistic estimate of these parameters than simply using the detection limit and reported by the laboratory. The validity of this approach is based on the assumption that the duplicate data set is representative of the whole database. The duplicate data set was generated by producing a laboratory duplicate sample for about every 17th prepared sample. The 375 duplicate samples represent 5.7% of all the samples in the database and they were analysed in batches along with the rest of the samples. The calculated median concentrations of elements are very similar in the duplicate data set and whole database. The percentage of samples below the lowest reliable concentration for each
element is similar for both the laboratory duplicate data set and the whole database. There is no systematic pattern; for some elements, the proportion of concentrations below the lowest reliable concentration is larger for the laboratory duplicate data set than for the whole database, whereas for other elements the opposite is true. On these bases, the estimates of lowest reliable concentration and precision can be considered valid for the whole database.

The median number of samples below the lowest reliable concentration for an element in the database is 194, which is three percent of all the samples. For 14 elements, more than 50% of the samples have concentrations below the lowest reliable concentration, which makes the estimating of the central tendency problematic. Elements with more than 90% of their data below the lowest reliable concentration (Au, B, Mo, Pd) are of very restricted use. However, since the number of samples below the lowest reliable concentration is not necessarily distributed evenly throughout the database, it is not possible to draw straightforward conclusions on the usability of the data for a particular element within a particular lithologic unit or geographic area.

4.2 Uses for the data

The Rock Geochemical Database of Finland was published in March 2007. The next phase of the work will be the determination and publishing of the chemical characteristics of the main lithologic units of the Finnish bedrock, based on the data in the database. This work is presently ongoing. Among the outputs will be background concentration maps of the bedrock of Finland for selected elements. The background concentration data will in turn be used in regional and crustal scale petrogenetic and exploration related studies. The possible uses of the database are by no means limited in the field of geology, several applications can be found in the fields of medicine and environmental sciences, for example.

ACKNOWLEDGEMENTS

The chemical laboratory of the Geological Survey of Finland is thanked for providing the raw concentration data without discriminating the values below the detection limits. We want to thank the various geologists who provided unpublished map material and guiding at sampling locations, and the numerous field assistants who took part in the sampling.

REFERENCES


ABSTRACT: The Talvivaara black-shale-hosted Ni-Cu-Zn deposits comprise one of the study sites for the EU 6th Framework Programme project BIOSHALE. This paper belongs to the geological modeling task. Special interest was given to Mn-rich and Ni-Cu-Zn-rich horizons and their correlation.

KEYWORDS: Black shale, geological modeling, nickel, sulphide deposits, Talvivaara, Finland

1 INTRODUCTION

The Talvivaara Ni-Cu-Zn deposits were comprehensively studied already by the Geological Survey of Finland between 1977 and 1982. 95 inclined drill holes averaging 200m in length and totaling 19.6km were drilled (Ervamaa & Heino, 1980).

The deposits are hosted by metamorphosed black shale (black schist) and contain as mineral resources at 0.15% Ni cut-off 338 Mt of low-grade ore 0.27% Ni, 0.14% Cu and 0.55% Zn in two deposits, Kuusilampi and Kolmisoppi. As a result of polyphase deformation the ore horizon has the maximum width of up to 400 m in the surface (Reino, personal communication).

Outokumpu Finnmines Ltd owned the rights to the deposit from 1985, but in 2004 a new company, Talvivaara Mining Company Ltd. has started extensive studies in the area.

The data used in this study is solely based on data collected during the Geological Survey of Finland drilling campaign. The data collected by the Outokumpu company and the Talvivaara Mining company were not available for the present study.

2 GEOLOGICAL SETTING

Talvivaara is located in the Kainuu schist belt which consists predominantly of metasediments like mica schists, quartzites, dolomites and metamorphosed black shales and was formed 2.2 to 1.9 billion years ago. The belt is narrow and roughly S-shaped, the length of the belt is 200km in north-south direction and the width is 40km in east-west direction. Metamorphosed black shale formations can be followed for hundreds of kilometers.

Rocks in the Kainuu schist belt have undergone several tectonic deformation phases. Regional metamorphism was of medium grade, amphibolite facies, in the area of Talvivaara. In the northern part of the belt regional metamorphism was not as high: the rocks have undergone greenschist facies metamorphism.

Ore grade black shale formation at Talvivaara is ca. 10 kilometers long and the maximum width is 400 meters. “Gangue” black shale formation in Talvivaara is 20 kilometers long, a few kilometers wide and up to 400 meters thick. Ore grade black shale is enveloped by the “gangue” black shale (Reino, personal communication). “Gangue” black shale is referred to black shale which is not of ore grade.

The thickness of the metamorphosed black shale formation has increased during tectonic deformation. The Talvivaara deposit is outcropped and is located topographically in a small hill in the area of the Kuusilampi deposit.

The horizon containing more than 0.8% Ni+Cu+Zn can be traced continuously for 10 km on the geophysical anomaly maps. A distinctive feature of the Talvivaara deposit is the presence of Mn-rich metamorphosed black shales with more than 0.8% Mn along a 3km-long and 50m-wide horizon parallel to the Ni-
Cu-Zn-rich horizon.

The metamorphosed black shales of Talvivaara exhibit folding, which is isoclinal in places, and the effects of several phases of deformation can be discerned (Loukola-Ruskeeniemi & Heino, 1996).

Two deposits occur in the Talvivaara area: Kolmisoppi is the northern ore body and Kuusilampi is the southern ore body. In this abstract only the Kuusilampi deposit has been illustrated.

The precursors to the Talvivaara black shales were metalliferous organic-rich muds deposited in anoxic conditions. The degree of pyritization of black shale suggests an anoxic depositional environment. Geochemical evidence for hydrothermal influx includes elevated Ni, Cu, Zn, and Mn values relative to those of average Finnish black shales (Loukola-Ruskeeniemi & Heino 1996). Layers in the Kuusilampi deposit are almost horizontal due to nearly horizontal folding in the area. The geological map of the Kuusilampi area is shown in Figure 1.

3 MODELS

The basis of these models is a database containing chemical analytical data of drill core samples analysed in the laboratories of the Geological Survey of Finland. Modeling was carried out using Surpac Vision v. 5.01.

In Figure 2 Mn-rich horizons and some Ni-Cu-Zn-rich horizons are illustrated. Mn-rich layers are drawn from drill core analyses where concentration of manganese exceeds 0.5%. Also, layers showing combined concentrations of Ni-Cu-Zn are drawn with concentration 1.0% or above.

More recent data owned by the Talvivaara company suggests that Mn-rich horizons are not as continuous as shown in the present model.

Figure 2 shows also drill core analyses from the Kuusilampi deposit by rock type depth-wise.

4 CONCLUSIONS

The models illustrate how the Mn-rich layers correlate with Ni-Cu-Zn-rich layers. As can be seen in Figure 1, Mn-rich layers and Ni-Cu-Zn-rich layers run parallel to each other.

These layers do not represent all layers in the Kuusilampi deposit but the layers can be interpreted to have undergone folding. Field observations from the area support the interpretation. The older folding phase observed was near horizontal with northbound strike. The newer folding phase was observed with strike of S-SE and dip of 50º.

The model shown in this abstract is an interpretation done with insufficient data, and therefore it is still under construction.

ACKNOWLEDGEMENTS

The present modeling task has been financed jointly by the BIOSHALE project, an EU 6th Framework project (bioshale.brgm.fr) and the Helsinki University of Technology, Geo-environmental Technology section (http://geo.tkk.fi/), but the data used in the modeling comes originally from the Geological Survey of Finland (www.gtk.fi).

We would like to thank Chief Geologist Jouni Reino from the Talvivaara Mining Company for valuable comments.
REFERENCES


Figure 2. A model of some of the layers in Kuusilampi deposit. The view is to the north. In the northern-most part of the model folding could be seen.
New geochemical and geophysical data of Northern Ireland

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ABSTRACT: The Geological Survey of Northern Ireland has completed new geochemical and airborne geophysical surveys over the whole country that will promote further mineral exploration. The geochemical surveys map the distribution of 60 elements in three sample media and geophysical imagery provides great detail on potentially mineralized structures. New anomalies in gold, platinum group elements and base metals have been mapped. Regionally, the airborne geophysical imagery refines and extends existing structural mapping. Prominent magnetic anomalies correspond with major intrusive complexes, the extensive Palaeogene lava flows and dykes. The electromagnetic and radiometric results display significant variations over different lithologies. At a local scale the imagery reveals outstanding structural detail.

KEYWORDS: Tellus Project, Northern Ireland, geochemistry, geophysics, gold, platinum, base metals

1 SURVEYS OF THE TELLUS PROJECT

The comprehensive geochemical and airborne geophysical surveys of Northern Ireland which began in 2004 were completed in 2006. Digital datasets and images will be released by the Geological Survey of Northern Ireland (GSNI) during 2007. These data are expected to encourage further mineral exploration in Northern Ireland, for gold, PGE’s and base metals.

The data were acquired by the Tellus Project, which has been funded by the Department of Enterprise, Trade and Investment and by the EU Building Sustainable Prosperity programme through the Department of Agriculture and Rural Development.

The project included three geochemical surveys across Northern Ireland under this programme and acquired the following data to the G-BASE standard established by the British Geological Survey (BGS). Soils were sampled at 20 and 50cm depths on a regular grid at one site per 2 km². Streams were sampled at an average of one site per 2.15 km². The following analytical methods for 60 elements and compounds were used:

- Soils: XRF and ICP with fire-assay for gold and PGEs,
- Stream sediments: XRF and fire-assay for gold and PGEs,
- Stream waters: ion chromatography and ICP.

Nearly 30,000 samples have been collected and analysed. Soils samples have been taken at a greater density in the urban areas of Belfast and Londonderry, primarily to establish an environmental baseline.

The low-level regional airborne geophysical survey was flown for the Tellus Project by the Joint Airborne-geoscience Capability, a partnership of the British Geological Survey and the Geological Survey of Finland, using a De Havilland Twin Otter aircraft. The survey parameters were:

- ground clearance: 56m over rural areas and 250m over populated areas,
- line spacing: 200m,
- line direction: 345° and 165°.

The following data were acquired:

- Total magnetic field and horizontal gradient,
- Electrical conductivity,
- Four channel gamma-ray spectrometry.

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The airborne magnetic results refine existing structural information, notably by extending the mapping of dyke swarms and delineating regional and local faults. The EM method maps predominantly shallow variations of electrical conductivity of geological, pedological or anthropogenic origins. Gamma-ray results show gross differences in the radioactivity of different lithologies and soils. The principal isotopes mapped are those of the uranium and thorium series and potassium-40.

2 PRECIOUS METALS

The styles of gold mineralization in Northern Ireland have been summarised by Arthurs and Earls (2004). Of these, the most important is the mesothermal quartz vein gold occurring in the Neoproterozoic Dalradian Supergroup close to the Omagh Thrust Fault in Co. Tyrone. In this area the new geochemical results show prominent gold and arsenic anomalies in streams and soils, which may be followed westward from known mineralization (Fig. 1).

The new magnetic images display detailed magnetic textures within the Dalradian and underlying Palaeozoic rocks, all intruded by extensive Palaeocene dykes (Fig. 2). The electrical conductivity images reveal gross differences in conductivity between the principal formations and prominent linear anomalies arising from the major fault planes (Fig. 3). Numerous, previously unmapped linear features have been revealed, many correlating with gold occurrences.

East of the Curraghinalt gold deposit, stratabound gold occurrences of the Glenwagna Formation and volcanogenic occurrences of the Tyrone Igneous Complex correlate with structural features revealed on conductivity and magnetic images (Figs. 2 and 3).

Prominent anomalies of gold, arsenic, antimony and other metals characterise the locality of another mesothermal vein gold deposit at Cargalisgorran in Co. Armagh. Intense arsenic anomalies have been recorded in Silurian greywackes and shales WSW and ENE of the Palaeogene granite intrusives of Counties Armagh and Down.

Significant alluvial gold has been found in panned stream sediment concentrates in and along the margins of these intrusives. The intrusives display characteristic but different expressions of magnetisation, conductivity and radiation. The detailed lineaments and textures revealed in the new magnetic and conductivity images reflect shear zones, subsidiary fracturing and other structural elements in these intrusives (Fig. 4).
Relatively high values of platinum were recorded in stream sediments and soils over the Antrim lavas, in the soils over the Co. Fermanagh and Co. Down dykes and in streams draining Upper Dalradian rocks in the Sperrin Mountains.

3 BASE METALS

Of the base metal geochemistry results so far analysed, the highest values of several metals occur in the soils and streams of the Antrim lavas. Copper, cobalt, chromium and nickel are all significantly higher than elsewhere in Northern Ireland. The lavas are clearly defined by the airborne magnetics and structures and lineaments within them are revealed or suppressed by different data transformations.

High nickel values are also associated with several of the dykes of Co. Fermanagh and a major dyke swarm in Co. Down. These trends beneath glacial cover are revealed clearly by the various magnetic transformations (Fig. 5).

REFERENCES

ABSTRACT: The management of New Zealand’s mineral resources is split between the central government and 86 regional and district councils. However, the council’s lack of recognition of the potential significance of the minerals sector has led to inconsistencies in the way minerals are managed and lost opportunities for mineral developments. To rectify this, we have carried out regional mineral resource and economic assessments to demonstrate the economic benefits of mineral resources to councils in prospective parts of New Zealand. Our aim is to encourage the councils to work cooperatively towards improving public awareness of the significance of minerals to regional economic activity, to better coordinate policy-making for minerals at regional and district levels, and to actively promote and market their mineral resource potential. In the case of the Otago region, this has led to the contribution of NZ$1 million from the Otago Regional Council toward regional airborne geophysical surveys to encourage mineral exploration, and underpin the region’s digital resource database that it is developing to foster economic growth.

KEYWORDS: minerals, potential, assessment, resources, local government

1 INTRODUCTION

For its land area of 270,000 km², New Zealand is well endowed with mineral resources and currently produces gold, silver, iron and industrial minerals (e.g. bentonite, clay, perlite, pumice, serpentine, silica sand and zeolite), limestone and rock aggregate, in addition to coal and petroleum. There is considerable potential for increased mineral production (Christie & Brathwaite 1999).

For metallic minerals and most industrial minerals, exploration and mining requires consents from three parties: the owner of the minerals (which may include the Crown i.e. the New Zealand Government), the landowner and the local authority (regional and district councils). The local authorities therefore have considerable influence on the discovery and development of New Zealand’s mineral resources. However, their lack of recognition of the significance of the minerals sector has led to inconsistencies in the way minerals are managed and lost opportunities for mineral developments, particularly because of regulations restricting access to mineral resources and sterilisation of mineral resources by other land uses (e.g. aggregate resources sterilised by urban development).

GNS Science, in partnership with the New Zealand Mineral Industry Association and Crown Minerals, have a research project aimed at providing mineral resource information to local governments for incorporation into regional and district policies and plans to allow the value of mineral resources to be reflected in land use decisions (Barker et al. 2006a, 2006b). Initially the project has targeted the Otago and Northland regions where a number of initiatives are now in progress. These initiatives have exceeded the initial expectations of the project, and include the contribution of NZ$1 million by the Otago Regional Council toward airborne geophysical surveys.

2 LEGISLATION

The Crown owns all gold and silver (and petroleum) in New Zealand while other minerals may be owned by the Crown, the owner of the land or some other person. The Crown (through Crown Minerals, an agency of the
central government) grants permits to explore and mine Crown-owned minerals and petroleum, and collects and maintains a database of reports on exploration. Access is negotiated with landowners (or administering agencies in the case of public land), while managing the environmental effects of activities is primarily the responsibility of regional and district councils.

The New Zealand Resource Management Act 1991 (RMA) requires the 86 local authorities to manage minerals, along with other resources, through the policies and plans that they produce under the RMA. They also manage the effects of activities (including mining) through a system of consents. Every regional council must prepare a regional policy statement, which provides an overview of the resource management issues of the region, and policies and methods to achieve integrated management of the natural and physical resources of the whole region.

Regional plans and district plans must give effect to regional policy statements. There are wide disparities in the way that regional policy statements deal with mineral resources, and the extent to which these policies are taken up in District Plans. Although a large quantity of minerals information is publicly available in digital products and on the www, to date there has been little uptake of this information by regional and district councils. Therefore the primary aim of our project was to assist incorporation of minerals information, and favourable provisions for minerals exploration and mining, in the plans and statements.

3 OUTREACH ACTIVITIES

Four regions dominate current mineral production and perceived mineral potential: Waikato, South Island West Coast, Otago, and Northland (Fig. 1). We have concentrated on two of these with significant undeveloped potential – Otago and Northland.

The Waikato is at present the focus of most exploration spending in New Zealand and a comprehensive regional programme of compiling information in the Taupo Volcanic Zone and parts of the Hauraki Goldfield has been in progress for several years by Glass Earth Ltd (Henderson et al. 2005, 2006). Minerals West Coast is developing a minerals strategy for the South Island West Coast region.

![Figure 1. Regions of New Zealand](image)
Subsequently the Otago Regional Council agreed to contribute NZ$1 million towards the cost of airborne EM and magnetic surveys of the region carried out by an explorer (Glass Earth Ltd) during early 2007, to increase the level of technical information, which may be used to attract further exploration and in groundwater management.

3.2 Northland initiative

Several meetings were held with the Northland regional and district councils from 2005. Enterprise Northland, the regional business development organisation, coordinated the establishment of a minerals focus group consisting of representatives of these organisations, and mineral companies active in Northland. GNS Science carried out a regional mineral resource assessment (Christie & Barker 2007; see below) and this was used as a basis for an economic study by the New Zealand Institute of Economic Research funded by Crown Minerals, and the Far North and Whangarei district councils. These studies highlighted the potential economic benefits of mineral development to the regions and districts. They have encouraged the councils to be more positive about mineral development and to actively promote the region’s mineral potential. The focus group is currently seeking local and central government funding for regional airborne geophysical surveys.

3.2.1 Northland mineral resource assessment

The Northland region contains a wide variety of mineral commodities and currently produces high quality ceramic clays, limestone for agriculture and cement, and rock and sand aggregates. Antimony, coal, copper, diatomite, kaolinite clay, kauri gum, manganese, mercury, peat, serpentine, silica sand and silver have been mined in the past and there are prospects for aluminium, chrome, feldspar sand, gold, lead, nickel, phosphate, zeolite and zinc.

Christie & Barker (2007) carried out a mineral resource assessment of the region using the US Geological Survey three step process (Singer 1993). This involved generating mineral deposit models, a geographic information system (GIS) of spatial data sets, and a counting method of assessment. Estimates of value for 16 metallic mineral deposit types total NZS$4,973 million, and for 14 non-metallic mineral deposit types they total NZS$23,699 million. A scenario was presented of increased mineral production 15 years hence, given that 1.) there is a sufficient level of exploration to define the new resources and 2.) new discoveries can be developed. In the scenario, the value of Northland’s mineral production would increase from the current NZS$58 million to more than NZS$354 million annually by:

- An increase in production of aggregate and limestone to past maximum annual levels
- Development of a gold-silver mine
- A second metalliferous mine (e.g. aluminium, copper or gold-silver),
- Silica sand mining,
- Small mining operations in one or more commodities such as coal, diatomite, feldspar, kauri gum, peat and zeolite.

3.2.2 Northland economic study

The results of the mineral resource assessment were further developed in an economic impact assessment by the New Zealand Institute of Economic Research. The proposed increase in output from the minerals sector was investigated in terms of the flow through effects in other sectors to evaluate the overall economic effects on local gross domestic product and employment.

4 CONCLUSIONS

The outreach initiative has shown that regional and district councils and regional development agencies are willing to include minerals and the mining sector in their economic development strategies when provided with information and technical support. Furthermore, when the economic benefits of mineral resource development are demonstrated some councils may be willing to fund activities to attract investment in mineral exploration and development.

Our experience to date suggests that while flexibility is essential, work in engaging additional regions should follow a four step process:

1. Presentations on mineral resources to local councils to get agreement to utilise minerals information;
2. A mineral resource assessment of the region to demonstrate local mineral potential;
3. An economic impact assessment to demonstrate economic benefits and returns specific to that region; and
4. Engagement of councils to seek support,
which may include funding exploration initiatives, and additional resource studies, if required.

The Otago example bypassed the third step because the councils considered that the economic benefits had already been demonstrated by current mining activity in the region (e.g. the open pit mine on the Macraes mesothermal gold deposit).

Regional government in New Zealand is developing resource databases to manage their resources more efficiently. Digital data on geology and mineral resources is now being incorporated into these databases as a result of the resource studies.

ACKNOWLEDGEMENTS

Ian Graham of GNS Science, and Doug Gordon - Executive Director, and Peter Atkinson - President of NZ Minerals Industry Association have supported the project with constructive advice and assistance throughout. Funding for the project was provided by the Foundation for Research, Science and Technology.

REFERENCES


ABSTRACT: Far-field alteration halos to the Antamina, Cerro de Pasco, Colquijirca, Iscaycruz, Milpo, Uchucchacua, Yauricocha polymetallic deposits, central Perú, were examined to identify features characteristic to the escape of spent ore fluids in carbonate rock-hosted systems. Alteration features examined include the metamorphic aureole, proximal and distal veins, metal zonation, and other geochemical dispersion halos. Predictable visible and cryptic alteration patterns extend a minimum of 500 to 800m from sulphide ore bodies. Locally, evidence can be found as much as 1 to 3km from the sulphides. A critical element in using the predictable patterns as exploration vectors is recognizing the permeability structure along which hydrothermal fluids may have exhausted from an ore-forming environment that does not crop out. Visible and cryptic alteration defines high to low temperature zonation features that are continuous between skarn and massive sulphide replacement deposits, strengthening a genetic linkage between these two deposit types.

1 INTRODUCTION

Carbonate rocks intruded by shallow level stocks are host to zoned polymetallic ore systems (Einaudi et al., 1981; Titley, 1993; Meinert et al., 1997; Megaw, 1998; 2001), including some of the largest deposits in the world. The districts have a core of intrusive rocks that may contain porphyry-style base-metal deposits. Skarn lies at the intrusive contact with the host carbonate rocks, with replacement massive sulphide (CRD) deposits that are concordant “manto” type deposits or discordant cross cutting chimney deposits up to several kilometers away from the magmatic core (Beaty et al., 1990; Megaw, 2001). Discrete veins and auriferous jasperoid deposits lie in a more distal position, as much as 1km away from the magmatic core (Noble & Alvarez, 1988; Pareja, 1995; Noble et al., 2000). The outward succession of deposit types accompanies a decrease in temperature of formation and a transition from Cu±Au dominated metal assemblages to Pb-Zn±Ag assemblages in distal replacement and vein deposits that are rich in manganese. In distal deposits, the connection between the distal deposits and a causative intrusive complex may not be evident or supported geochemically (Megaw, 1998).

Our studies of distal alteration in carbonate rock-hosted polymetallic deposits in central Perú (Antamina, Cerro de Pasco, Colquijirca, Iscaycruz, Milpo, Uchucchacua, Yauricocha) identify similarities in alteration halos to skarn, CRD, base metal vein, and auriferous jasperoid deposits (Fig. 1). Structural architecture, igneous geometry, dip of host carbonate strata, and composition of host carbonate rocks exert a fundamental control on mineralization and escape of the spent hydrothermal fluids. As a first order control, the size of distal alteration halo is dependent in part on the size of the mineralized zones, the size of associated intrusions, and the permeability structure (bedding geometry, fracture and fault mesh, etc.). Other factors to consider include the metamorphic aureole, proximal and distal veins, metal zoning, geochemical dispersion halos, and alteration. Taken together, visible and cryptic alteration defines high to low temperature zonation features that are continuous across the skarn-CRD-distal vein transition, strengthening a genetic linkage between these deposit types. The zonation in alteration can also provide vectors toward sulphide deposits hosted in carbonate rocks.
Metamorphic aureoles around high-level intrusion form much larger exploration targets than the individual mineralized zones. The most pronounced visible alteration features are thermal metamorphism and fluid flow effects surrounding intrusion-centered systems. Visible effects include recrystallization, bleaching, and conversion of calcareous rocks to hornfels or to marble, depending upon the protolith composition. At Antamina, bedding-controlled and fracture-controlled bleaching extends as much as 300m vertically and 200m laterally from the skarn whereas unbleached gray marble and hornfels extend up to 800m laterally and 300m vertically above the skarn. Yauricocha contains an inner zone of bedding and structurally controlled bleached marble, and an outer zone of gray marble that extends at least 500m into the carbonate rocks.

Surrounding carbonate-hosted ore zones are veinlet networks or swarms of thin (hairline to 2cm) wavy-planar veins that represent escape pathways for the fluids responsible for sulphide mineralization. The vein swarms also connect different mineralized zones and form halos extending up to 800m laterally and >500m vertically from mineralized zones. The veinlets are important exploration guides, as they will contain anomalous geochemistry that varies outward from the thermal source. The veinlets contain variable amounts of carbonate (calcite, ferroan, or dolomite) ± quartz ± calcicarbonate minerals with pyrite and base-metal sulphides. Distinct orange carbonate veins surround virtually all the deposits; the orange colour is due to the weathering of sulphide. Geochemically the veins contain elevated base metals and Mn with or without elevated Ag as well as the epithermal suite As, Hg, Sb, and Tl in the shallower deposits such as Cerro de Pasco or at the distal fringes of deeper deposits such as Yauricocha. In some deposits (Iskaycruz), these veins are concentrated along favorable beds, therefore forming an asymmetrical halo extending outward from mineralized zones, and diminishing in intensity away from mineralization. The vein swarms follow the permeability structure, and recognizing them and their structural control is important for exploration.

Larger Ag-base metal veins of potential economic interest, analogous to the veins at Uchucchacua, lie distal to some skarns above and lateral to the main skarn (Antamina). At Antamina, the distal veins are present over a 9-km² surface area, extending at least 1km laterally from the main skarn and extending over 400m vertically above it. At Yauricocha, similar veins extend up to 3km laterally from the main zones. These Ag-base metal veins provide a significantly larger exploration target than the main mineralized skarn-CRD bodies or any proximal veinlets.

At Yauricocha, Uchucchacua, and Antamina, proximal and distal carbonate-dominated veins locally contain unique ultraviolet fluorescent (UV) characteristics, with many fluorescing a distinct red-orange colour. Less common fluorescent colours include yellow and white. The shades of red-orange fluorescence colour is related to the concentration of Mn in the calcite, thus provide a link to the hydrothermal system. The other fluorescent
colours reflect other trace elements in the calcite. Mapping of core or underground exposures with a hand held UV light potentially provides a cheap and easy prospecting tool as the density of red-orange fluorescing veins increases in proximity to mineralized zones.

4 METAL ZONING

Lateral metal zoning is evident in several of the districts. Low-grade porphyry style Cu ± Mo mineralization occurs at the core of many of the deeper deposits. Proximal to the porphyry-carbonate contacts are Cu-rich zones (locally with high sulphidation mineralogy) grading outward to more Zn-rich zones. Outboard of the porphyry-carbonate contacts are Zn-Pb-Ag dominated zones lacking high sulphidation mineral assemblages. The most distal mineralization occurs as Pb-Zn-Ag veins located as far as 3 km laterally from the center of the districts. In shallow level deposits such as Colquijirca, high sulphidation ore mineral assemblages associated with Cu (±Au) mineralization in the center of the district are flanked laterally by more Zn-rich mineralization (Bendezú & Fontboté, 2002, 2003, 2004). Many of the individual ore bodies are not significantly zoned over vertical extents exceeding 300 to 400m.

Skarn and CRD mineralization closely associated or proximal to porphyry intrusions are hosted entirely within the zone of bleached marble and are surrounded by a network of thin proximal carbonate-sulphide veinlets. Distal Ag-base metal veins lie above and lateral from porphyry intrusions. Zones of high fluid permeability, specifically at dike margins, control distal Zn-rich skarn and CRD at Iscaycruz and distal Ag-Pb-Zn-Mn veins at Uchucchacua and Fortuna (Antamina). Mineralization in these zones lies outside the marble aureole within limestone. At Iscaycruz, the host carbonate strata have near vertical dips and the zones of mineralization, dolomitization, and jasperoid alteration. At Colquijirca the host calcareous strata are shallowly dipping resulting in the sub-horizontal mineralized zones and dolomite alteration and jasperoid bodies.

5 GEOCHEMICAL DISPERSION HALOS

Geochemical studies at Antamina, Yauricocha, Cerro de Pasco, and Uchucchacua permit some generalizations to be made. The dispersion halo rising above a skarn and through veins such as those at Uchucchacua is variable, are broadest at depth in rocks and narrow at shallower levels in the hydrothermal system along the fluid escape channels. Elements typical of higher temperature environments, such as Cu, Bi, and Mo, are enriched in at depth. Conversely, elements typical of low temperature environments, such as As, Mn, Sb, and Tl are those that will be enriched in the lower temperature veins found at shallower crustal levels. A similar suite of anomalous elements is present in carbonate veins forming the distal fringes up to 800m from the polymetallic deposits Yauricocha.

Oxygen isotopes provide an additional tool to recognize magmatic-derived hydrothermal systems. For example, distal Ag-Mn-Pb-Zn veins and white, grey and brown carbonate veins at about 400 m vertically above the top of the Antamina skarn and through the vertical extent of the Uchucchacua veins have $\delta^{18}O$ VSMOW values between 11 and 15‰, indicating a dominantly magmatic-hydrothermal origin. Depletion halos, where $\delta^{18}O$ values are <20‰, in the host carbonate rocks are variable. They lie within the zone of visible alteration in the skarn environment but extend almost 100 meters out in visibly unaltered rocks as a cryptic alteration for up to 400m vertically above the Antamina skarn. In the shallow, distal vein environment represented by Uchucchacua, the depletion halo lies within the main fluid escape structure represented by the white calcite vein.

6 IDENTIFYING HYDROTHERMAL DOLOMITE AND JASPEROID

Dolomitic rocks and chert are common in calcareous rock terranes where they principally reflect syn-depositional or diagenetic processes. However, around many, shallow level, carbonate rock-hosted polymetallic deposits, large areas of jasperoid and dolomite are present where they partially overlap the main ore bodies (eg. Colquijirca, Cerro de Pasco, Iscaycruz) but also extend as much as 1km from the sulphide orebody. Detailed study at Cerro de Pasco has shown that wholesale depletion of Sr from the host rock distinguishes hydrothermal from diagenetic dolomitization. Hydrothermal jasperoids contain the epithermal suite of elements (As, Sb, Tl, Hg ± Cs, Li) in anomalous concentrations, whereas diagenetic chert or siliceous horizons in the limestone show no evidence for the input of these elements. At Yauricocha,
these elements are associated with low-grade distal Au in the Purisima Concepción prospect (Alvarez & Noble, 1988; Noble et al., 2000).

7 CONCLUSIONS

Work around carbonate rock hosted polymetallic deposits in central Peru has defined predictable visible and cryptic alteration patterns that extend a minimum of 500 to 800 m from the sulphide ore body. Locally, evidence can be found as much as 1 to 3 km from the sulphides. A critical element in using the predictable patterns as exploration vectors is recognizing the permeability structure along which hydrothermal fluids may have exhausted from an ore-forming environment that does not crop out. The alteration patterns are continuous across the skarn-CRD transition, strengthening a genetic linkage between these deposit types.

ACKNOWLEDGEMENTS

BHP Billiton, Cia. de Minas Buenaventura, Cia, Minera Antamina, Noranda, Phelps Dodge and Teck Cominco provided financial and logistical support for the project. Additional financial support was provided by a Cooperative Research and Development grant from the Natural Sciences and Engineering Research Council of Canada. Sociedad Minera Corona and Volcan Compania Miñera provided additional logistical support to the project.

REFERENCES


Lead isotope constraint on lead-zinc deposits across Sichuan-Yunnan-Guizhou boundaries, China

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ABSTRACT: Lead-zinc deposits are widely distributed in Sichuan-Yunnan-Guizhou (Chuan-Dian-Qian) boundaries area in China. The Pb-Zn deposits are hosted in carbonate rock from later Proterozoic to Permian. The ore bodies are apparently controlled by the faults, with strong calcitization and dolomitization. Some researchers think these deposits are the results of Emeishan basalt eruption. In this paper, we summarized the extensive data of lead isotopes of ores and crustal rocks from Sichuan-Yunnan-Guizhou area (southwest Yangtze craton). Our results show that ore-forming materials are derived mainly from the country rock. Metallogenetic epoch of Pb-Zn deposits in this area is consistent with the subduction of Jinshajiang-Ailaoshan and Ganzi-Litang Ocean down to Yangtze craton in Indosinian.

KEYWORDS: Chuan-Dian-Qian area, lead isotopes, ore deposits, country rock

1 INTRODUCTION

Lead isotopes of Pb-Zn deposits had been studied by many geologists, especially on the origin of single deposit regional mineralization (Doe et al. 1974 Macfarlane & Peterson, 1990; Kesler et al., 1994; Zhu, et al., 1998; Chang et al., 2003;), and the sources of the metallogenic materials. In this paper, we have summarized the data of lead isotopes of ores and country rocks. In order to check lead isotope variations in this study area, discuss metal sources of the Pb-Zn deposits and establish the relationship between the structural evolution and mineralization.

2 GEOLOGICAL SETTING

Early Yangtze block formed after Xiaohé movement at 1700Ma. Owing to the Jinning movement (900~800Ma), Yangtze block solidified and became the basement of succeeding sedimentary cover. The extensional environment spread all over the world and led to the break-up of Pangea from Early Sinian (850-700Ma). At the same time, post orogenesis and rifting took place. Then Shimian-Chengjiang rift zone formed in the west of Yangtze block.

This region was in the period of passive continental margin from late Sinian to late Palaeozoic. After late Sinian, west margin of Yangtze block turned into typical craton basin and widely deposited the platform facies carbonate rocks.

Jinshajiang-Ailaoshan Ocean, Babu Ocean and Ganzi-Litang Ocean formed at the margin of Yangtze craton. Emeishan basalt extensively erupted large area around the west of Yangtze craton at late Permian. Eruption of basalt was possibly related to the open of Ganzi-Litang Ocean. Early and middle Triassic Ganzi-Litang Ocean kept on spreading and formed oceanic basin. Jinshajiang- Ailaoshan, and Ganzi-Litang Ocean closed in Indosinian (T₂-T₃) (Zhang et al., 2006). As a result, Baoshan block, Changdu-Lanping-Simao block and Yidun block collaged gradually to the west of Yangtze craton and formed the foreland basin belt characterized by Chuanxi and Chuxiong basin. This basin belt formed from late Triassic to middle Jurassic. Compressional structure environment maintained from Indosinian to Yanshanian (T₃-K₁) at west of Yangtze craton. So, west of Yangtze craton still was foreland basin belt.

Since middle Cretaceous, shear extensional environment appeared at west of Yangtze craton.
East of Tibet and Songpan-Ganzi block was extruded eastward because of the collision from Indonidian plate subducting beneath Eurasia. As a result, Jinshajiang and Ailaoshan-Honghe faults occurred long distance slide (Tapponnier & Peltzer, 1988; Tapponnier & Lacassin, 1990).

3 DISTRIBUTION OF THE PB-ZN DEPOSITS

The boundaries of Sichuan, Yunnan and Guizhou Provinces (Chuan-Dian-Qian), one of the most important ore concentrated areas for base metal in China, are located on the southwest margin of the Yangtze craton. More than four thousands ore deposits and occurrences are found here. There occurred fault activities in the region, but magmatism was lacking. The only magmatite is Emeishan basalt erupted at late Permian. The Pb-Zn deposits (occurrences) distribute among Shimian-Xiaojiang (Fig.1①), Aninghe (Fig.1②) and Yadu-Ziyun faults (Fig.1③). Many deposits, distributed along deep faults, especially at the intersection of the faults, are apparently controlled by faults. Almost all deposits occurred in the carbonate rocks. The ages of ore-hosting layers from Pb-Zn deposits become gradually younger from northwest to southeast. The age of Huize Pb-Zn deposit concentrates in Indosinian period (Huang, 2005; Zhang et al., 2005). So Huang (2005), Li (2003) and Zhang (2006) think that the formation of the deposits is the result of Emeishan basalt activity. Emeishan basalt offered the material and energy for the Huize deposit.

4 INTERPRETATION MODELS FOR PB ISOTOPES

Lead isotope is a powerful tool to trace the sources of metals in ore deposits and to discriminate terranes (Zhu, 1998;), as well as being applied in geochemical exploration and evaluation of ore deposits (Chang, 2003), Massimo (2006) particularize the advantages using the lead isotopes than other isotopes: (1) Pb isotope compositions can be easily measured on rocks and ore minerals, thus providing an insight on the interaction of hydrothermal fluids (and not only magmas) with the crustal basement and on the metal sources for ore deposits; (2) three radiogenic Pb isotopes ($^{206}$Pb, $^{207}$Pb, $^{208}$Pb) are derived from three different radioactive nuclides ($^{238}$U, $^{235}$U, $^{232}$Th, respectively), thus allowing investigation of the Pb isotope system in a tridimensional space compared to the other isotope system.

The common lead isotopic signatures of ore minerals can judge the structural setting and the origin of materials according to sample position.

Fig.1 The distributing map of the lead-zinc deposits in Chuan-Dian-Qian area

Fig.2 $^{207}$Pb/$^{206}$Pb vs $^{206}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb vs $^{206}$Pb/$^{204}$Pb diagrams of ore minerals investigated in this study. The coloured areas represent the compositional fields of country rock and Emeishan basalt. The upper crust (UC), orogen (OR), mantle (M) and lower crust evolution curves are from Zartman and Haines (1988).

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on the $\Delta\beta$-$\Delta\gamma$ plot. Zhu et al. (1998) find the variety of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ is the best tool to response the resources. However, the variety of $^{206}\text{Pb}/^{204}\text{Pb}$ is sensitive to metallogenic epoch. For emphasizing the variety of Th, Pb and the correlation between Th, Pb and U, Pb, lead isotope was calculated on the relative deviation with the contemporaneou mantle as follows:

$$\Delta\beta = \left[ \frac{(207\text{Pb}/204\text{Pb})_{\text{CP}}}{(207\text{Pb}/204\text{Pb})_{\text{MP}}} - 1 \right] \times 1000;$$

$$\Delta\gamma = \left[ \frac{(208\text{Pb}/204\text{Pb})_{\text{CP}}}{(208\text{Pb}/204\text{Pb})_{\text{MP}}} - 1 \right] \times 1000.$$ 

There CP and MP express common lead and mantle lead respectively. For to sure the value of $(207\text{Pb}/204\text{Pb})_{\text{MP}}$ and $(208\text{Pb}/204\text{Pb})_{\text{MP}}$ at a certain epoch, we commonly use the mantle present values $(207\text{Pb}/204\text{Pb})_{\text{MP}}=15.51$, $(208\text{Pb}/204\text{Pb})_{\text{MP}}=37.63$, $\mu=7.9$, $232\text{Th}/204\text{Pb}=31.92$, here, we adopt the age ($t=225\text{Ma}$) as the estimated age of these deposits. By using $\Delta\beta$-$\Delta\gamma$, the geological setting and the origin of materials of deposits can be judged according to positions on the $\Delta\beta$-$\Delta\gamma$ plot.

5 RESULTS

Lead isotopes of the samples in country rock have the consistent results (Table 1). Only two samples from Huize deposit and one sample from Tianbaoshan deposit have the more radiogenic than that of others, suggesting an open-system environment, but they response the tendency of lead isotope. One sample from Xiaoshifang deposit have the low value similar to the values of Xiaoshifang lead-zinc ore, $\text{Xiaoshifang lead-zinc ore}$

<table>
<thead>
<tr>
<th>Deposit district</th>
<th>Pb$^{206}$Pb/Pb$^{204}$</th>
<th>Pb$^{207}$Pb/Pb$^{204}$</th>
<th>Pb$^{208}$Pb/Pb$^{204}$</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xiaoshifang(2)</td>
<td>17.194–18.189</td>
<td>15.617–15.689</td>
<td>37.033–38.486</td>
<td>1</td>
</tr>
<tr>
<td>Daliangzi(9)</td>
<td>18.246–18.625</td>
<td>15.593–15.777</td>
<td>38.247–38.809</td>
<td>2, 3</td>
</tr>
<tr>
<td>Shanshulin(1)</td>
<td>18.828</td>
<td>15.677</td>
<td>38.93</td>
<td>4</td>
</tr>
<tr>
<td>Tianqiao(1)</td>
<td>18.397</td>
<td>15.545</td>
<td>38.463</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1. Lead isotopes of country rocks from the Pb-Zn deposits of Chuan-Dian-Qian area

Table 2. Lead isotopes of sulphides from the Pb-Zn deposits of Chuan-Dian-Qian area

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Pb$^{206}$Pb/Pb$^{204}$</th>
<th>Pb$^{207}$Pb/Pb$^{204}$</th>
<th>Pb$^{208}$Pb/Pb$^{204}$</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daliangzi(22)</td>
<td>17.687–18.969</td>
<td>15.217–15.882</td>
<td>37.274–39.586</td>
<td>1, 2, 3</td>
</tr>
<tr>
<td>Fushan(10)</td>
<td>18.925–21.352</td>
<td>15.386–16.067</td>
<td>38.846–41.972</td>
<td>4, 5, 6</td>
</tr>
<tr>
<td>Chipu(3)</td>
<td>18.073–18.112</td>
<td>15.615–15.67</td>
<td>38.237–38.430</td>
<td>8</td>
</tr>
<tr>
<td>Leshong(1)</td>
<td>20.34</td>
<td>15.81</td>
<td>39.42</td>
<td>11</td>
</tr>
</tbody>
</table>


Lead isotopes of the sulphide samples in ore deposits in the study area have relatively consistent results (Table 2). Only six samples from Jinsmchang deposit have the anomalous high values, that maybe due to an open-system behavior. All samples of these deposits plot a cluster between the orogen and upper crust evolution curves in the uranogenic plot (Fig. 2a) and just above the orogen curve in the thorogenic plot (Fig. 2b). Most of the ore samples plot distinct filed overlapping on the zone of subduction in $\Delta\beta$-$\Delta\gamma$ plot, only several samples values fall in the area of orogen and metamorphism. The samples of Xiaoshifang deposit are confined in retrograde metamorphism area (Fig. 3).

6 DISCUSSION

The lead isotope can offer the following information: one provides the resource of the ore lead at the large-scale (upper crust, lower crust, orogen or mantle) and the regional (country rock) boundary. The other brings forth the relationship between the lead isotope and the distribution of the lead-zinc deposits in the investigated terrane. Despite different ages and lithologies, all the country rocks of different deposits have consistent lead isotope signatures within the region suggesting that terrane lithologies had a dominant control on the isotope composition of magmatic and hydrothermal activities (Massimo, 2006). In the uranogenic and thorogenic plots, lead isotopes of most Pb-Zn deposits of this area have the consistent values, so these deposits have the same resources of upper crust and orogen in large-scale. This interpretation is consistent with orogen environment at the middle and late
Triassic, Jinshajiang-Ailaoshan, Ganzi-Litang Ocean subducted down to southwest Yangtze craton when the locations of these deposits are on continental margin. It is also supported by the research about MVT deposits by Leach et al. (2001). On the other hand, the ore lead isotopes plot above the area of Emeishan basalts from mantle plume than depleted mantle and have the high $^{206}\text{Pb}/^{204}\text{Pb}$ values (Fig. 2b). These features display that ore lead composition come mainly from the upper crust. Emeishan mantle plume had not contribution to these deposits. Xiaoshifang samples have the low $^{206}\text{Pb}/^{204}\text{Pb}$ values which represent this deposit had different resources from other deposits. Virtually, Xiaoshifang deposit is associated with Huili Group basement rock (Lin, 1995) and lead isotopes derived from the basement rock located on lower crust with retrograde metamorphism (Fig. 3).

Corresponding to the variety of the country rock, the lead isotopes of ore samples have similar signatures. From northwest to southeast, the lead isotopes values increase in $^{206}\text{Pb}/^{204}\text{Pb}$ and decrease in $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ (Fig. 2). Xiaoshifang deposit separates distinctly with other deposits because of the old resources and country rocks (Huili Group) and it maybe formed earlier than other deposits. Lehong, Jinshachang and Maoping deposits are different from others (Fig.2), because they are completely controlled by faults. In addition, many ore samples occurred in the faults had been oxidized for these deposits. So, they have the open-system during and after the metallogenic process. Considering other geologic feature (Wang, 2002), we think these deposits belong to the Mississippi-Valley type deposits. The lead isotope compositions of these deposits have the variety of increasing on radiogenic lead from northwest to southeast. It is maybe related to younger of the age ore-hosting strata similar with the change of lead isotope compositions.

7 CONCLUSION

The ore-forming substances came from country rock strata, not from Emeishan basalt and other deep seated magma. The forming of the these Pb-Zn deposits are related to the collision between Jinshajiang-Ailaoshan, Ganzi-Litang Ocean and Yangtze craton in middle and late Triassic. They are MVT deposits with the signature of lacking magma activity and epigenetic origin.

ACKNOWLEDGEMENTS

The study is supported by China Geological Survey Project (1212010634001) and China National Science Key Foundation grant (40434011).

KEY REFERENCES


Hocartite and Stannite-Kesterite series from Silver-Lead-Zinc Deposits of the Kolyma-Verkhoyansk Fold Belt: Implications for Ore Genesis

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ABSTRACT: Hocartite and stannite-kesterite series, their paragenetic sequence, intergrowths and chemical composition from silver-lead-zinc deposits of the Kolyma-Verkhoyansk Fold Belt have been studied. A substantial compositional variation of these minerals has been revealed. Mineral formation temperatures are estimated using the sphalerite-stannite geothermometer.

KEYWORDS: hocartite, stannite-kesterite series

INTRODUCTION

The silver-lead-zinc deposits of the Kolyma-Verkhoyansk Fold Belt, Russia, contain numerous bismuth minerals of the bismuthinite-aikinite and lillianite-gustavite series, and bismuth-bearing minerals such as ramdohrite, the andorite series and the freibergite-tetrahedrite series. In this paper, particular attention is given to hocartite and minerals of the stannite-kesterite series which have been studied for their paragenetic relationships, composition, and conditions of formation.

1 GEOLOGICAL SETTING

The formation of tin–silver–base-metal deposits is related to the activity of granitic magmatic–hydrothermal systems. Their creation occurred when the Kolyma-Omolon superterrane collided with the Siberian continent, resulting in the formation of steeply dipping faults that controlled the distribution of transverse granite belts (Fig. 1). The tin deposits are confined to the endo- and exocontacts of these granitic massifs. The accretion processes, which took place along the Okhotsk active continental margin, lead to the reactivation of north–west trending regional faults. This resulted in the injection of siliceous sub-volcanic magmas and generation of the fluids responsible for the formation of the Ag–Pb–Zn veins. A prominent feature of these veins is their rhythmic-zoned and banded fabrics. Such banded

Figure 1. Main tectonic units of the East Yakutia and location of Sn–Pb–Ag deposits
fabrics of carbonates, quartz, and sulphides, are widespread and mainly comprise multiple alternating bands of siderite, sphalerite, and galena. In addition, monomineral (carbonate, quartz or sphalerite) zones also occur with individual bands being visually distinguished by colour and grain shape/size. The following sequence of banding is typical: galena–sphalerite–quartz → quartz–chalcopyrite–stannite–sphalerite–galena → chalcopyrite–stannite–sphalerite–galena in the rhythmically banded veins and each is considered to be a single paragenetic mineral assemblage.

2 MINERAL INTERGROWTHS AND CHEMISTRY

Hocartite (Ag$_2$SnFeS$_4$)

Hocartite is the most widespread sulphostannate mineral in the deposits. This mineral is observed as aggregates up to 1cm within cavities in quartz (Fig. 2a) usually in association with galena. The hocartite aggregates are cross-cut by late, thin veinlets, composed of Ag-stannite (containing up to 18 wt.% Ag). These veinlets are generally less than 2 µm. (Fig. 2b). It is possible that high silver content in stannite is an artifact which results from intimately intergrown hocartite.

Minerals of the stannite-kesterite series (Cu$_2$SnFeS$_4$-Cu$_2$SnZnS$_4$) are usually observed in association with sphalerite as veinlets or tiny inclusions distributed along crystal growth zones (Fig. 3a). Flame-like stannite, observed within an outer zone, is oriented in the direction of growth of sphalerite crystals, whilst an inner zone displays mutual boundaries without any evidence of replacement. This means that in each successive stannite rhythmite overgrows a new zone of the sphalerite crystal. This zoning is evidence for the temporal fluctuation of the composition of ore-forming fluid. In rare cases, the minerals of the stannite-kesterite series were found as individual grains. The chemical composition of minerals of this series displays a considerable variation of Fe and Zn contents. In general, the Fe content ranges from 0.5 to 13.7 wt. %, whilst the Zn content varies from 0.2 to 13.8 wt. %. An expected reverse correlation between the Fe and Zn contents with a value of 0.96 was revealed in these minerals. The data obtained in this study from electron microprobe analyses seems to indicate a nearly complete compositional series between ksterite and stannite. However, Springer (1972) found an immiscibility gap between synthetic Cu$_2$FeSnS$_4$ and Cu$_2$ZnSnS$_4$. This gap is considered to be a consequence of the difference in the crystal structures of stannite and ksterite. Kostov & Mincheva-Stefanova (1981) found that this difference is the result of the re-ordering of atoms in the crystal lattices of these minerals.
The present study confirms the compositional gap in the natural kesterite-stannite series. The intergrowths of stannite and kesterite with mutual boundaries along the crystallographic edges were observed in samples from the deposits studied (Fig. 3b, Table 1). The Fe/Zn ratio in stannite is equal to 12 (Zn admixture is of 1 wt. %), while this ratio in coexisting kesterite is 0.4 (Zn=9.9 wt. %, Fe=3.81 wt. %).

Table 1. Electron microprobe data for stannite (St) and kesterite (Kt)

<table>
<thead>
<tr>
<th>№</th>
<th>Mineral</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
<th>Sn</th>
<th>S</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kt</td>
<td>30.2</td>
<td>9.9</td>
<td>3.8</td>
<td>26.8</td>
<td>29.1</td>
<td>99.8</td>
</tr>
<tr>
<td>2</td>
<td>St</td>
<td>30.1</td>
<td>1.1</td>
<td>11.9</td>
<td>28.4</td>
<td>29.0</td>
<td>100.5</td>
</tr>
</tbody>
</table>

*№ analyses correspond to those in fig.3b

3 SPHALERITE-STANNITE GEOTHERMOMETER

Sphalerite and stannite are minerals that widespread in many of the silver-lead-zinc deposits of the Kolyma-Verkhoyansk fold belt. This allows us to estimate mineral formation temperatures using the Zn and Fe ratios between the sphalerite–stannite pairs. The coexisting stannite and sphalerite grains, with mutual boundaries that infers their simultaneous deposition under equilibrium conditions, were analyzed by EPMA (Table 2).

The sphalerite–stannite geothermometer is based on the experimentally established variations in iron and zinc distribution between this mineral pair (Nekrasov et al., 1979; Nakamura & Shima, 1982). The equilibrium fractionation of these elements is described by the hypothetical reaction:

\[ \text{Cu}_2\text{FeSnS}_4 + \text{ZnS} = \text{Cu}_2\text{ZnSnS}_4 + \text{FeS} \]  

The distribution coefficient

\[ K_D = \frac{(\text{Fe/Zn})_{\text{sphalerite}}}{(\text{Fe/Zn})_{\text{stannite}}} \]  

is equivalent to the equilibrium constant of this reaction and is independent of the compositions of stannite and sphalerite solid solutions (Nekrasov et al., 1979).

Two equations for the temperature dependence of \( K_D \) and corresponding thermometric expressions have been proposed:

\[ T^\circ C = \frac{1274}{(1.174 - \log K_D)} - 273 \]  

(Nekrasov et al., 1979) and;

\[ T^\circ C = \frac{2800}{(3.5 - \log K_D)} - 273 \]  

(Nakamura & Shima, 1982).

Calculated temperatures ranged from 40° to 345°C based on equation 3 and from 133° to 350°C based on equation 4 (Table 2). Temperatures estimated on the base of equation 4 seem to be more reliable as mineral formation temperatures.

Table 2. Zn and Fe content in co-existing sphalerite (Sl) and stannite (St) and calculated mineral formation temperatures

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Fe</th>
<th>Zn</th>
<th>Fe/Zn</th>
<th>KD</th>
<th>( T^\circ C ) (1)*</th>
<th>( T^\circ C ) (2) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>St</td>
<td>11.8</td>
<td>2.2</td>
<td>5.5</td>
<td>20.3</td>
<td>240</td>
<td>309</td>
</tr>
<tr>
<td>Sl</td>
<td>13.3</td>
<td>49.5</td>
<td>0.3</td>
<td>52.7</td>
<td>170</td>
<td>263</td>
</tr>
<tr>
<td>St</td>
<td>3.9</td>
<td>15.8</td>
<td>0.3</td>
<td>128.4</td>
<td>115</td>
<td>226</td>
</tr>
<tr>
<td>Sl</td>
<td>0.3</td>
<td>63.5</td>
<td>0.04</td>
<td>435.6</td>
<td>61</td>
<td>183</td>
</tr>
<tr>
<td>St</td>
<td>11.8</td>
<td>1.5</td>
<td>7.8</td>
<td>12.4</td>
<td>46.5</td>
<td>14.7</td>
</tr>
<tr>
<td>Sl</td>
<td>3.4</td>
<td>55.5</td>
<td>0.06</td>
<td>32.8</td>
<td>200</td>
<td>285</td>
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<tr>
<td>St</td>
<td>11.7</td>
<td>0.9</td>
<td>12.8</td>
<td>11.7</td>
<td>4.1</td>
<td>12.8</td>
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<tr>
<td>Sl</td>
<td>4.1</td>
<td>60.8</td>
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<td>263</td>
<td>322</td>
</tr>
<tr>
<td>St</td>
<td>8.5</td>
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<td>1.6</td>
<td>6.0</td>
<td>59.8</td>
<td>0.1</td>
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<tr>
<td>Sl</td>
<td>0.6</td>
<td>13.0</td>
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<td>0.4</td>
<td>63.1</td>
<td>0.01</td>
</tr>
<tr>
<td>St</td>
<td>9.6</td>
<td>4.0</td>
<td>2.4</td>
<td>0.4</td>
<td>66.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Sl</td>
<td>5.1</td>
<td>8.5</td>
<td>0.6</td>
<td>0.1</td>
<td>66.7</td>
<td>0.001</td>
</tr>
<tr>
<td>St</td>
<td>12.4</td>
<td>0.9</td>
<td>14.1</td>
<td>2.3</td>
<td>64.5</td>
<td>0.04</td>
</tr>
<tr>
<td>Sl</td>
<td>12.0</td>
<td>2.6</td>
<td>4.6</td>
<td>10.2</td>
<td>53.2</td>
<td>0.2</td>
</tr>
<tr>
<td>St</td>
<td>12.0</td>
<td>2.6</td>
<td>4.6</td>
<td>10.2</td>
<td>53.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* Calculated temperature based on eq. (3)  
** Calculated temperature based on eq. (4)

4 CONCLUSIONS

This study has shown that minerals of the stannite group (hocartite, stannite, kesterite and their varieties) are common constituents in the late-stage mineral assemblages of the silver-lead-zinc deposits of the Kolyma-Verkhoyansk fold belt. The wide variations of the isomorphic components in these minerals and their crystal zoning suggest a sharp change of ore mineralizing fluid parameters during the course of their deposition. Thinly banded aggregates, in which minerals described are observed, confirm the alternating changes in the chemistry of the mineral forming solutions. This could be the result of a rapid drop of the temperature and the pressure, the removal of a gas phase through fluid boiling or by a dilution due to mixing with cold meteoric waters. Such a situation is typical of the deposition of such mineral associations un-
der conditions at shallow depths, often in open void spaces. This is confirmed by the wide occurrence of festoon, cockade and crustified fabrics of mineral aggregates at these deposits. (Anikina et al., 2003). Therefore, sulphostanate minerals in these deposits were deposited at between 133° and 350°C from dramatically evolving fluids.

ACKNOWLEDGEMENTS

This study was supported by the Russian Foundation for Basic Research (project 06-05-64369) and Department of Earth Sciences of Russian Academy of Sciences (Program: “Large and superlarge ore deposits and their origin”).

REFERENCES


Transport in mine tailings: Geophysical monitoring and reactive transport modelling

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ABSTRACT: Reactive transport in low sulphide and low carbonate mine tailings has been studied using column tests. Conductivity measurements, which are indicative of pore water salinity, were performed at 20 depth levels and at different time steps. The results correlate well with the measured changes in the bulk ion content of the pore fluid, and also with measured and calculated fluid conductivities. Geophysical monitoring measurements, therefore, could yield valuable data on temporal changes in bulk ion content due to transport processes, and, thus, provide the required data for the calibration and/or verification of reactive transport models.

KEYWORDS: fluid conductivity, reactive transport modeling, geophysical monitoring, pore water chemistry

1 INTRODUCTION

Knowledge of reactive transport characteristics of mine and ore processing residues is essential to estimate the potential of the material to build hardpans. Thereto, column tests have been developed (e.g. Jung 2003). In order to avoid multiple expensive and time consuming experiments, reactive transport modelling has been applied (e.g. Molson et al. 2005; Brookfield et al. 2006). Although there are numerous possibilities to characterise the initial and final hydrological, geochemical and mineralogical states of column experiments, the possibilities to monitor chemical processes during column experiments are limited.

As a new approach, we used geoelectrical conductivity measurements at 20 depth levels as a monitoring tool. Since the electrical conductivity is a function of inter alia water saturation and pore water salinity (Archie 1942; Sen et al. 1981; Chinh 2000), changes in electrical conductivity can be attributed to changes in the ion content of the fluid at steady hydrologic conditions. The method has been tested using column experiments filled with material from low sulphide and low carbonate mine tailings (Freiberg mine district, Germany).

2 EXPERIMENTAL LAYOUT

The investigated material was taken from a zone underlying oxidized tailings at depths between 1.20 and 1.50 m (Graupner et al. 2007). The dried material (grain size < 500 µm, porosity $\phi = 0.46$) was filled into 50 cm long, 5 cm diameter and 80 µm thick polyethylene tubes (Figure 1). Half of the inner surface of the tube was covered with a thin foil containing multilevel contacts for conductivity measurements at different depth levels. The contacts were arranged in 20 levels with decreasing level distance towards the top. Each level consisted of four electrodes (two current injection electrodes outermost, two potential electrodes innermost) with an azimuth angle of 36.7 degrees between each other. Conductivity measurements were carried out at distinct time steps.

The uppermost 15 cm of the column were filled with quartz sand ($\phi = 0.44$), aimed at obtaining a sufficient chemical contrast for transported elements, as water flow was directed upward by evaporation driven capillary transport. The base of the pipe was sealed and connected to a reservoir containing artificial rain water by a valve. Water entered the column at the bottom and evaporated at the top. Time and volume of water entering the column were recorded to analyse the water consumption of the
column minus the water fixed in gels and secondary phases, as a function of time. After about 18 days, the water consumption became nearly constant and a stable water distribution was reached. The lowermost 10 cm of the column were water-saturated due to the valve-controlled water table.

![Diagram of experimental layout](image)

Figure 1: Schematic view of the experimental layout of the column experiment.

3 MEASUREMENTS

3.1 Conductivity measurements

The electrical contact to the medium was realized by galvanic connection. Since the tailings/quartz sand matrix can be interpreted as an isolator, at least a continuous fluid film along the grains between the electrodes is necessary to enable the electrical contact. The first complete set of conductivity measurements over the whole depth range was obtained once the moisture reached the top of the column and started to evaporate.

At each depth level an appropriate current $I$ (max. 10 mA) was injected into the material and the potential difference $U$ was measured between the two potential electrodes. The conductivity $\sigma$ is defined as

$$\sigma = \frac{I}{U} \cdot k_n$$

with $k_n$ as the geometric factor for the n-th depth level. The results of measurements at three different time steps are shown in Figure 2a.

3.2 Pore water analysis

After 146 days, the experiment was terminated. The water content was determined for 50 depth ranges throughout the whole column (Figure 2c). Pore water was extracted by centrifugation for eight depth ranges. Pore water pH and conductivity were measured, and the chemical composition determined by ICP-OES analysis (Figure 2b).

![Graphs showing conductivity and water content](image)

Figure 2: (a) In situ conductivity measured at three time steps, (b) concentration of selected elements within the pore water and (c) water content after 146 days.

4 MODELLING

The reactive transport model FLOTRAN90 (Lichtner 2005) was used to simulate (oxidative) weathering of primary minerals, upward transport of dissolved ions and precipitation of secondary phases. Included in the model were the following reactive primary tailings minerals as determined by SEM analysis: sulphides (e.g. arsenopyrite (FeAsS), iron-bearing sphalerite ((Zn,Fe)S)) and aluco-silicates (biotite, muscovite, plagioclase).
Gypsum (CaSO$_4$·2H$_2$O), jarosite-group minerals (e.g. KFe$_3$(OH)$_6$/(SO$_4$)$_2$), as well as iron and possibly also aluminium hydroxides were found to precipitate in both, the tailings material and quartz sand regions, respectively. Boundary conditions were set as described in the experimental section.

The relationship between electrical conductivity ($\sigma_w$, in mS/cm) and the total amounts of cations or anions (in eq/l) as described by Appeleo and Postma (1996) was used to estimate the fluid conductivity from the pore water chemistry:

$$\sigma_w = \sum \text{anions} \times 100 = \sum \text{cations} \times 100$$

The formation of ion pairs was accounted for using the Debye-Huckel algorithm for calculation of activity coefficients. This relation is valid for $\sigma_w$ values up to ~ 2.0 S/m. At higher $\sigma_w$ values, solutions behave increasingly non-ideal due to the electrostatic attraction between ions of opposite charge as well as because of friction of ions against solvation molecules of surrounding ions.

5 RESULTS AND CONCLUSION

We used Archie’s law (Archie 1942)

$$\sigma = \frac{\Phi^m}{a} \sigma_w S_w^n$$

To estimate the fluid conductivity $\sigma_w$. The Archie parameters a, n and m for the mine tailings and the quartz sand were determined for the final state (i.e. day 146, Table 1). With this parameter set and the assumption of a stable moisture distribution, the fluid conductivities at the other time steps can be estimated.

<table>
<thead>
<tr>
<th>parameter</th>
<th>n</th>
<th>a</th>
<th>m</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mine tailings</td>
<td>2</td>
<td>1</td>
<td>1.7</td>
<td>0.46</td>
</tr>
<tr>
<td>quartz sand</td>
<td>2</td>
<td>0.5</td>
<td>1.4</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 1: Archie parameters for the mine tailings and the quartz sand in the column test, respectively.

There is a good correspondence between the measured pore water conductivity and that conductivity estimated on the basis of geoelectrical measurements and geochemical calculations within the scope of application of the used model (Figure 3). In addition, the results are in agreement with measured changes in the bulk ion content of the fluid (Figure 2b). Geophysical monitoring measurements, therefore, may give a valuable insight into the temporal changes in fluid conductivity caused by ion transport.

In a further step, the temporal changes recognized by geophysical monitoring, will be compared to the results of the 1D-reactive transport model.

**ACKNOWLEDGEMENTS**

We thank Dr. Mollée from the Saxonia Standortentwicklungs- und Verwaltungsgesellschaft mbH, Freiberg, Germany, for the continuous support during the project. This work is part of the research project “Hardpan formation on mining dumps”, financed by the German Federal Ministry of Education and Research (BMBF, contract number 0330523).
REFERENCES


ABSTRACT: Fine laminated oxidized tailings with cemented layers formed at a low sulphide and low carbonate mine tailings dam within the polymetallic sulphide mine district of Freiberg (Germany) have been studied in detail. EDAX mapping and subsequent data processing (AnalySIS©) were used to estimate the distribution characteristics of major primary and secondary mineral phases and of open or partially filled pores in the cemented/unconsolidated sediment layers for a typical depth profile (~2cm long). This profile showed strong contrasts at mm scale. As a result, different types of cemented layers could be clearly defined in the oxidized zone. Furthermore, the results contribute to a better understanding of the effects of cemented layer formation for the retention of contaminants (especially As) within the oxidized tailings.

KEYWORDS: tailings dam, Freiberg mine district, cemented layer, mineral and pore distribution

1 SITE DESCRIPTION

The studied tailings dam is located close to the village of Halsbruecke (Germany, Saxony) and covers an area of ~60,000 m². It was used to deposit low sulphide- and low carbonate-bearing tailings from 1955 to 1968. The metal content of the heaped material was determined as ~0.1 wt.% Pb, ~0.2 wt.% Zn, ~1.4 wt.% S, ~0.02 wt.% Cu and ~0.1 wt.% As (ACD report, 1993). The tailings are partly covered with coarse sand and topsoil.

2 MINERALOGICAL COMPOSITION

The major primary phases at the tailings dam are fragments of the Lower Freiberg gneiss as well as gangue and ore minerals from the mined polymetallic ore veins (quartz >> barite, fluorite > pyrite, arsenopyrite, sphalerite, galena). The most frequent secondary phases include gypsum, Fe sulphates, jarosite-group minerals, Si-, Fe-As- and Fe-Si-rich gels, Fe(III) oxyhydroxides and clay minerals (Graupner et al., submitted).

3 METHODS

In order to estimate the distribution of the primary and secondary mineral phases a typical profile covering oxidized fine laminated tailings with and without cementation was investigated. In addition to this the distribution of open and partially filled pores in the sediments was studied in the same profile. Dry polished thin sections were prepared at the University of Wuerzburg. Adjacent fields covering all layers of interest were mapped using the EDAX module of a Quanta 600 FEG system (FEI Company). A resolution of 512 x 512 was employed.

The distribution of the phases within cemented layers and adjacent unconsolidated sediments was estimated. The area percentage calculation is based on the distribution of elements typical of individual mineral phases. Applying AnalySIS©, the false coloured images of the element distributions as produced by the EDAX module were processed. The images were edited using different software tools (mainly filters) to optimize the fitting threshold. A two step procedure was applied: (1) Definition of rectangular regions of interest (ROI’s) for (a) cemented and (b) unconsolidated parts of the mapped areas based on microscopic investigations. The ROI’s were positioned within the layers in the thin sections as revealed by microscopy and by the false coloured images of
the carbon distribution; high carbon count rates generally stand for open pores filled with embedding medium. Narrow transition zones at the margins of the cemented layers and the unconsolidated sediments were excluded from the ROI’s.

(2) The TIFF images of the element distribution in the mapped areas were converted into grey values. The signal intensities were increased by multiple reversing and squaring. The averaging filter was applied to erase artefacts. The data shows that the four types of phases can be described individually by an appropriate element signature for each phase: (i) major phases that are present as individual grains or parts of grains, (ii) minor phases that occur as layers covering mineral grains, (iii) embedding medium infilling open pore space, and (iv) embedding medium infilling partially filled pore space. Combinations of elements were used to separate minerals or mineral groups; e.g., gypsum was defined by multiplying the processed images of Ca and S – artefacts were subsequently erased by a standard averaging filter (Ave). The gypsum images were further processed to identify fluorite in the thin sections.

Table 1 specifies the elemental signatures used for each studied phase as well as the filters and operations applied. As-bearing phases were studied by a MIA (multiple image alignment), merging all As images for the studied profile.

Area percentages were calculated for the individual ROI’s using AnalySIS©. For the MIA of the As-bearing phases an intensity histogram was developed.

4 RESULTS

Sediment layers characterized predominantly by contrasting major secondary phases (sulphate minerals vs. Fe-rich gel phases) in individual layers and by variable degrees of cementation by the secondary phases, have been defined. These show significant differences concerning the estimated area percentages of filled area, porosity, quartz, gypsum and gel-like phases; e.g., a gypsum-rich cemented layer was characterized by a reduced porosity and high gypsum values. The results of the investigation are listed in Table 2.

Figure 1 shows MIA’s from the upper part of the profile: (a) processed As images and (b) processed carbon images. The As MIA, plotted as a function of depth, is overlain by an intensity histogram. It clearly shows the distribution of As within the profile. The highest As intensities were detected in the upper gypsum-rich cemented layer; other layers contained insignificant As contents only.

Figure 1b shows a MIA of the carbon distribution. Bright colours stand for increased carbon contents and the brightness is proportional to the porosity. Especially the intensely cemented gel-rich layer is clearly defined by a very low density of carbon and, consequently, a very low porosity (< 1 area %). Contrary to this, two layers higher in the profile, a gypsum-enriched oxidized tailings layer and a gypsum-rich cemented layer, cannot be distinguished clearly from each other in Figure 1b.

5 CONCLUSIONS

Thin sections of a ~2 cm long vertical pro-

---

<table>
<thead>
<tr>
<th>Phase</th>
<th>Filters</th>
<th>Operations</th>
<th>EDAX - Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>pore space</td>
<td>N×N</td>
<td>--</td>
<td>Ca Kα</td>
</tr>
<tr>
<td>barite</td>
<td>Ave</td>
<td>--</td>
<td>Ba L</td>
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<td>S Kα, Fe Kα</td>
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<tr>
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<td>Ave</td>
<td>Ca Kα * S Kα</td>
<td>Ca Kα, S Kα</td>
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<tr>
<td>fluorite</td>
<td>DCE, Ave</td>
<td>gypsum(reverse) * Ca Kα</td>
<td>Ca Kα, gypsum</td>
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<tr>
<td>quartz</td>
<td>DCE, Ave</td>
<td>reverse Fe Kα, K Kα, ...</td>
<td>Si Kα</td>
</tr>
<tr>
<td>silicates (excl. quartz)</td>
<td>N×N, Ave</td>
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<td>Si Kα, quartz</td>
</tr>
<tr>
<td>Fe phases (excl. sulphides)</td>
<td>Ave</td>
<td>sulphide (reverse) * Si Kα</td>
<td>Si Kα, sulphide</td>
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<tr>
<td>As-bearing phases (MIA)</td>
<td>N×N</td>
<td>coordinate the images without correlation</td>
<td>As Kα</td>
</tr>
</tbody>
</table>

Table 1: Methods used in AnalySIS© for data processing of the profile.

Legend: AV (Averaging filter): smoothing effect → minimises the noise; DCE (differential contrast enhancement): faint features (either bright or dark) become clearly visible → enhancement of image contrast; N×N: definition of the parameter for averaging filter with optional square matrix → reduction of the shot noise; Sigma: filtering of the shot noise – pixels with intense grey values, compared to the surrounding area, will not be influenced by the sigma filter.

"Digging Deeper" C.J. Andrew et al (editors)
file through a typical part of a tailings dam have been studied using EDAX and AnalySIS©. Different types of sediment layers within the profile and their mineralogical composition could be defined clearly. These sediment layers are characterized by the predominance of different secondary phases and also by variable degrees of cementation.

The advantage of using AnalySIS© is the independence (to a large extend) of the method from chemical variations within one mineral or gel-like phase. Phases could also be subdivided easily into several sub-assembly groups as defined by variable chemistry; e.g. by creating transitional phases like the partially filled area.

The possibility of automating several operations to get a quick and quite accurate estimation of e.g. cemented and porous parts within mapped profiles is another advantage of AnalySIS©.

The results confirm the assumption that the retention of As within the studied profile not only depends on the intensity of cementation, but, more importantly, on the mineralogy of the cementing secondary phases (e.g. Morin et al., 2003; Rammlmair et al., 2006); that means, it is clearly favoured by an accumulation of Fe-rich gels with strong retention capacity for As.

ACKNOWLEDGEMENTS

The authors are grateful to A. Wittenberg and D. Rammlmair for their continuous scientific support. The study was part of a project which was financed by grant No. 0330523 provided by the Bundesministerium für Bildung und Forschung (BMBF, PT Jülich) of Germany.

REFERENCES


Table 2: Distribution of phases in the different layers within the tailings. All values are given in area percent.

Legend: (1) Gypsum- and (fluorite)-enriched oxidised tailings: Moderate porosity and increased fluorite and gypsum conc.; (2) Gypsum-rich cemented layer: Low porosity and high gypsum conc.; (3) Gel-rich cemented layer: Low porosity and quartz conc.; high conc. of gel phases; (4) Oxidised tailings: High porosity; (5) Gel-rich partially cemented tailings: Reduced porosity and high gel conc. (6) Partially cemented oxidised tailings: High porosity, but lower values than (4); (7) Gel-enriched layers and lenses: Relatively high gel conc., but lower values than (3); (8) similar to (4)

Origin of diapir-related Zn-Pb deposits in the Basque-Cantabrian Basin, (Northern Spain)

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ABSTRACT: Zn-Pb stratabound mineralization related to diapirs of Triassic age is found in the Basque-Cantabrian Basin (northern Spain). Mineralogy consists of sphalerite, galena, pyrite and minor marcasite, accompanied by calcite, dolomite, quartz, barite and bitumen. Fluid inclusion (microthermometry, crush-leach) and stable and radiogenic isotope (δ34S, δ13C, δ18O, 87Sr/86Sr) data suggest basinal brines and fluids that dissolved diapiric evaporites were involved in the formation of the ore.

KEYWORDS: diapirs, Zn-Pb sulphides, Basque-Cantabrian Basin, bitumen

1 INTRODUCTION

In northern Spain and North Africa, stratabound Zn-Pb deposits are known to occur in association with diapirs derived from Triassic evaporite successions, cross-cutting sediments of Mesozoic and Cenozoic age. In Tunisia, these deposits have become an important source of metals (Sheppard et al. 1996, and references therein). Similar diapiric structures are found in the Basque-Cantabrian Basin (N. Spain) where Zn-Pb occurrences and small old mining workings are known, especially around the Murguía and Orduña diapirs (Fig. 1). In 1998, the Ente Vasco de Energía (EVE) and Outukumpu Minera España (OME) started an exploration and drilling program around the Murguía diapir (Álava Province) in order to assess the mineral potential of the structure. As a result of this, two mineralized horizons (up to 2 metres thick with ore grades of 8% Zn) were recognised, with mineralization (sphalerite and galena) replacing platform facies sandstones (Valmaseda Formation) and extending around the diapir. The aim of this work is to characterise the mineralisation related to the Murguía and Orduña diapirs, in terms of fluid origin and formation conditions, and to evaluate the role of the diapiric structures and the enclosing sediments in the location of the deposits. To achieve this, a petrographic and geochemical study has been carried out.

2 GEOLOGICAL SETTING

The Orduña and Murguía diapirs are located SW of the Basque Cantabrian Basin (BCB), in the northern part of the Iberian Peninsula (Fig. 1). The BCB is composed of sediments of Mesozoic and Tertiary age, which are occasionally intruded by evaporite diapirs consisting of Upper Triassic rocks. Diapirs are aligned NW-SE over an area of 100x25 km and SW-NE over an area of 75x15 km, and are concentrated around the depocenters of the Aptian-Albian basin (García-Mondéjar et al. 1996). The diapiric structures were active from at least the late Cretaceous and were deformed by the Alpine orogeny. The diapirs are made up of clays, gypsum and halite of early Triassic age (Keuper facies), with occasional detached blocks of Jurassic dolostones, and intrude a thick succession of Lower to Upper Cretaceous rocks. The Lower Cretaceous rocks are composed of siliciclastics of late Albian to early Cenomanian age (Valmaseda Formation). The late Cretaceous includes carbonates and marls with ages ranging from late Cenomanian to late Campanian (EVE 1996). Mineralization has been classified into three groups according to the host rock association: Type 1 in sandstones of the Valmaseda Fm; Type 2 in carbonates and carbonate breccias of Jurassic and Turonian age enclosed within the diapirs; and Type 3 in black shales at the Cenomanian-Turonian boundary.
PETROGRAPHY AND MINERALOGY

Mineralization in the Valmaseda Fm (Type 1) is the most interesting economically. Sulfides are mainly hosted by arkoses and subarkoses. The most important example is the Altube deposit, situated on the NW margin of the Murguía diapir. The ore minerals are sphalerite, galena and pyrite that occur as replacive disseminations of millimetric crystals, semimassive bodies and veins (up to a few cm wide) associated with dolomite, calcite and quartz. Bitumen is commonly observed with the Zn-Pb sulphides.

Type 2 mineralization occurs in dolomitized limestones of Turonian age and in dolostone breccias of Jurassic age (fragments within the diapirs). Examples are the Jugo and Monteleón deposits, located at the Eastern edge of the Murguía diapir and at the NW side of the Orduña diapir, respectively. Mineralization consists of replacive disseminations, stockworks, breccias and veins. Ore minerals are sphalerite, galena and pyrite, associated with dolomite, calcite, quartz and albite.

Paul is the only example of Type 3 mineralization, located at the southern edge of the Orduña diapir. It is hosted by black shales that correspond to the C-T Anoxic Oceanic Event of the Cenomanian-Turonian boundary. Mineralization consists of idiomorphic millimetric sized sphalerite, galena and pyrite crystals, disseminated in the black shales as well as centimetric thick veins of sphalerite, galena, pyrite and dolomite.

Organic matter is found in relation to all the mineralization types. It occurs as solid bitumen in the sandstone replacing detrital quartz grains in Type 1 deposits and occurs in the breccia and veins in Type 2 deposits. Textural, reflectivity and Rock-Eval pyrolysis studies showed that solid bitumen formed after liquid hydrocarbons. Solidification could have occurred before or during the formation of the Zn-Pb deposits, as fractures and vesicules in the bitumen are filled with sulphides, barite and ore-related carbonates. The wide range of reflectivity and Rock-Eval data from one locality to another points to organic matter maturation related to local thermal anomalies rather than to regional burial.

MICROTHERMOMETRY AND CRUSH-LEACH ANALYSIS

Fluid inclusion studies on sphalerite and quartz yielded a range in homogenization temperature (Th) from 80 to 240°C and ice melting temperatures (Tmi) from -2.8 to -27.5°C (Fig. 2). A positive correlation is observed between Th and bitumen reflectivity pointing to a relationship between fluid circulation and the heterogeneous maturation of organic matter.
(Cl/Br)\textsubscript{molar} and (Na/Br)\textsubscript{molar} ratios derived from fluid inclusion crush-leach analyses of sphalerite, quartz and ore-stage carbonates (Fig. 3) suggest the presence of some fluids related to evaporated sea water but mostly halite dissolution brines.

4 ISOPTIC GEOCHEMISTRY

The sulphur isotope composition of sulphides is similar in all three type of deposits, with $\delta^{34}$S values ranging from +3.4 to +28.3‰ for pyrite, from +7.4 to +14.6‰ for sphalerite and from +4.1 to +12.0‰ for galena. Barite compositions range from +16.2 to +24.3‰. Gypsum from the Keuper facies (diapiric) has $\delta^{34}$S values ranging from +13.5 to +17.4‰. The $\delta^{34}$S of sulphides is compatible with a sulphur source related to the reduction of sulphate (probably thermochemical, TSR) of evaporitic origin. The higher $\delta^{34}$S values of some barite samples compared to gypsum may be related to the isotopically heavy residual sulphate.

Carbon and oxygen isotope compositions of carbonates fall into two different groups. In Type 1 mineralization $\delta^{18}$O\textsubscript{SMOW} of ore-stage carbonates ranges from +17.7 to +20.6‰ and $\delta^{13}$C from -4.9 to +2.3‰; in Type 2 and 3 mineralization $\delta^{18}$O\textsubscript{SMOW} of ore-stage carbonates ranges from +20.8 to +27.1‰ and $\delta^{13}$C\textsubscript{PDB} from -10.3 to +3.0‰. These variations could be related both to temperature variations during ore-stage carbonate formation and to differences in host rock lithology. According to calculated mixing and water/rock interaction models, and assuming a formation temperature similar to the sulphides (120-240°C), the $\delta^{18}$O of the ore-forming fluids could have been between +5 and +14‰. The negative values of $\delta^{13}$C in some carbonates suggest the presence of organic-derived C in the fluids.

$^{87}$Sr/$^{86}$Sr ratios of ore-stage carbonates discriminate between the different types of mineralization: from 0.71052 to 0.71202 in Type 1 and from 0.70801 to 0.71116 in Types 2 and 3. This suggests a strong influence of the host rocks (detrital or carbonate) on the ore-forming fluids.

5 CONCLUSIONS

In the BCB, three main diapir-related Zn-Pb deposit types are found: sandstone-hosted disseminations and veins (Type 1); carbonate-hosted disseminations and veins (Type 2) and disseminations in black-shales and related veins (Type 3). According to textural evidence, both Type 1 and 2 mineralization is epigenetic, and Type 3 seems to be syngenetic. The conceptual model for Type 1 and 2 involves basinal brines that were channeled around the diapirs and interacted with the evaporites. As suggested by $\delta^{34}$S data, H\textsubscript{2}S could have been produced through sulphate-reduction (likely thermochemical) of diapiric sulphate, in the presence...
of hydrocarbons, at temperatures as high as 240°C as indicated by Th data from fluid inclusions. The interaction of fluids with hydrocarbons is supported by the formation of methane clathrate in some of the fluid inclusions during freezing studies, and the negative δ13C data in carbonates. Some surficial fluids derived from seawater evaporation were also present at some stage. The genetic model is similar to that proposed by Orgeval (1994), Posey et al. (1994) and Sheppard et al. (1996) for diapir-related Zn-Pb deposits in the North-African and Gulf Coast diapirs. In the BCB, the Type 1 deposits are the most economically interesting. A potentially important volume of mineralization is located in the Valmaseda Formation at Altube (NW margin of the Murguía diapir). Our study also confirms the importance of the Valmaseda Formation as a host rock for sulphides around the diapiric structures since new showings were discovered in the Villasana de Mena diapir, situated 40 km to the NW of Murguía (Fig. 1).

ACKNOWLEDGEMENTS

This work has been financed through the Spanish Ministry of Education and Culture PB1998-0901 Project. The authors wish to thank Juan García (EVE) and Joaquin Beck (Outukumpu Minera Española) for their help in the field and for allowing us access to the drill core samples. We also thank Jean-Robert Disnar and Fatima Laggoun-Défarge (Institut des Sciences de la Terre d’Orléans) for their help with the bitumen Rock-Eval and reflectance study.

REFERENCES


ABSTRACT: REE in fluorite from Asturias show different content and distribution patterns from east (Berbes) to west (Villabona). The linear trend of the data in a Tb/Ca vs. Tb/La diagram hints at crystallization from a single hydrothermal event, Berbes being the early stage and Villabona occurring later. $^{87}$Sr/$^{86}$Sr ratios of fluorite are distinct in each area and vary from 0.70802 to 0.71052. This is consistent with the presence of two Sr sources: seawater of Lower Jurassic age and a more radiogenic source of basinal origin that interacted with basement rocks. REE patterns and Tb/Ca ratios are compatible with the presence of a unique hydrothermal system that probably flowed from east to west leaching different rocks during early Jurassic times.

KEYWORDS: fluorite, Rare Earth Elements, Sr isotopes, Asturias, hydrothermal

1 INTRODUCTION

The most important fluorite deposits of the Iberian Peninsula are located in Asturias (N Spain) and have produced more than 7Mt of ore since the 1970’s. The deposits are found in three areas, named from east to west, Caravia-Berbes, La Collada and Villabona.

They occur as veins enclosed in limestones within the Palaeozoic basement and as vein and stratabound bodies in highly silicified red-bed sediments (carbonates, marls and sandstones) of Permo-Triassic age (García Iglesias and Loredo, 1994). The red-beds contain interbedded lavas of basaltic composition (Valverde, 1992). Mineral paragenesis is composed of fluorite, quartz, barite, calcite, dolomite and minor sulphides (galena, chalcopyrite, pyrite and marcasite).

Fluid inclusion data indicate that two types of fluids were involved in fluorite precipitation: a low salinity solution (between 0 and 8.5 wt% NaCl eq) and a high salinity CaCl$_2$-rich fluid (from 9 to 26 wt% NaCl eq) (Sánchez et al. 2006a). Homogenization temperatures (Th) range from 100 to 160°C in Berbes (eastern area), 80 to 160°C in La Collada and from 80 to 140°C in Villabona (westernmost area). In Berbes, solid organic matter embedded with fluorite and late-stage quartz fluid inclusions are found. Cl/Br and Br/Na ratios obtained from crush-leach indicate that the mineralizing fluids involved in the process were evaporated seawater and brines formed after the dissolution of evaporites (Sánchez et al. 2006a). Mixing was probably the cause of fluorite precipitation (García Iglesias & Loredo, 1994; Sánchez et al. 2006a).

The age of the Villabona deposit was constrained by analyzing the Sm-Nd isotope ratios in fluorite (Sánchez et al 2006b). This method yield an age of 185±29 Ma, which is consistent with the hydrothermal event widely described in Western Europe that took place during the Early Jurassic, related to the opening of the North Atlantic Ocean.

In the present work, REE and Sr isotope data from fluorites of the Berbes, La Collada and Villabona areas are presented in order to gain further insights on the origin and evolution of the mineralizing fluids. REE geochemistry may be a powerful tool to gather information about the source of these elements, migration and precipitation processes as well as the chemical composition of the fluid (Möller et al. 1984) whereas Sr isotopes may help to identify the solute sources and fluid paths.
Fifteen samples of fluorite and two samples of Permo-Triassic volcanic rocks were analyzed for their REE content. Analyses were carried out at ACTLABS, Canada, by ICP-MS. Results were normalized to the Post-Archaean Australian Shale (PAAS). $^{87}\text{Sr}^{86}\text{Sr}$ ratio was measured in 27 samples of fluorite. Analyses were performed at the CAI (Universidad Complutense, Madrid, Spain).

Fluorites have a low $\Sigma$REE content, with mean concentration values of 0.4 ppm in Berbes, 1.1 ppm in La Collada and 9.3 ppm in Villabona. The distribution of REE shows a roof-shaped pattern with an enrichment of HREE with respect to LREE (Fig. 1), which is more prominent in samples from La Collada. A positive Ce anomaly in fluorites from Berbes is observed, contrasting with fluorites from La Collada and Villabona where no Ce anomaly is present. Volcanic rocks of Permian age have the highest $\Sigma$REE content: 13.7 ppm and their distribution depicts an almost flat pattern with a minor positive Eu anomaly.

$^{87}\text{Sr}^{86}\text{Sr}$ ratios vary from 0.70802 to 0.71052, with a different range of values according to the district. Thus in Berbes, $^{87}\text{Sr}^{86}\text{Sr}$ range from 0.70802 to 0.70964, from 0.70945 to 0.71052 in La Collada and from 0.70826 to 0.70881 in Villabona (Fig. 2).

3 DISCUSSION

Fluorites from the three districts show significant differences in terms of REE and Sr isotope signatures. The $\Sigma$REE content increases from the Berbes deposit (situated to the East) to Villabona (the westernmost mineralization) by an order of magnitude. The La/Lu ratio depicts an opposite trend, decreasing from a mean value of 0.36 in Berbes, to 0.17 in La Collada and 0.09 in Villabona. These low ratios imply a strong fractionation between LREE and HREE, which is more pronounced in Villabona. As the degree of REE fractionation is controlled by the source rock and by processes in the fluid during transport (Schwinn & Merkl, 2005), the hydrothermal fluids either leached different rocks or the physico-chemical conditions during fluid flow were different in the three deposits. However, this hypothesis is also compatible with a gradual variation of these conditions from east (Berbes) towards west (Villabona).

In a Tb/Ca vs. Tb/La diagram (Fig. 3) samples plot within the sedimentary field, like most MVT deposits, indicating an assimilation of calcium-rich carbonate rocks by the ore-forming solutions (Möller et al., 1976). The linear trend and positive slope of data from Berbes and La Collada indicates a progressive increase in the REE fractionation, probably related to the timing of mineralization, from early to late stages. Thus, precipitation of fluorite probably proceeded from Berbes (early, lower Tb/Ca and Tb/La ratios) to La Collada (late, higher Tb/Ca and Tb/La ratios). Samples from Villabona also depict a linear trend but at higher Tb/Ca ratios than fluorite from the other deposits. These higher ratios could be due either to a different source for the REE or to a precipitation from fluids that also interacted with siliciclastic or volcanic rocks.
A good linear correlation between the La/Tb and the La/Yb ratios of fluorite from three areas is also seen in Figure 4. The mean La/Yb ratio of each deposit, that is, the degree of fractionation between HREE and LREE, also correlates with the mean Th’s of fluid inclusions. Berbes has the highest La/Yb ratio (0.29) and Th (140°C and 135°C for the low and high salinity fluids, respectively); Villabona has the lowest values for La/Yb ratios (0.06) and Th (90°C) and La Collada presents intermediate values for both La/Yb ratios (0.09) and Th (120 and 95°C, respectively). These data reinforces the idea of a single large-scale hydrothermal system with a gradual change in the leaching and/or transport conditions of the REE from east to west.

The positive Ce anomaly found in samples from Berbes can be explained through two processes: 1) reduction of Ce(IV) to Ce(III) at the deposition site increasing the Ce content of the fluid available to be incorporated into fluorite and 2) the Ce content of the fluids was high in Ce(III) before fluorite precipitation (inherited anomaly). The first hypothesis is favored as the Ce anomaly is only observed in the deposit (Berbes) where organic matter is found. The Ce anomaly differentiates the easternmost fluorites (Berbes), from the westernmost ones (La Collada and Villabona).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios in fluorites display a wide variation, from 0.70802 to 0.71052. Fluorite from Berbes shows the largest $^{87}\text{Sr}/^{86}\text{Sr}$ range, whereas fluorite from Villabona has the lowest and most homogeneous $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Assuming a similar age for all the deposits, this range is consistent with the presence of two sources of Sr with different isotopic ratios that mixed in different proportions at each deposit. As suggested by halogen data (Sánchez et al. 2006a), one of the fluid sources could be related to evolved seawater ($^{87}\text{Sr}/^{86}\text{Sr}$ during Lower Jurassic ≈ 0.70750; Burke et al. 1982) whereas the more radiogenic source should be related to a basinal brine which interacted with basement rocks (carbonates, sandstones, volcanics...). The distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios shows a higher abundance of basinal brines at La Collada, whereas at Villabona the mixture was dominated by modified seawater.

Fluorite from Villabona shows distinct REE, Sr isotope compositions and lower homogenization temperatures of fluid inclusions compared to La Collada and Berbes. Therefore, the latter deposits could be related to a deeper system dominated by basinal brines and Villabona to a more superficial system, where seawater was the major component. Assuming a similar age for all the deposits, these differences could reflect the presence of two separate hydrothermal systems that leached rocks at different depths. However, a unique hydrothermal system could be envisaged, as data from homogenization temperatures, total REE content and Tb/Ca ratios from La Collada are mostly intermediate between those from Berbes and Villabona. The hypothesis of a single hydrothermal system seems more plausible and is compatible with the Jurassic basin topography, deeper in the NE and shallower towards the W (Garcia-Ramos & Gutiérrez, 1995).
4 CONCLUSIONS

Fluorite from the Berbes, La Collada and Villabona deposits show a ΣREE increase from east (Berbes) to west (Villabona). A strong fractionation between LREE and HREE, especially in Villabona is observed. The linear trend in the Tb/Ca-Tb/La diagram suggests crystallization from the same hydrothermal event. Thus, Berbes would form at early stages and Villabona at late stages of mineralization. The higher Tb/Ca ratios in fluorite from Villabona could be related to fluids that preferentially interacted with low-Ca bearing rocks. The positive Ce anomaly in fluorites from Berbes is probably related to a more reducing environment compared to the other two deposits.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios show a distribution from higher values in La Collada (0.71052) to lower values in Villabona (0.70826), consistent with the presence of two sources of Sr that mixed in different proportions: seawater of Lower Jurassic age ($^{87}\text{Sr}/^{86}\text{Sr} \approx 0.70750$) and a more radiogenic source of basinal origin which interacted with basement rocks. Homogenization temperatures and REE patterns are compatible with the presence of a unique hydrothermal system flowing from east to west and leaching different types of rocks. Fluorite precipitation took place during early Jurassic times as a result of mixing.

ACKNOWLEDGEMENTS

This study has been financed through a CI-CYT project (BTE2003-01346). V. S. has benefited from a FPI grant (Spanish Ministry of Education and Science).

REFERENCES


Origin of fluids associated to gangue minerals in fluorite deposits of Asturias (N Spain)

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ABSTRACT: Barite, carbonates, quartz and sulphides are present as gangue minerals in fluorite deposits from Berbes, La Collada and Villabona (Asturias, N Spain). Calculated $\delta^{18}O$ of fluids ranged from -1.1 to +6.7‰ during barite precipitation, from +2 to +6‰ during quartz formation and around +3‰ during carbonate deposition. $\delta^{34}S$ of barite (+17 to +56‰) is explained from sulphate reduction processes (either TSR or BSR) in systems closed to sulphate. $\delta^{34}S$ of sulphides (+0.6 to -32‰) are compatible with these processes. Isotopically light pyrite and marcasite (-7.6 to -32‰) would be related to late stage cooling and oxidation of the hydrothermal system. Organic matter derived carbon was an important source of C in the fluids especially in Villabona ($\delta^{13}C$= -14.8 to -3.2‰ in calcites and from -7.9 to -2.2‰ in dolomites).

KEYWORDS: stable isotopes, fluorite, Asturias, sulphate reduction

1 INTRODUCTION

The Asturian fluor spar district (N Spain) is one of the most important in Europe. Some of the deposits as Villabona, La Collada and Berbes are currently in operation. They occur as veins within the Palaeozoic basement, hosted by limestones of Upper Carboniferous age and as vein and stratabound bodies in highly silicified red-bed sediments (carbonates, marls and sandstones) of Permo-Triassic age (Garcia Iglesias & Loredo, 1994). The red-beds contain interbedded lavas and pyroclastic rocks of trachytic to basaltic composition (Valverde, 1992). Mineralogy comprises fluorite, quartz, barite, calcite, dolomite and minor sulphides (pyrite, marcasite, galena and chalcopyrite). The paragenetic succession shows the presence of 3 stages of quartz precipitation (Fig. 1). The first stage comprises a widespread silicification of the enclosing rocks (Q1) previous to fluorite formation; the second stage (Q2) is composed of small idiomorphic crystals, and Q3 quartz is characterized by the hydrocarbon inclusions and the idiomorphic shape (“diamond-type”). The Q3 quartz is only found in the Berbes deposit. Two generations of barite precipitated after fluorite, which are morphologically distinct, being the later one only found in Villabona.

Solid organic matter occurs in the Berbes deposit and hydrocarbons are found in fluid inclusions trapped in fluorite and late-stage quartz (Q3). Cl/Br and Br/Na ratios obtained from crush-leach indicate that the mineralizing fluids involved in the process were evaporated seawater and brines formed after the dissolution of evaporites (Sanchez et al. 2006a). Fluorite from Villabona was dated at 185±29Ma from the Sm-Nd method (Sánchez et al 2006b), indicating that the hydrothermal event occurred during the Early Jurassic, related to the opening of the North Atlantic Ocean. The age is consistent with other similar fluorite deposits of Western Europe. Here, we present a stable isotope study of gangue minerals (carbonates, barite, sulphides and quartz) in order to elucidate the origin of the fluids responsible for, and the mechanisms of gangue mineral deposition.

2 ANALYTICAL RESULTS

24 barites and 16 sulphides (marcasite, pyrite and galena) from the three deposits (Berbes, Villabona and La Collada) were analyzed for their S isotope composition. Results are shown in Fig. 2 and display a wide range of values both in barite and sulphides. $\delta^{34}S$ vary between +17.2 and +30‰ in barite from Berbes.
and from +31.3 to +56‰ in barite from Villabona. $\delta^{34}$S of sulphides (pyrite and marcasite) from Berbes range from +0.6 to +8.5‰, from +9.9 to -32‰ in La Collada and from -16.5 to -7.6‰ in Villabona. A galena sample from La Collada gave a $\delta^{34}$S value of +5.3‰. The oxygen isotope composition of 11 barites from Berbes and Villabona were also analyzed and the $\delta^{18}$O values ranged from +14.7 to +17.7‰.

Figure 1. Paragenetic sequence in Asturias deposits

<table>
<thead>
<tr>
<th>QUARTZ</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
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<tr>
<td>FLUORITE</td>
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<tr>
<td>SULPHIDES</td>
<td>Pyrite</td>
<td>Marcasite</td>
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<tr>
<td>BARITE</td>
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<td>DOLOMITE</td>
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<td>CALCITE</td>
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37 samples of carbonates (calcite and dolomite) were analyzed for their C and O isotope composition. The $\delta^{13}$C values for calcites and dolomites from Berbes and La Collada deposits are similar and range from 0.7 to +6.1‰. However, $\delta^{13}$C of carbonates from Villabona are distinctly lower, ranging from -14.8 to -3.2‰ in calcites and from -7.9 to -2.2‰ in dolomites. The $\delta^{18}$O of both carbonates in the three deposits show similar values, between +17.4 and +27.6‰.

The $\delta^{18}$O values of early quartz (Q2) from Berbes and La Collada (5 samples) range from +19.3 to 23.9‰; late idiomorphic (“diamond type”) quartz only found in Berbes (Q3) has higher values that vary from +23 to +24.5‰ (5 samples).

3 DISCUSSION

The high $\delta^{34}$S values of barite, especially in Villabona, suggest a sulphate source related to either a thermochemical sulphate reduction (TSR) or bacteriogenic sulphate reduction (BSR) in a system partially closed to sulphate. The ultimate source of sulphate could be either seawater or sulphate derived from dissolution of evaporites of Jurassic age ($\delta^{34}$S $\approx$ +17 to +20‰). In both cases, the reduction processes would be enhanced by the presence of organic matter at the depositional sites. The wide range of $\delta^{34}$S values could be due to different reduction degrees in the sulphate reservoirs before barite deposition or, alternatively, to a mixing between sulphate sources having contrasting $\delta^{34}$S values. As high amounts of Ba cannot be transported in sulphate-rich solutions, the second hypothesis would involve a Ba-rich, sulphate-poor fluid with a $\delta^{34}$S $\approx$ +17 to +20‰ and a sulphate-rich solution having a $\delta^{34}$S $>$ +50‰. Homogenization temperatures in barite from Berbes (150 to 165°C; mode: 155°C) are higher than those from Villabona (80-125°C; mode: 90°C), suggesting that the main sulphate reduction process in Berbes would be of TSR type whereas at Villabona BSR would dominate. Moreover, the positive correlation between $\delta^{34}$S and $\delta^{18}$O in barites at Berbes (Fig. 3) supports sulphate reduction at the depositional site. Assuming isotopic equilibrium between sulphate and water and a T=150°C, the $\delta^{18}$O of the fluid would range between +3.7 and +6.7‰ at Berbes and between -1.1 and +0.4‰ in Villabona taking a T=90°C. In both cases fluids are isotopically compatible with surface wa-

Figure 2. $\delta^{34}$S histogram for sulphates and sulphides from Asturias deposits

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sulphide deposition in these deposits generally exceeded conditions capable of sustaining efficient bacterial processes (> 120°C), biogenic reduction, if present, should have occurred away from the ore zone and/or prior to the hydrothermal event. The very low $\delta^{34}S$ values of some pyrite and marcasite samples from La Collada and Berbes and especially from Villabona ($\delta^{34}S$ from -17 to -7‰) are consistent with BSR and are possibly related to episodes of cooling (low temperature conditions) and oxidation that accompany the final stages of the hydrothermal environment (Plumlee & Rye, 1992).

In a $\delta^{13}C$/$\delta^{18}O$ diagram (Fig. 4), carbonates from the three deposits plot within a similar $\delta^{18}O$ range (+17.5 to +25.8‰). $\delta^{18}O$ of hydrothermal calcite and dolomite range from +17.5 to +22.7‰, variation that could be explained if carbonates precipitated from a fluid having a $\delta^{18}O = +3$‰, during a temperature decrease (from 130 to 80°C as found in FI (Sánchez et al., 2006a; fractionation equation of O’Neil et al., 1969). The assumed $\delta^{18}O$ of the fluid is compatible with modified surface waters (meteoric or seawater). However, compared with Berbes and La Collada, the $\delta^{13}C$ of carbonates from Villabona has more negative values (down to -14.7‰), probably related to a presence of organic-derived carbon in this deposit during precipitation.

The $\delta^{18}O$ of quartz are distributed in two groups. The first group corresponds to quartz II with values from +19.3 to 23.9‰ and the second to quartz III (diamond type, with hydrocarbon-bearing fluid inclusions) with $\delta^{18}O$ values between +23 and +24.5‰. Assuming a T of formation (deduced from microthermometry of fluid inclusions) for quartz II around 130°C (Sánchez et al., 2006a), the calculated $\delta^{18}O$ of the fluid ranges from +2 to +6‰ (Clayton et al., 1972), consistent with a surface water modified through water-rock interaction. No microthermometric data are available from quartz III. The heavy $\delta^{18}O$ values could be explained by a temperature decrease (from 130 to 80°C) if, during the hydrothermal process, the isotopic composition of water remained unchanged.

4 CONCLUSIONS

Stable isotope composition of gangue minerals (barite, carbonates, sulphides and quartz) show that hydrothermal fluids involved in the precipitation of these minerals were of surface origin (either meteoric or seawater), which had likely been isotopically modified after interaction with the basement (mainly carbonates) and/or enclosing rocks (sandstones and marls). At Berbes, mean $\delta^{18}O$ of fluids during quartz II, hydrothermal carbonates and barite precipitation were +4‰, +3‰ and +5‰ respectively, assuming a mean T of 130°C. Similar values have been calculated for Villabona except for late barite where $\delta^{18}O$ of fluids was around 0‰. Organic matter-derived carbon must have been an important source of C in the fluids, especially in Villabona where very negative $\delta^{13}C$ values were obtained.

The high $\delta^{34}S$ of barite is explained from BSR and/or TSR in systems partially closed to sulphate. Organic mater was locally abundant and played an essential role as the reducing agent in sulphate-reduction processes. $\delta^{34}S$ of sulphides (+0.6 to -32‰) are compatible with
BSR, which took place before mixing with the basin-derived hydrothermal fluid. The most negative $\delta^{34}S$ values (-7.6 to -32‰) correspond to late stage pyrite and marcasite and would be related to a precipitation from cooling and oxidation during the waning stages of the hydrothermal system. The gangue minerals in the fluorite deposits of Asturias (N Spain) were probably precipitated after the mixing of a sulphate-rich water of surface origin, undergoing sulphate reduction, with a sulphate-poor, Ba and base-metal bearing brine at the deposition site (either red-beds of Permian age or basement fractures).

ACKNOWLEDGEMENTS

This study has been supported by a CICYT project (BTE2003-01346) and a FPI grant to V.S. (Spanish Ministry of Education and Science). Special thanks to MINERSA for the fieldwork and sampling facilities.

REFERENCES


Pb-Zn-Ba mineralization from the Tazekka Pb-Zn district, eastern Morocco

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ABSTRACT: The Tazekka Pb-Zn district, eastern Morocco, includes both mineralized veins and stockworks in the Paleozoic basement and stratabound deposits in the Liassic carbonate cover rocks. The purpose of this study is to examine the relationship between mineralization seen in the basement and cover by combining field observations, mineralogy, fluid inclusion data and previous stable isotope data and use these information to present a unified model for the formation of the Pb-Zn ores. The results suggest that the general fluid evolution is similar in most of the deposits and is independent of host rock age. High salinity, low temperature fluids are present in the cover where they predate mineralization. The wide range of salinities suggests fluid mixing has occurred, possibly between an evaporated seawater brine and a lower salinity fluid. Sphalerite appears to be related to fluids of intermediate salinity with deposition probably associated with the mixing process. The resemblance between the results and data from other Pb-Zn ore deposits in Europe suggests water-rock interaction during downward migration of the fluids is important for ore genesis.

KEYWORDS: Pb, Zn, basement, carbonate, mineralization, Tazekka, Morocco

1 INTRODUCTION

The Palaeozoic basement and Liassic carbonate rocks of the Tazekka district of eastern Morocco host numerous Pb-Zn- (Cu, Fe) and Ba deposits (Fig. 1). Veins of sphalerite, galena, pyrite and chalcopyrite, together with stockworks of quartz and barite are present in Lower Ordovician schists, in an Upper Visean-Namurian volcano-sedimentary complex and in the Tazekka granite. The overlying Liassic carbonate platform sequence contains stratiform Pb-Zn sulphide deposits lying above an unconformity between the Lower and Upper Lias (Auajjar 1987). The general geological characteristics of the Tazekka district have been described in Auajjar (1994) and Auajjar & Boulègue (1999). The purpose of this study is to examine the relationship between mineralization seen in the basement and cover by combining field observations, fluid inclusion data and previously published lead and sulphur isotope geochemistry. This information is used to present a unified model for the formation of the Pb-Zn ores of the Tazekka district.

2 METHODOLOGY

The characteristics of the mineralization were determined by optical microscopy of thick and thin sections. Microthermometry of fluid inclusions was performed on polished thick sections using Chaixmeca and Linkam THMSG600 heating-freezing stages. The ionic composition of fluid inclusions was determined by the crush–leach technique. The anions F-, Cl, Br\(^-\) and SO\(_4\)^{2-} were analysed by ion chromatography on double-distilled water leaches using a Dionex 45001.

3 MINERALIZATION

Deposits of the Palaeozoic basement

Mineralization in the form of quartz-sulphide veins and quartz-barite veins and stockworks is hosted by schists, volcano-sedimentary rocks and granites of the Tazekka district (Fig. 1).

The quartz-sulphide veins are typically either NE-SW (Dar Bou Azza, Dar Izid) or E-W (Bab Sedra, Dar Asri, Bab El Hajjaj) trending, with thicknesses ranging from 1 to 7m and lengths of a few hundred metres to several kilometres. Barite veins and stockworks are developed only in the Upper Visean-Namurian volcano-sedimentary complex, and are observed at Bab Bou Idir, Koudiat Lakhâa and Douar Tsâima. A few veins, e.g. veins N80 (Douar Tsâima), N70 (Koudiat Lakhâa) and N20 (Bab Bou Idir) contain sulphide mineralization. The Bab El Hajjaj vein is the only E-W-trending vein rich in barite.

The quartz–sulphide veins contain quartz, sphalerite, galena, pyrite, chalcopyrite, tetrahedrite and barite; secondary malachite and pyromorphite appear locally. Pyrite and sphalerite occur only in the NE-SW-trending group. The quartz may be grey and microcrystalline (quartz 1), white, macrocrystalline and translucent with comb or rosette textures (quartz 2), or locally pyramidal (quartz 3). Barite forms pink, fine grained massive aggregate (barite 1), large white crystals (barite 2) or "cockscomb" crystal aggregates (barite 3).

The NE-SW-trending veins show a well-defined mineralogical sequence: barite 1-pyrite -sphalerite 1 -F1- quartz 1-galena 1-tetrahedrite 1 -F2- sphalerite 2-chalcopyrite 1 -F3- galena 2-tetrahedrite 2-quartz 2-F4- barite 2-quartz 3-barite 3-galena 3 (where F1, F2, F3 and F4 represent fracturing events). For the E-W-trending veins, a contrasting mineralogical sequence is suggested since F1 and F2 fracturing events are not present. The sequence is: chalcopyrite -F3- galena and tetrahedrite -F4- barite 2-quartz 3-barite 3-galena 3.

In the quartz - barite stockworks and veins, barite forms either large crystals (barite 2) or barite 3 in geodes.

Deposits of the Liassic cover

The Liassic-hosted Pb-Zn mineralization is focused along the Mesozoic basin margin, controlled by grabens formed during the major Toarcian-Bathonian Middle Atlas tectonic event. Deposits onlap from NE to SW close to the North Middle Atlas fault (N30E). The deposits comprise stratiform (Aïn Hallouf, Bou Khalifa, Ain Tarselt, Asdi Ben Zehra, and Ain Kheebb) and open-space filling ores (Sidi Abdellah) (Fig. 1). Stratiform sulphide Pb-Zn mineralization is hosted by hydrothermal dolomites overlying the unconformity between the Lower and the Middle Liassic.

Sulphides typically form massive aggregates hosted by three hydrothermal dolomite types: early hydrothermal dolomites (types 1 and 2) and later saddle dolomite (type 3). The early hydrothermal dolomite 1 is a dolospar containing microdolospar residual zones. Dolomite 2 is well represented at the Sidi Abdellah deposit. This dolomite is black, coarsely crystalline and is cut by veins of dolomite 3 up to 15 cm thick. Dolomite 3 is coarsely crystalline and in some geodes is overlain by bitumen.

The three types of hydrothermal dolomite are characterized by different δ¹⁸O values. For dolomite 1, which hosts the stratiform ores, δ¹⁸O values vary from -7.2 to -8.2‰ (average -7.8‰). Dolomite 2 hosting the Sidi Abdellah deposit has δ¹⁸O values around -9.8‰. Dolomite 3 (saddle dolomite) is slightly more variable with δ¹⁸O values of -7.57 to -12.58‰ (average -9.4‰) (Auajjar & Boulègue 2002).

At Bou Khalifa and Ain Hallouf, centimetre-sized crystals of sphalerite and galena and pyrite and chalcopyrite are found in dolomite 1.
Sphalerite occurs as transparent or translucent red or yellow crystals forming a ribbon or banded texture and contains microscopic inclusions of chalcopyrite and pyrite. Euhedral dolomite 3 crystals also occur crosscutting the galena cleavage. At Bou Khalifa, brecciated sphalerite is cemented by dolomite 3.

At Sidi Abdellah, crystals of sphalerite and galena are associated with chalcopyrite and pyrite. Together, they form massive aggregates in dolomite 2. Microscopic inclusions of chalcopyrite are present in sphalerite and microscopic inclusions of tetrahedrite occur in chalcopyrite. Fractured galena and sphalerite and curved cleavage planes in galena indicate deformation after mineralization. In this deposit chalcopyrite forms cement enclosing brecciated crystals of pyrite. Pyrite occurs in aggregates of subhedral and euhedral crystals. Microscopic inclusions of bournonite are present within the galena. A phase of supergene alteration of earlier minerals is represented by smithsonite, malachite, covellite and Fe-oxides.

4 FLUID INCLUSION DATA

Fluid inclusion studies were performed on all three hydrothermal dolomite types and sphalerite from the cover; quartz 1, barite 1 and sphalerite 1 from the basement. Two main fluid inclusion types have been recognised: L1 - H₂O–NaCl-(CaCl₂); and L2 - H₂O–CaCl₂-NaCl. L1 occur in secondary fluid inclusion planes (FIP) in sphalerite 1 and quartz 1; as pseudo-secondary inclusions in barite 1 from the basement, and as primary inclusions in sphalerite and dolomite 3 from the cover. L2 are present as secondary inclusions in dolomite 1 and as pseudosecondary inclusions in dolomite 2.

Ice melting temperatures (Tm_{ice}) of L1 in sphalerite are between -11 and -3°C (-11 to -5°C in the cover and -8 to -3°C in the basement); in dolomite 3 between -7.2 and -6.5°C; in barite between -11 and -6°C; and in quartz between -6 and -0.5°C. Homogenisation temperatures (Th) vary between 110 and 159°C in sphalerite (generally lower temperatures in the basement); between 110 and 160°C in dolomite 3; between 190 and 290°C in barite; and between 200 and 320°C in quartz (Fig. 2).

L2 inclusions are characterised by Tm_{ice} between -23.0 and -11°C and Th between 90 and 100°C (Fig. 2).

5 HALOGEN DATA

The halogen content of inclusions hosted by quartz and barite from the Palaeozoic basement and of inclusions hosted by dolomite 2 and dolomite 3 from the Liassic cover are shown in Figure 3. It is clear that the fluids from the different samples have a similar range of halogen compositions and that they have a lower Cl/Br than seawater. The trend in the data could be interpreted as due to dilution moving from the cover dolomites to basement barite and quartz.

6 DISCUSSION AND CONCLUSIONS

The lack of any observable cross-cutting relationships between deposits in the Liassic cover and the basement rocks or geochronological data mean that it is difficult to confirm a genetic relationship between the two types. However, the petrographic, stable iso-
Topo and fluid inclusion studies suggest that the general fluid evolution is similar in most of the studied deposits and is independent of the host rock.

In the mineralized structures, the fluids do not exhibit significant compositional variations and the fluids associated with sphalerite (low-moderate salinity, low Th) are similar in both the cover and in the basement. In contrast, the high salinity and low temperature fluids are only present in the cover, where they occur associated with dolomite 2, prior to deposition of sulphides.

The evolution of the fluids could be interpreted as a mixing and dilution of the high salinity fluids (possibly evaporated seawater brines) trapped in dolomite 2 from cover with lower salinity fluids trapped in barite 1 and quartz 1 from the basement. Sphalerite deposition appears to be related to fluids of intermediate salinity probably associated with the mixing process.

The resemblance between the present results and previous work on other Pb-Zn ore deposits in Europe that focused on the origin and evolution of the mineralising fluids, suggests water-rock interaction related to a downward migration of the fluids into the basin and even into the basement was an important process (e.g. Canals & Cardellach 1997; Gaspararrini et al. 2003; Bouch et al. 2006).

ACKNOWLEDGEMENTS

This work was developed through the Grices (Portugal) - CNRST (Morocco) cooperation and also supported by POCI 2010. The authors thank Jamie Wilkinson for improving the manuscript.

REFERENCES


A contribution to the knowledge of the Hammam Zriba and Bou Jaber Pb-Zn-Ba-F ore deposits (Tunisia)

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ABSTRACT: The Hammam Zriba and Bou Jaber ore deposits are two important examples of carbonate-hosted F-Ba-Zn-Pb mineralization in Tunisia. Petrography, microthermometry, Raman spectroscopy and fluorescence microscopy were carried out on fluid inclusions hosted by fluorite and barite from these deposits. The wide range of salinity observed suggests mixing of two fluids of different composition. It is likely that this fluid mixture transported an immiscible petroleum phase as preserved in liquid hydrocarbon fluid inclusions. Fluorescence microscopy indicates that the petroleum fluid inclusions have an aliphatic composition in both ore deposits. Preliminary Pb isotope data suggest a similar source of lead for both ore deposits. Geological and fluid characteristics are consistent with a MVT classification for this mineralization.

KEYWORDS: Hammam Zriba, Bou Jaber, fluorite, barite, fluid inclusions, MVT deposits

1 INTRODUCTION

The Hammam Zriba (HZ) and Bou Jaber (BJ) ore deposits, located in the north of Tunisia, are two examples of carbonate-hosted F-Ba-Zn-Pb mineralization in the Mahgreb region (Figs. 1 and 2). HZ is located southwest of the Zaghouan fault, about 8 km from Zaghouan village and 68 km south of Tunis. BJ is located about 250 km west-southwest of the Tunisian capital and 6 km south of the small village of Kalaat-es-Sunam, near to the Algerian border. Based on fluid characterization, the present study intends to contribute to the understanding of the origin of these F-Ba-Zn-Pb deposits.

2 GEOLOGICAL SETTING

HZ belongs to the so-called “Tunisian Fluor Province” and is a stratiform ore deposit located at an unconformity between Portlandian limestones and Campanian limestones and marls. BJ is located in the so-called “Diapir zone”, characterized by the occurrence of diapirs of Triassic evaporite. The deposit occurs in karst cavities within Aptian limestones and in a N75E fault at the contact between Aptian limestones and Cenomanian black marls. Both areas are characterized by the occurrence of NS, NE-SW and ENE-WSW faults; some of these are still active and are associated with hot springs.

3 MINERALOGY

At HZ, mineralization is essentially composed of barite-celestite, fluorite, sphalerite, galena, pyrite and calcite. Thibieroz (1976) and Bouhlel et al. (1988) defined three fluorite ore
types: i) rubané ore consisting of fluorite (HZ F₁) associated with white, fibrous, massive barite; ii) intrakarstic ore consisting of fluorite (HZ F₁II) associated with massive barite and, occasionally, well-developed calcite crystals; and iii) geodic structures, fractures or late veins filled with fluorite (HZ F₁III).

At BJ, mineralization is composed of barite, sphalerite, galena, pyrite, fluorite and calcite. There are two main types of ores: i) intrakarst massive ore with sulphides (sphalerite and galena), ankerite, barite and fluorite; and ii) fault-controlled “vein” ore composed of sphalerite, galena, barite and violet fluorite. Several types of barite can be distinguished: i) well-developed white or transparent barite crystals in the footwall of the massive ore (BJ B₁); ii) barite rich rubané ore (BJ B₁II); and iii) white, radial fibrous, remobilised barite. Fluorite usually occurs as large, transparent crystals (BJ F₁) that formed prior to barite (Amouri 1986).

5 FLUID INCLUSION STUDIES

5.1 Methodology

Petrography and fluid inclusion studies were carried out on barite (B₁ and B₁II) and fluorite (F₁, F₁II and F₁III) from both ore deposits. Non-destructive methods were employed: microthermometry, micro-Raman spectroscopy and fluorescence microscopy. Microthermometric characterisation of the fluid inclusions was performed on doubly polished thick sections (<300 µm) using a “Chaixmeca” heating-freeze stage (Poty et al. 1976) and a “Linkam 600” stage (Shepherd 1981). Both stages were calibrated using natural and synthetic fluid-inclusions. In addition, the analysis of the gas phase composition and the petroleum phase was undertaken with a Labram Raman microspectrometer. The fluorescence studies were performed using a binocular reflection microscope equipped with a LEITZ MVP Combi photometer with a Pol-OPak illuminator, a 50x oil immersion objective (nₑ = 1.5180), 10x oculars and equipped with two illumination fonts and theirs stabilizers: one of white light and the other of HBO 100W high pressure mercury for fluorescence.

5.2 Microthermometry

Aqueous and immiscible petroleum-rich fluid inclusions were observed in both deposits. Additionally, in the BJ ore deposit, carbonic and aqueous-carbonic fluids were also observed. These inclusions were classified into several types: aqueous FI (Lw), petroleum-rich FI (Lp), immiscible liquid FI (Lw-p-c, Lp-w-c, Lp-c), carbonic FI (Lc) and aqueous-carbonic FI (Lw-c).

In both ore deposits a wide variation in the composition of primary Lw inclusions (found isolated or in crystal growth zones) was observed. These fluids are low to high salinity (HZ: 3.1 to 25.2 wt % eq. NaCl; BJ: 0 to 26.2 wt % eq. NaCl). In the immiscible liquid FI, the aqueous phase composition is very similar to the aqueous FI (HZ: 1.9 to 24.0 wt % eq. NaCl; BJ: 15.2 to 19.6 wt % eq. NaCl) (Fig. 3). Primary aqueous and petroleum-rich FI in both deposits have similar homogenisation temperatures (HZ (Lw): 99 to 170ºC; HZ (Lp): 99 to 142ºC; BJ (Lw): 92 to 213ºC; BJ (Lp): 102 to 110ºC; Figures 3 and 4). Only petroleum-rich FI hosted by B₁ from BJ show relatively higher homogenisation temperatures (149 to 190ºC; Fig. 4).

4 LEAD ISOTOPES


"Digging Deeper" C.J. Andrew et al (editors)

5.3 Micro-Raman spectroscopy

Using micro-Raman spectroscopy to analyze petroleum inclusions was not conclusive due to the inexistence, at the time, of an adequate filter to remove the fluorescence effect of the hydrocarbons present in the inclusions. CO₂ and CH₄ peaks were identified by micro-Raman spectroscopy in Lw-c inclusions. These gave a vapour phase composition of 73.3 to 100 mol% CO₂ and 0.0 to 26.7 mol% CH₄.

5.4 Fluorescence

Fluorescence microscopy revealed fluorescence colours in the HZ petroleum-rich FI between blue and white-blue. The Q_{650/500} and I₅₄₆ parameters estimated for primary FI vary from 0.158 to 0.496 and from 2.308 to 10.304, respectively. For secondary FI the estimated values were Q_{650/500} =0.514 and I₅₄₆ = 18.775, suggesting a more aliphatic-rich composition. The fluorescence colours observed in the BJ petroleum rich FI vary between white-blue, blue, yellow and green-yellow. The Q_{650/500} and the I₅₄₆ parameters estimated for primary FI vary from 0.276 to 0.405 and from 8.782 to 21.03, respectively. These results indicate, as in the case of HZ, an aliphatic-dominant composition, although with a higher content of aromatic compounds than at HZ.

6 CONCLUSIONS

The microthermometric data and the fluorescence microscopy reveal that the fluids present in barite and fluorite from HZ and BJ are very similar in composition. These data, together with similar lead isotopic compositions of galena from both deposits, imply a common genesis. The fluid inclusion data suggest that in both HZ and BJ mixing of two aqueous fluids with different salinities occurred. The similar salinity of the aqueous phase in the Lw and Lw+Lp inclusions, the identical genesis (primary and secondary) of the three type of inclusions (Lw, Lp and Lw+Lp) and the comparable range of homogenisation temperatures suggests coeval entrapment of immiscible petroleum and aqueous fluids. Although we cannot determine the origin of these fluids, it is obvious that hydrocarbons were present during fluorite and barite deposition and probably during base metal mineralization.

It is inferred that tectonic activity drove fluid circulation through karst cavities that behaved as traps for the mineralization. Gharbi et al. (1981) proposed a Néogène age for karst formation and ore recrystallization at Bou Jaber. The source of the brines is unknown, but they could have been derived by dissolution of evaporites within the Triassic series (Benchilla et al. 2003) and/or may represent post-collisional basinal fluids (cf. Bradley & Leach 2003).

ACKNOWLEDGEMENTS

This work was developed through the GRICES cooperation project (Portugal)/INRST (Tunisia) and supported by POCI 2010.

REFERENCES

Amouri M (1986) Le gisement de Bou Jaber (Atlas Tunisien Central). Un exemple de mineralisation Pb-


Investigations on the Chemistry of Mineralizing Fluids of Vein Type Mineralizations Related to the Diapiric Zone in Northern Algeria

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ABSTRACT: The mineralizations presented in this paper are closely related to the “peri diapiric” zone in NE Algeria and are characterized by the occurrence of numerous Triassic diapirs hosted mainly by different lithologies of the Cretaceous series. This series hosts numerous Pb-Zn, Ba-F, Fe and Cu mineralizations that were mined in the past. Siderite mines in this area (Ouenza in Algeria and Jerissa in Tunisia) are still operating. Mineralization occurs in swarms of steeply dipping veins and is usually accompanied by intense dolomitization and silicification. Fluid inclusion homogenization and freezing data, along with Na-Cl-Br leachates, permit the characterization of the mineralizing fluids. This data confirms that the mineralizations have formed during the Atlasic orogenic event. In the Na-Cl-Br diagram the composition of the mineralizing fluids lies well on the halite dissolution trend indicating that the fluids acquired their salinities by the dissolution of halite.

KEYWORDS: Algeria, siderite, barite, fluorite, fluid chemistry

1 INTRODUCTION

Numerous Pb-Zn-Ba-F and siderite mineralizations of appreciable economic importance occur in Northern Algeria as well as in Tunisia. These mineralizations are generally hosted within strata of Aptian to Turonian-age and are closely related to a zone of Triassic diapirs piercing the Cretaceous series.

The “peri diapiric” mineralizations in the NE of Algeria share many features with the Tunisian occurrences. According to Sheppard et al. (1996), the mineralization can be divided into different types based on their location in and around the diapirs. A variety of different mineralizations in this area have been sampled for this investigation - Ouenza (siderite), M'kririga (F, Ba, Pb/Zn), Ouasta (Pb/Zn), Essouaba (F, Ba, Pb/Zn), Hammeimat (F, Ba), Mesloula (Pb/Zn) etc.

A major aspect of this paper is to characterize the fluids responsible for the formation of these deposits. The method applied is the chemical analysis of inclusion fluids. The chemical composition of palaeo-fluids can be used as a geochemical tracer to investigate the original signature and origin of different kinds of inclusion fluids. Analytical work on the chemistry of the inclusion fluids (F, Cl, Br, I, Na, K, Ca, etc.) can contribute substantially to the question as to the origin of mineralizing fluids. This paper focuses on the question as to where the fluids of the investigated mineralizations acquired their high salinities.

2 GEOLOGIC SETTING OF THE INVESTIGATED MINERALIZATIONS

The eastern Saharan Atlas fold belt of north Africa coincides roughly with the well-known zone of diapirs (“Zone des Diapirs”) which is characterized by numerous bodies of Triassic evaporites piercing the cores of anticlinal structures in a NE-SW trending zone. Throughout the Zone des Diapirs Pb/Zn, Ba-F, and Cu-mineralization has been mined in the past. The ore occurrences are enclosed within platform carbonates of Aptian or Turonian age. Morphologically, they range from disseminations, “nests” and breccia fillings to vein types.
In this zone the Triassic rocks outcrop in several places piercing the overlying Cretaceous formations. The Triassic rocks consist of a sequence of argillites, marls, sandstones and gypsum-bearing units containing rock fragments of black dolomite, micaceous sandstone, limestone and altered dolerite.

This Triassic formation is overlain by a well fractured, dolomitized and silicified carbonate formation of Aptian age. It is typically overturned and dipping 70-80° SW. The contact between the Triassic rocks and Cretaceous rocks is also tectonic and is represented by a breccia zone and a ferro-oxide and barite- celestite mineralization called “zone ferro-barytique”. These observations indicate that the contact is tectonic.

In this area mineralization occurs in four types of configurations:

**Type 1** corresponds to the “Zone ferro-barytique” marking the contact between the Triassic formation and the Aptian formation (Sami et al. 2003). It is marked by the presence of anhydrite, gypsum and celestite and minor barite. The mineralization is mainly brecciated and shows a reddish colour. It consists of brecciated aggregates that host ferric hydroxides and, rarely, some crystalline galena. Massive mineralization is also present.

**Type 2** consists of disseminated fine grained syngenetic sulphides in the well bedded and often dolomitized biomicrite of the Cenomanian-Turonian aged “Bahloul facies”.

**Type 3** consists of fluorite, barite and galena filling fractures as well as lenticular bodies or as disseminations. Banded textures are common. This type is essentially hosted by the sandy limestone and marl series.

**Type 4** corresponds to fluorite-galena, barite- and copper sulphosalts in veins and stringers. They occur throughout the Aptian limestones and define centimeter-scale veins generally aligned parallel to the NE-SW trending faults. Vein fluorite occurs as centimeter to decimeter scale vughs. Purple or white fluorites appear as cubic crystals, 0.2 to 3cm in size. Fluorite is mostly associated with large disseminated patches and well-formed crystalline galena.

Figure 1. Geological map showing the major geological units and mineralizations of the investigated area in Northern Algeria.
3 ANALYTICAL METHOD

The method used to analyze the inclusion fluids was described by Bottrell et al. (1988). Different gangue minerals such as barite, fluorite, quartz, and carbonates, were selected and manually separated for the extraction of soluble salts. The samples were crushed to a grain size between 0.25 and 1 mm and carefully cleaned. 1 g of the cleaned sample and 5 ml of the leaching solution (DDW) were transferred to the thoroughly cleaned mortar and crushed. Because of its significance for the origin of the fluids, special attention was given to the analyses of anions. The samples were analyzed by ion chromatography. A Dionex system (DX-500) with a micro membrane suppressor was used. Na, K, Li, Ca and Mg were analyzed by ion chromatography using aliquots of the same solution.

4 CHARACTERISTICS OF THE FLUIDS

The use of the Br-content to characterize the origin of brines was introduced by Rittenhouse in 1967. It is important that only very conservative systems that are not buffered and changed by ambient mineral reactions in the alteration zones are taken into consideration. Thus Cl-Br and to some extent I-systematics are more suitable to provide clues to the identity of the highly saline fluids than other element ratios which may be changed by wallrock alterations. Evidently Cl-Br-ratios are very difficult to be modified by fluid/rock reactions thus providing a tracer for hydrothermal fluids at least as “robust” as hydrogen isotope composition.

Despite the similar ionic radii of chlorine (1.81 Å) and bromine (1.96 Å) the fractionation of these elements in evaporitic processes is quite different. In an initial stage of evaporation Na, Cl, and Br are concentrated in a hypersaline environment, and their ratios do not change. At an evaporation index of > 10, halite is precipitated. Br has a very conservative behavior and is not incorporated into the halite lattice. At an evaporation index of approximately 70, Mg-salts start to precipitate and Br is still concentrated in the residual brines. The cation systematics changed from an original Na-preponderance to Mg- and K-dominated systems (McCaffrey et al. 1987).

In a Cl/Br- versus Na/Br-molar ratio diagram (Fig. 2) the evolution of the fluids by fractionation of halite from seawater is demonstrated. Accordingly the composition of an evaporitic brine is shifting along the “evaporation trend” when halite starts to precipitate at an evaporation index of about 10. On the other hand fluids percolating through the crust acquiring salinity by dissolution of halite, plot towards higher Cl/Br- and Na/Br-molar ratios and their composition is close to the “halite dissolution trend”.

All investigated samples give high yields when crushing and extracting the salts indicating an overall high salinity. An important feature of the fluid composition is the general low Br-content. Fig. 2 shows that the majority of the investigated samples is situated on the halite dissolution trend, that means that the fluids acquired their salinity by the dissolution of halite. A slight shift of the trend towards lower Na-contents (that means lower Na/Br-ratios) can be explained by lowering the Na content of the mineralizing fluids by albitization processes. A similar trend is formed by siderite samples from the Fe-deposit of Jerissa in Tunisia which seems to have a similar genetic history.

Fluid inclusions in fissure-hosted quartz from the investigated mineralizations suggest temperatures fluctuating between ca. 130 and 380°C. The fluids are aqueous NaCl–CaCl2–H2O solutions where the temperatures of first ice melting range between -50 and -60°C. Accordingly the fluids show medium salinities of 12.5 to 17 wt% NaCl eq. In Fig. 3 the basic microthermometric data for the Ouasta ore deposit are presented.

The most common brine type found in the “peri diapiric” zone has a relatively restricted
range of freezing temperatures but a large range of homogenization temperature extending from slightly below 150°C to more than 340°C. Brines with these salinities and high temperatures were found in inclusions from some minerals in the Hodna domain and recently in the Aurès Massif (Boutaleb 2001).

5 CONCLUSIONS

The investigated diaper-related vein-type deposits in NE-Algeria are structurally controlled and are part of the late Alpine geotectonic event of the eastern Saharan Atlas fold belt. The mineralizations are restricted to platform carbonates of Aptian or Turonian age. The style of mineralization varies from pockets to breccia-fillings to veins. Alteration phenomena are intense dolomitization and silicification with nacrite, dickite, and kaolinite as most important alteration minerals.

Usually the fluids forming these mineralizations exhibit salinities between 12.5 and 17.0 wt% NaCl eq. The main chemical feature of the inclusion fluids is the low Br-content with respect to Cl and Na. This indicates that the mineralizing fluids acquired their salinity by dissolution of halite. Evidently Cretaceous hydrothermal fluids percolating through the crust partly dissolved the Triassic diapirs. This is in agreement with the late Alpine tectonic history of that area.

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
Vertical zoning patterns and magmatic-hydrothermal evolution of the Geumseong Mo deposit, South Korea

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ABSTRACT: The Geumseong Mo deposit, South Korea, formed in the Palaeozoic sedimentary rocks following the emplacement of the Cretaceous leucocratic intrusions, representing the apical part of relatively shallow-level plutons. The Geumseong deposit comprises two kinds of ore bodies with different styles of mineralization, which include the Mo skarn deposit and the Mo-bearing aplitic cupola. The Geumseong skarns are both calcic and magnesian, but calcic ones are most common. Some aplitic cupolas are geochemically highly evolved, and have well-developed comb quartz and aplitic layers. The vertical scale alteration patterns of the deposit in the mine show Mo-bearing aplitic apical zone with proximal Fe skarn through transitional Mo skarn to distal haematite zone. The ore-bearing fluids migrated from the relatively deep contact zone of the hidden cupolas to the upper carbonate wall rocks to form different types of skarn and mineralization under physical conditions of decreasing temperature and oxidation state.

KEYWORDS: Geumseong, Mo mineralization, skarn, Korea, unidirectional solidification texture

1 INTRODUCTION

In general, the skarn deposits in South Korea are considered as economically significant sources for W, Mo, Fe, Zn, Pb and Cu and are genetically related to the emplacement of Late Cretaceous granitoids (Yun 1983). Numerous skarns and veins hosting Mo-W minerals have been identified in the Hwanggangri area, the central South Korea. (Reedman et al. 1973).

The Geumseong molybdenite deposit is one among the largest Mo producers in South Korea with production/reserves of 1.45 Mt averaging 0.48 MoS₂ (Koh et al. 2003). Mo mineralization represents the most important deposit within the area. The Mo-bearing skarns and aplitic cupolas are still under exploration by diamond drillings, and its lower limits have not been established yet. This paper focuses on the magmatic-hydrothermal evolution of the Geumseong Mo deposit with special emphasis on the vertical distribution pattern of the metasomatic facies.

2 GEOLOGICAL SETTING

Tectonostratigraphic units in the South Korea include the Gyeonggi Massif, the Okcheon belt, the Yeongnam Massif, and the Gyeongsang Basin from north to south. The two Precambrian massifs form the basement of South Korea and comprise the late Archaean to Neoproterozoic high-grade metamorphic rocks (Fig. 1). The NE-trending thrust-fold belt, the Okcheon-Taebaek belt, is composed of the Neoproterozoic-early Palaeozoic Okcheon zone to the southwest, and the Palaeozoic Taebaek basin to the northeast (Oh et al. 2004).

A trimodal distribution of Mesozoic magmatism has been recognized in Korea (Sagong et al. 2005): Triassic (Songrim), Jurassic (Daebo) and Cretaceous (Bulguksa) episodes. Magmatic-hydrothermal activities are known to be associated with the Jurassic and the Late Cretaceous granitic magmatisms (Choi et al. 2005). However, the most important Mo-W mineralization of the South Korea is reported in the Hwanggangri-Taebaek area (So et al. 1983), the northeastern part of the Okcheon basin, where these two events of granitoids overprinted repeatedly (Fig. 1).

The Guemseong mine is located at the southern margin of the Jurassic Jecheon granitoids and near the northern area of the Cretaceous Muamssa granite together with the Cambro-Ordovician mixed dolostone-limestone
series of the Yeongweol Group, Choseon Supergroup along the NW- and NE-trending fault systems.

The Jecheon granitoids yielded K-Ar whole rock ages of 179 ± 6 Ma (Ishihara et al. 2002) and 169 ± 5 Ma (Shibata et al. 1983), whereas the partly altered aplite dike associated with Mo mineralization gave K-Ar age of 107.5 ± 2.3 Ma. The aplitic intrusions show deep negative Eu anomaly and M-type tetrad effects in REE patterns on a chondrite normalized diagram, indicating extreme magmatic fractionation. In contrast, the Jecheon granitoids display LREE-enriched patterns and exhibit smooth, right-dipping curves, indicating adakitic signatures (Ishihara et al. 2005).

3 MINERALIZATION AND METASOMATIC FACIES ZONATION

Field observations and diamond drilling data in the Geumseong mine have revealed the occurrence of two main types of skarn and one barren oxidized zone: (1) lower magnesian skarn zone as Fe skarn, developed at the contact between Mo-bearing aplitic cupola and dolomitic marble, (2) upper calcic skarn zone as Mo skarn, developed in marble, and (3) uppermost disseminated haematite zone in marble. The Guemseong skarn is chiefly an exoskarn in both the lower and upper skarn zones. However, the endoskarn found in the lower skarn zone is limited to only a few centimeters in width. The skarn is more developed in the upper skarn zone than in the lower zone. The pyroxene and garnet present in these two zones are visually and compositionally distinct.

Fig. 2. Slab photograph of the Geumseong aplitic cupola showing comb-textured quartz layer and aplitic layer.

3.1 Felsic Intrusion

The Geumseong skarn is spatially and genetically associated with the leucocratic subvolcanic intrusions, comprising fine-grained biotite granite with related pegmatite, aplitic cupolas and dikes. Aplitic cupolas are reported here for the first time from South Korea. They have characteristic interlayered texture with well-developed comb quartz layers containing disseminated molybdenite and aplitic layers (Fig. 2). Comb quartz layers typically consist of unidirectional solidification and crenulated textures with zoned quartz megacrysts. Aplitic layers consist mainly of a fine-grained mixture of quartz, sericite, orthoclase, albite and muscovite with minor apatite and monazite. Petrological and geochemical data of the felsic intrusions indicate highly-evolved and oxidized, silicic epizonal intrusions.

3.2 The Lower Skarn

Metasomatic alteration in the lower dolomitic strata of the Yeongweol Group at the aplitic contact produced a relatively thin (about 2m to 10m) magnesian skarn. The magnesian skarn is primarily made up of pyroxene, olivine and interbedded magnetite. These minerals underwent varying degrees of retrograde alteration to a mixture of tremolite, serpentine, talc, chlorite and phlogopite. In dolomitic marble,
skarn is marked by an increase in grain size and the formation of serpentine, amphibole, chlorite, magnetite, phlogopite, pyrite and quartz along the skarn-marble contact. A noticeable feature of the skarn is barren of molybdenite with the lack of garnet. Pyroxene from all parts of the lower skarn is nearly pure diopside (Di$_{80-100}$), and olivine is relatively pure forsterite (Fo$_{70-85}$).

3.3 The Upper Skarn

Molybdenite mineralization occurs with the pyroxene-garnet skarn. The dimensions of this skarn are > 450m along E-W strike with a thickness of 50m to 200m (Park 1982). This skarn is very large in comparison with lower magnesian skarn. It has altered intensively and hence the zonation is very clear. The upper skarn is characterized by calcic exoskarn assemblage that is dominated by pyroxene and grandite garnet with minor epidote, amphibole, sericite, chlorite and quartz.

The upper skarn is zoned from massive pyroxene-garnet skarn in the central part to monomineralic garnet skarn at the contact between skarn and marble. The main pyroxene-garnet skarn zone consists of dark green pyroxene and dark reddish brown garnet in a ratio of 5:1 to 3:1. This zone constitutes approximately 70% of the total upper skarn volume and contains relatively high-grade molybdenite. This skarn is overprinted by late quartz, epidote and amphibole. Here molybdenite is more abundant than pyrite and chalcopyrite. The marginal garnet zone in the upper skarn consists of abundant zoned garnet and minor magnetite, epidote, amphibole, chlorite, quartz and calcite instead of wollastonite. Garnet exhibits a wide range in color from reddish brown to greenish yellow towards the marble contact. Some local zones of haematite and pyrite at the contact of skarn and marble are also noticed. Molybdenite in the upper skarn increases towards the central pyroxene-garnet skarn, but magnetite, haematite and pyrite are more abundant toward the marble contact.

The pyroxene and garnet in this skarn are visually and compositionally distinct. The pyroxene composition for the central main zone is more Fe-rich (Hd$_{69-90}$) than the outermost-zone pyroxene (Hd$_{45-61}$). The composition range of garnets in the garnet skarn zone is Ad$_{63-100}$, and is slightly enriched in Fe relative to those in pyroxene-garnet skarn (Fig.3). In addition to the zonation in ratios of clinopyroxene:garnet in the upper skarn, there is also a progressive Fe$^{3+}$ enrichment in mineral assemblage with distance from the central main skarn to the skarn margin.

Fig. 3. Composition of garnet and pyroxene from the Geumseong skarn. Clinopyroxenes from upper skarn display hedenbergitic composition, whereas diopsidic composition is recorded by those from lower skarn.

3.4 The Haematite Zone

The haematite zone, which represents the uppermost replacement zone in the Geumseong deposit, occurs as relatively flat-lying body (about 10m to 30m in thickness) with disseminated haematite within the marble. This zone consists of a reddish brown rock with a finely banded texture made up of recrystallized calcite crystals and a very fine-crystalline haematite. A characteristic of this zone is barren of molybdenite with the lack of skarn minerals.

4 DISCUSSION

The Geumseong skarn is spatially and genetically associated with the leucocratic sub-volcanic intrusions. Previous K-Ar and Rb-Sr ages (Shibata et al. 1983; Jin et al. 1992; Ishihara et al. 2002) from the Jecheon granitoids inferred an origin for the Daebo orogeny unrelated to the aplitic-associated Geumseong Mo occurrence.

The Geumseong magmatic-hydrothermal system is vertically zoned from a central low-grade Mo cupola with proximal Fe skarn through transitional Mo skarn to distral haema-
tite layers surrounded by bleached marble. Development of the lower skarn is probably coeval with emplacement of the aplitic cupola. In the lower magnesian skarn, the composition of the main skarn minerals such as diopside, forsterite and serpentine, do not contain much Fe. Thus, the available Fe in solution tends to form magnetite rather than garnet, olivine and pyroxene. In contrast, the upper calcic skarn display systematic compositional variations from the central pyroxene-garnet to marginal garnet zone. The abundance of pyroxene relative to garnet in the central main part and the high Fe^{2+}/Fe^{3+} values of both pyroxene and garnet are indicative of relatively reduced conditions. On the contrary, the mono-mineralic abundance of garnet and rarity of pyroxene in the skarn margin is relatively barren of molybdenite, and is consistent with the presence of both magnetite and haematite toward the marble front. The high fO2 indicated by the oxide mineral assemblage favors the crystallization of andraditic garnet over the intermediate diopside. Differences in oxidation state correlate well with the skarn zonation pattern and mineralization.

ACKNOWLEDGEMENTS

This work was supported by a grant (No. R01-2006-000-10553-0) from Korea Science and Engineering Foundation (KOSEF) under the Basic Research Program.

REFERENCES


ABSTRACT:: Brecciation is a common feature of many mineralized systems including vein gold and Fe-Cu-Au deposits. In this paper we use a particle code (PFC2D) to simulate the brecciation process. Breccias of the Cloncurry district (Australia) are believed to form in response to a pulse of overpressured fluid released from a cooling intrusion and we set out to explore this model here. Results are presented for two fluid boundary conditions. One involves a fluid flux applied to the base of a pre-stressed, cohesive particle assembly as may occur at the top of an intrusion releasing fluid. This results in lifting of the entire mass, with minimal fracturing at the base of the material. An alternative approach involves an isolated pulse of overpressured fluid moving through the material. This produces fracturing ahead of the migrating pulse with subsequent collapse of the fractured rock into the space left in the wake of the pulse. This simulates brecciation as a fluid-driven (hydraulic) fracturing, followed by fluidization of the resulting fragments.

KEYWORDS: particle flow codes, brecciation, fluidisation

1 GEOLOGICAL BACKGROUND AND RATIONALE

Breccia, the Italian word for 'breach', is typically a rock composed of fragments (both angular or rounded) of a previously homogeneous rock, cemented in a matrix that may be of a similar or a different material. This study involves the numerical simulation of breccia formation using a “particle code” which is a form of discrete element codes. Particular application is to the economically important and well studied breccias of the Cloncurry region in Queensland. Milled breccias containing both exotic and local fragments are the typical hosts to chalcopyrite-gold-magnetite-calcite orebodies in the Cloncurry Fe-ox-Cu-Au district. The relationship between these breccias and the ore-forming fluids is not well understood beyond the clear spatial relationship, in which, for example, ore minerals form part of the matrix to the breccias with rounded, altered fragments. Some geometries of the breccias require substantial fragment transport distances, up to 1000m, in sheet-like bodies. It is suggested that a key driver for the system in Cloncurry was a strong initial pressure gradient between the fluidized mass at the starting point and some distal point in the Soldiers Cap Group (Oliver et al., 2006). This research aims to test this hypothesis through exploring the relationships between applied flux of fluid into the system, the mechanical strength of the original rock mass, and the resulting patterns of the fracture systems and breccias.

The approach described here represents a development of existing research in characterising large-scale collective motion of particles in fluidized beds. Fluidized beds are widely used in the chemical and fossilfuel processing industries to mix particulate solids and fluids (gases or liquids). A typical fluidized bed consists of a vertically oriented chamber, a bed of particulate solids, and a fluid flow distributor at the bottom of the chamber. The fluid flows upward through the particles, creating a drag force that counteracts gravity. With sufficiently high flow, the solids are levitated and move in complex, turbulent patterns (hence the name “fluidized”). This turbulence promotes heat and mass transfer as well as chemical reactions between the fluid and the solids.
Experimental results (see Chapter 7 in Brennen, 2005) demonstrate a sequence of macroscopic behaviour as the gas flow is increased:
(a) small-amplitude highly complex behavior, (b) large-amplitude approximately periodic behavior, (c) periodic behavior intermittently interrupted by “stutters,” and (d) “turbulent” behavior. This project explores whether or not such transitions occur for weak rock masses and if characteristic breccia textures are developed that allow the physical conditions of brecciation to be identified in the field. At a later stage reaction-transport modeling will be coupled to these models to allow precipitation of minerals in the breccias and alteration of the fragments.

2 METHODOLOGY

2.1. PFC2D

This paper presents the findings of a preliminary evaluation of a particle code (PFC2D; Itasca Consulting Group; http://www.itascacg.com/pfc.html) for simulating the geological process of brecciation. Particle codes represent a cohesive rock as a series of bonded particles with specified contact relationships. The code can accommodate large displacements and rotations of rock fragments, which would be impossible in a continuum code. To model this phenomenon requires a particle based simulation and cannot be achieved with classical continuum codes. Although widely used in chemistry modeling and chemical engineering (see Xu, 2003), the applications of this methodology to geological simulations are in their infancy (Ord et al., 2006; Imber et al., 2004).

2.2. Model setup

2.2.1. Particles

The key parameters are given below. For convenience they are taken from previous studies where it has been shown that such parameters reproduce real rock behaviour (Ord et al., 2006)

Sample size: 0.6m x 0.2m
Porosity: 0.13
Particle density: 2226 kg/m³
Particle size: 2 – 3mm

Normal & shear stiffness of balls and walls: 1.16x10¹⁰ N/m

Figure 1. Initial particle assembly with stress-controlled boundary walls. Details of compressive contact forces shown in black.

2.2.2. Boundaries

The boundaries of the model represent ‘servo-controlled’ walls, which were used to maintain the specified confining stress on the model boundaries. The walls adjust their movement during cycling of the model to maintain a given stress on the assembly.

2.2.3. Fluid

Fluid flow is calculated on a fixed grid overlying the particle assembly, taking account of the interaction between fluid and particles (Shimizu, 2006). The fluid mesh was created after initialization of stresses in the model, and the model was then cycled to stable equilibrium state with a hydrostatic fluid pressure gradient.

3. SIMULATIONS

3.1. Brecciation driven by fluid flow

The following images illustrate the effect of applying a fluid flux to the base of the model, following initialization and equilibration. The incompressible flow algorithm ensures that the flow field instantaneously attains the steady state appropriate to the boundary conditions. Subsequent adjustments to the flow field reflect the movement of particles. The applied fluid flux has the effect of raising the entire block of particles, with a small degree of breakage at the base of the particle assembly. Figure 2 shows the effect of varying the bond strength (cohesion) between particles. There appears to be a narrow range of properties that produces fracturing. Varying the fluid velocity produced a similar range of behaviors.

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Figure 2. Effect of varying bond strength on fracturing driven by fluid flow from the base. Cohesion decreases from top to bottom. Black lines represent fractures, so that the greatest fracturing is seen to be in the bottom figure.

Figure 3. Effect of adding stationary side regions representing cohesive walls. Coloured bands indicate layers of cohesionless particles.

Figure 4. Effect of varying flow rate and bond strength on the behaviour of the system with cohesive sidewalls.

To simulate boundary interactions with the country rock, the assembly was modified by adding stationary sides to the model; sections 0.1m wide on either side of the model that have a fixed wall at the top to prevent the particles from moving upwards. These fixed side regions act as walls to which the particles in the middle section adhere.

Figures 3 and 4 illustrate the behaviour of the system with these cohesive sidewalls, again with fluid flow from the base. The grey bands are layers of cohesionless particles, which were inserted to facilitate fragmentation of the rock mass. The middle section is lifted by the fluid, with fracturing that propagates downwards from the top boundary, producing geologically realistic structures. These types of models have
the capability of transporting fragments considerable distances as in the Cloncurry situations but such models have not yet been run

3.2. Brecciation driven by a pressure pulse

As an alternative scenario, we explored the effect of a pulse of overpressured fluid moving through the system.

Figure 5 illustrates some aspects of the resulting behaviour. Compression ahead of the pulse results in fracturing, then the fragments collapse into the space left by the pulse once it has passed through the system. The fracture pattern and ultimate assembly of rock fragments looks realistic and representative of a breccia, although this particular example does not represent long-distance transport of fragments which has been inferred from some natural examples (Oliver et al., 2006).

Figure 5. Brecciation caused by upward migration of a rigid wall.

4. DISCUSSION

The simulations presented in this paper represent a preliminary investigation of the potential of PFC2D for modelling brecciation. Applying a fluid flux to the base of the model using the fixed coarse grid fluid scheme has much the same effect as mechanically lifting the lower boundary; the rock may undergo some fracturing at the base, but the fragments have nowhere to go because in the present experiments, the fluid pressure is sustained. Our alternative approach of forcing a pressure pulse through the particle assembly produces more obviously promising results. These results suggest that compressible flow may be an important “ingredient” for modelling brecciation; in particular, the ability to model a pulse of overpressured fluid that creates space into which the fractured rock can collapse, appears to be essential.

5. ACKNOWLEDGEMENTS

S. Mikula thanks iVEC (http://www.ivec.org) for their support of her throughout this research as an iVEC intern. This work is supported by iVEC and by the Predictive Mineral Discovery Cooperative Research Centre.

REFERENCES


New considerations about the La Paz vein deposit: Telescoped skarn-vein system

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ABSTRACT: The La Paz district is located on the eastern border of the Mesa Central, Mexico. It is formed by a Range and Basin geomorphology determined by a Cretaceous sedimentary sequence showing a plicative deformation, developing an eastward recumbent anticline with an N-S axis. This part forms the Range zone (western side) whilst towards the eastern side is located the Basin zone formed by a flat ground covered by recent alluvial material on top of the Cretaceous sedimentary sequence. The emplacement of granodiorite intrusives occurs in both zones and has developed a metasomatic aureole. In the Range zone skarn-hosted Cu-Au mineralization occurs. The vein systems crosscut lithostratigraphy as much in the range zone as in the basin zone, and have a well developed lateral zoning from west to east: Ag-Pb-Zn-Cu-Au in the range zone, Cu-Ag-Zn-Pb in the western side of the Basin zone, and Ag-Pb-Zn in the eastern side. Geochemical composition (major and trace elements) of the granitoids reveals a complete difference between the granitoids from the Range and those from the Basin. The tendency, in terms of major elements, within the granitoids and skarns, is for the La Paz granitoids to be concentrated in the field of Cu-rich, and Fe-Au-rich skarns, corresponding to high K calc-alkaline rocks. The results of the U-Pb dating of the intrusives from the Range and Basin zones shows approximately 1Ma of difference.

KEYWORDS: Au-Cu skarn, Ag-Pb-Zn veins, Mesa central, U/Pb dating, magmatism, Mexico

1 INTRODUCTION

The La Paz district is located 200km north from San Luis Potosí City, SLP state, México. The Ag-Pb-Zn epithermal veins have been known and exploited since the XVII Century. Different authors (Machado, 1970, Cajero, 1975, Castro-Larragoitia, 1990, Gunnesch, et al., 1994) along the time increment the initial description of the epithermal vein system (García, 1967). The discovery and recent exploitation of the Au-Cu skarn zone, and in particular its Gold heterogeneity distribution, imply the necessity of complete new geological review of the district.

The first report on the skarn area was by Spurr et al. (1912). Minerals were first produced from the Dolores Mine on Ag-Pb-Zn-Cu veins. The Ag-Pb-Zn vein structures in the San Agustin, El Pilar, and San Acacio mines were closed down by 1992, because the high cost of production and the low price of the metals at the time. Proved ore reserves remain about seven million tonnes in situ. However, Cu-Au mineralization from skarn mines (Dolores) are still being exploited. The mines are owned and operated by Negociacion Minera Santa Maria de La Paz, S.A. de C.V.

In this paper we present new metalogenic data supported by new field, petrographic, mineralogic, geochemical, and U-Pb dating studies.

2.- GEOLOGICAL SETTING

The La Paz district is located in the eastern border of the Mesa Central, Mexico. The Mesa Central is an elevated plateau mainly covered by Cenozoic volcanic sequences crosscut by deep continental basins filled with alluvial and lacustrine sediments. Towards the east margin appears a Jurassic to Cretaceous sedimentary sequence, showing plicative deformation and
reverse faulting due to the Laramidian orogeny.

The study area extends through a basin and range system. The range part is composed by Albian-Cenomanian to Maastrichtian-aged limestones (Garcia, 1967; Barbosa et al., 2004). The Laramide Orogeny affects the entire sedimentary sequence and developed an eastward verging recumbent syncline - anticline fold styles, along a N-S axis (Campa & Coney, 1984). These recumbent folds are cut by a granodiorite intrusion with a well developed metasomatic aureole throughout the sedimentary series associated with Au-Cu skarn mineralization. The Basin is filled with Pleistocene (?) to Recent alluvial sediments (Garcia, 1967). Similar granodiorite apophyses are emplaced in the western part of this basin (San Agustin Mine; Figure 1). Cenozoic volcanic rocks are not present in La Paz district.

The Basin and Range system is delimited by a N-S deep fault structure, the Taxco-San Miguel Fault, which defines the eastern border of the Mesa Central domain (Nieto-Samaniego et al., 2005). Locally, this is known as the Dolores Fault and has a vertical displacement estimated to be between 500 and 1000m (Spurr et al., 1912). An ENE-WSW fault system appears to control the Ag-Pb-Zn-Cu vein systems, principally developed in the Basin, and less importantly in the range part. The vein system crosscuts the skarn aureole in both Range and Basin areas. The veins have developed a mineralogical zoning from (Cu-Ag-Pb-Zn-Au) in the western skarn (Range) area to (Ag-Pb-Zn-Cu) in the eastern veins area (central Basin), and (Ag-Pb-Zn) towards the eastern end of the mineralized structures (Figure 1).

2 STRUCTURAL ANALYSIS

The strike and dip of the veins, fault and skarn contacts have been systematically measured in both Basin and Range parts. In both part, all structures present vertical to sub vertical dip. In the Basin the faults are developed in two main directions NNE and ENE. The NNE faults diminish progressively away from the Range towards the centre of the Basin where ENE faults predominate.

The NNE fractures seem to be a structural accommodation between the two main structural direction, the major N-S fault and the ENE veins structures. The strike of the veins are the same as the faults in both parts of the system, ENE to NE. The skarn contacts in the Range do not show any preferred directions, but in the Basin, the skarn contacts have the same preferred directions as the ENE veins. This is interpreted to imply that the fractures controlling the Ag-Pb-Zn Cu veins were developed earlier, possibly contemporaneous to the granodiorite emplacement.

Figure 1: Geological sketch map of the La Paz district. in blue: the sedimentary formations (undefined); in red: the granodiorite intrusives; in green: the skarn aureole; in yellow: the Ag-Pb-Zn-Cu mineralized veins.
3 DESCRIPTION OF SKARN AND VEINS

Most of the granodiorite stocks and dykes show a porphyritic texture, where the phenocrysts are essentially plagioclase (oligoclase-andesine, 35-40%), K-feldspar (orthoclase-microcline, 30-25%), quartz (20-25%), and mafic minerals (biotite, hornblende, 8-10%), the phenocrysts are set in a fine grained groundmass formed of microcrystalline quartz and feldspar. The intrusives and dykes develop metasomatic aureoles in the host rock associated with propylitic retrograde alteration.

The shape of the metasomatic aureole, induced by the granodiorite intrusions is related to the nature of the host sedimentary rocks.

Endoskarn is not more than a metre thick and comprises diopside, grossularite and titanite. The exoskarns are very well developed, with a variable thickness of between 10 and 100m. They present a classic mineralogical zonation: 1) hedenbergite/andradite at the intrusive contact. 2) andradite/diopside. 3) grossular/wollastonite at the distal part. The marble and recrystallized limestone aureole is about a further 10 to 50m thick.

The principal sulphide minerals in the skarn are: pyrite, arsenopyrite, chalcopyrite, bornite, pyrrhotite, tetrahedrite, boulangerite and molybdenite. The retrograde alteration affects the metasomatic aureole and the intrusives. It is characterized by an intense stockwork structure with thin mineralized veinlets showing propylitic alteration (actinolite, tremolite, chlorite, epidote, sericite, calcite, quartz) and sulphide minerals (pyrite, native gold, electrum, galena, sphalerite, chalcopyrite). There is no evidence of potassic alteration.

Most of the gold present in the metasomatic aureole is associated with the retrograde veinlets.

The vein mineralogy shows a lateral Cu-Au zonation variation from the Range to the Basin center. In the Range and the western part of the Basin, the vein mineralogy is composed of sphalerite, argentiferous galena, tetrahedrite, pyrargyrite, chalcopyrite and native gold in a gangue of quartz, calcite and late, green to translucent fluorite. In the Basin center (San Acacio Shaft) the vein mineralogy is characterized by tetrahedrite, pyrargyrite, argentiferous galena and sphalerite in a gangue of quartz, calcite and late, deep blue fluorite.

4 MAJOR AND TRACE ELEMENTS

The La Paz granitoids have an average content of SiO$_2$ = 67.26% (Range) and 61.91% (Basin), Al$_2$O$_3$ = 15.38% (Range) and 15.99% (Basin) a K$_2$O/Na$_2$O = 1.45 (Range) and 2.65 (Basin) and Al$_2$O$_3$/(CaO+Na$_2$O+K$_2$O) molar ratio of about 1.33 (Range) and 1.26 (Basin). The Fe$_2$O$_3$+MgO+MnO+TiO$_2$ = 4.66% (Range) and 5.98% (Basin), they are respectively slightly lower in comparison with the normal values of typical calc-alkaline volcanic arcs (ca. 6%). They have moderate magnesium numbers (Mg$^#$ = 100 x MgO / (MgO + Fe$_2$O$_3$), molar) ranging from 19 to 53. Major element variation diagrams show a correlation between SiO$_2$ vs. K$_2$O and MgO. The reported values for different types of skarn (Fe, Au, Cu, Zn–Pb, W, Sn and Mo) also have been plotted (Meinert, 1995).

The tendency, in terms of major elements, for the plutonic rocks associated to different types of skarn is towards calc-alkaline composition. Most of the samples from the La Paz granitoids are concentrated in the field of Cu-rich, and Fe–Au-rich skarns, corresponding to high K calc-alkaline rocks.

La Paz REE elements have the tendency to be rich in light elements (LREE) and depleted in heavy elements (HREE). REE patterns display a steep negative slope with an inflection at Tb, and low Eu anomalies (Eu/Eu*= 0.77 (Dolores) and 0.82 (Basin) are observed.

5 INTRUSIVES U-PB DATING

Twenty-five LA-ICPMS analyses (Valencia; Arizona University) for prismatic zircons, showing regular magmatic zonation yielded $^{206}$Pb/$^{238}$U ages dispersed between 36.0 ± 0.6 Ma to 1356.9 ± 96 Ma for the Range intrusive (“Dolores Stock”). The weighted mean crystallization age for zircons from the Dolores granodiorite intrusion is calculated according to Ludwig (2003) as 36.8 ± 0.5 Ma (n=20; MSWD of 1.4). This age is concordant with the dating realized by Tuta et al. (1988) of ca. 36 Ma based on K-Ar on biotites from the Dolores intrusive. Twenty-two LA-ICPMS analyses for prismatic zircons, showing regular magmatic zonation provided $^{206}$Pb/$^{238}$U ages dispersed between 33.0 ± 3.2 Ma to 384 ± 14 Ma for granodiorite dyke from the Basin area (“San Acacio dyke”). The weighted mean crystallization age for zircons from the San Acacio granodiorite dyke calculated according to Ludwig (2003) is
35.0 ± 0.5 Ma, (n=20; MSWD of 1.5). This age distribution highlights the magmatic pulse style emplacement events from the Dolores stock 36.8 ± 0.5 Ma to the San Acacio dyke 35 ± 0.5 Ma.

6 CONCLUSIONS

The La Paz district is located across an asthenospheric structure called the Taxco-San Miguel Allende, Deep Fault which has a direct relation to the emplacement of several skarn ore deposits of different ages along a strike length of 350km from north to south: Providencia-Concepción del Oro, La Paz, La Maroma, San Juan de Guadalupe, Guadalcazar, San Pedro, La Negra. The magmatism, skarn and vein mineralization are controlled by the major N-S and secondary ENE faults. The interplay of both structural trends are recurrent. The varying intrusives and dykes represent significant chemical composition variations and U-Pb ages (ca. 1 Ma), illustrating the pulsative implacement along this zone. The first magmatic pulse (ca. 36 Ma) developed a large Au-Cu mineralized metasomatic aureole. It is possible to correlate by chemical composition and ages these magmatic events with the volcanic effusives ones mentioned by Orozco, et al. (2002; ca. 33 Ma and ca. 27 Ma).

The ENE mineralized veins which crosscut the skarn aureole and intrusives in both Basin and Range area only contain significant Au-Cu values where they crosscut the Au-Cu skarns. In addition the colour of the late fluorite shows a change from translucent in the veins hosted in skarns to deep purple when the wall rocks are marbles.

According to the regional geology it is possible to estimate the ages of the mineralized vein structures to ca. 30 Ma. This is a result of studying Sm/Nd in a fluorite sample from the veins.

The Ag-Pb-Zn-Cu La Paz vein system is similar in strike, mineralization, and age to the Ag-Pb-Zn Fresnillo vein system, therefore, they can be related to the same metallogenic event.

ACKNOWLEDGEMENTS

Our deep gratitude to José Cerrillo Chowell, General Director Negociacion Minera Santa Maria de La Paz y Anexas, S.A. de C.V. for the support received for the fulfillment of the present study, and for allowing its publication.

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
El Tule stratabound F-Sr deposit: a key to understand the origin and mobilization of basinal brines in NE México.

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ABSTRACT: The Mesozoic platform limestones that outcrop in NE México contain abundant small to medium size stratabound, almost monomineralic celestine deposits. These deposits usually display a very monotonous fluid history with no major changes both in fluid temperature and composition. El Tule deposit stands out as a rare example of a transitional deposit between the celestine lenses and mantos, well represented at the south of the Coahuila State (La Paila and Alamitos Ranges), and the fluoritic mantos that are characteristic of the upper Cretaceous sediments at the north of the Coahuila State (i.e. La Encantada-Buenavista). This deposit records a history of fluid expulsion during and after the Laramide Orogeny in NE Mexico.

KEYWORDS: celestine, fluorite, Cretaceous carbonates, MVT, NE México.

1 INTRODUCTION

In North-East Mexico, several low-temperature, epigenetic, stratabound Pb-Zn-F-Ba ore deposits outcrop forming a newly defined MVT province (Tritilla et al., 2006). These deposits appear scattered throughout the whole Mesozoic carbonate platform in the Coahuila, Chihuahua, Nuevo León and San Luis Potosí States. These deposits often present a close association with organic matter, either liquid hydrocarbons or bitumen; they display a very simple mineralogy (hypogene: barite, celestine, fluorite, sphalerite, galena) and present low formation temperatures (90-105°C) coupled with variable salinities.

Almost monomineralic celestine deposits are commonly found within the Acatita and Aurora Fm. (Albian) at the central part of the Coahuila Platform (Alamitos, Australia and La Paila Ranges); some other small and isolated celestine deposits are also found north of the San Marcos Fault and in the SE margin of the Parras Basin (Puente-Solis, 2005). Even though these deposits represent one of the biggest accumulation of celestine in the world; yet, this district received little attention from the scientific and mining world mainly due to the small and disperse character of the single ore bodies.

These celestine deposits appear as "mantos" (flats) made up by medium size, white celestine crystals that contain variable amounts of remnants of the enclosing limestone. When the celestine lenses are pure, it is usual to find pockets and cavities filled up by idiomorphic crystals of celestine up to 10cm in length, with minor quantities of native sulphur, fluorite and gypsum. Very recently Ramos-Rosique et al. (2005) and Tritilla et al. (2004, 2005, 2006)
studied some of the celestine lenses from Los Alamitos Ranges (El Venado, El Volcán, La Tinaja, La Vibora, El Diablo mines), presenting the first microthermometric data on these deposits and preliminary results on the brine halogen composition.

2 EL TULE DEPOSIT

An unusual mixed celestine-fluorite ore deposit is located at El Tule locality, north of Muzquiz (Coahuila). This deposit stands out as the northern last important celestine-bearing body, grading into zone with fluorite-dominated ore bodies (La Encantada-Buenavista district).

2.1 Geology and structure.

El Tule deposit is enclosed within the limestones of the Buda Formation (Washita Group, Upper Cretaceous). It is made up by a single stratatabound mineralized body whose disposition is controlled by sub-horizontal stratification joints with clear evidences of layer-parallel slip, acquiring a "pinch and swell" overall shape. The mineralized structure presents a very variable thickness, with local mineralized zones up to 2 m thick (Lamadrid, et al., 2006).

The deposit is celestine-dominated, with minor fluorite. An early celestine generation show evidences of deformation during crystal growth (crystals bends, undulose extinction, mechanical twinning), while the latest, dominant celestine generation grew in a deformation-free environment presenting similar open space filling textures than the celestine-bearing deposits mentioned above (rhythmites, tabular centimetric to decimetric euhedral crystals, fetidness, etc.). After celestine precipitation ceased, minor quantities of fluorite formed as a late phase partially filling the remnant cavities and vugs in a passive succession. This fluorite always appear as bluish to colorless, zoned, idiomorphic cubic crystals growing on top of the celestine crystals.

Figure 2. First generation of celestine (deformed).

Both celestine and fluorite also occur within the enclosing limestone, scattered filling up a fenestral porosity originated after the dissolution of pre-existing euhedral anhydrite crystals.

2.2 Fluid Inclusions study.

Celestine contains abundant aqueous, two-phase fluid inclusions with evidences of post-trapping changes (necking-down mainly). Homogenization temperatures are between 80 and 120°C with very variable salinities between 5 and 11 wt% NaCl eq. (Lamadrid, unpublished personal data). Raman analyses indicate no traces of other gases than water vapor. The Th vs salinity plot suggest a mixing of fluids as the main mechanism for celestine precipitation, despite the heavy dispersion of data.

Fluorite contains two fluid inclusion types. The brine-bearing fluid inclusions are bi-phase (L+V) to poly-phase (L+V+S trapped). The trapped solids are euhedral quartz crystals or high birrefringence minerals identified as calcite crystals. Raman analyses indicate the presence of variable amounts of CH₄, H₂S and CO₂ within the gas phase.

The hydrocarbon-bearing fluid inclusions are dark brown in color (heavy oils) and poly-phase (L+V+B), due to the presence of variable amounts of solid bitumen.

Homogenization temperatures and salinities for the aqueous fluid inclusions are between...
120 and 150 °C and salinities between 11.7 and 16 wt% eq. of NaCl respectively (Lamadrid, unpublished personal data), showing much less dispersion than the celestine inclusions. In a Th vs salinity plot, the data disposition suggest that fluorite precipitated mainly by cooling after mixing of two, contrasted fluids.

Petrographic analysis give clear evidences of coeval trapping of hydrocarbon-bearing and brine-bearing fluid inclusions within the same growth zone. FTIR analyses and CLSM volumetric reconstructions of the hydrocarbon-bearing fluids indicate the presence of heavy oils.

Figure 3. Coeval hydrocarbon-bearing (HC) and aqueous-bearing (AQ) fluid inclusions in fluorite.

Raman analyses of the gas phase of the brine-bearing fluid inclusions in fluorite indicate the presence of variable amounts of CH₄, H₂S and CO₂. All these data allow the PVT modelling of the fluorite precipitation conditions using the PIT software (Thiery et al, 2000).

2.3 Discussion.

The mineralogical change from celestine to fluorite precipitation probably reflects a change on the fluid regime and composition from a compressive regime (Laramide orogeny) to the subsequent post-laramide distension.

Celestine precipitated within opened sedimentary joint during and after the Laramide deformation, partially substituting the enclosing limestone, filling up the fenestral porosity after anhydrite dissolution. Then, the most plausible origin for the sulphate is the dissolution of the pre-existing evaporites as suggested for other deposits in the region (Tritlla et al., 2006).

Fluorite precipitated after a dramatic change of the fluid composition, probably precluding the ongoing of celestine formation, during the mixing of the remaining brine after celestine precipitation, likely enriched in residual Ca²⁺, with an external emulsion of brine and hydrocarbons, resulting in a partial degradation of the organic matter by means of TSR reactions and the generation of CH₄, H₂S and CO₂ found in the gas phase of the brine-bearing fluid inclusions.

The in situ origin for the small amounts of hydrocarbons found is unlikely, as the local -rock- source of organic matter was almost certainly depleted by the excess of sulphate during celestine formation.

3 CONCLUSIONS.

El Tule deposit represents a rare example of a transitional deposit between the celestine lenses and mantos, well represented at the south of the Coahuila State (La Paila and Alamitos Ranges), and the fluoritic mantos that are characteristic of the upper Cretaceous sediments at the north of the Coahuila State (i.e. La Encantada-Buenavista). This deposit contains the most complete history of fluid expulsion during the Laramide and post-laramide tectonic phases, reflecting a change in both fluid regime and chemistry.

4 ACKNOWLEDGEMENTS

We would like to acknowledge Fluorita de México S.A. de C.V. and specially Ingenieros Agustín Rodriguez and Samuel Baca for the permission, help and geological discussions on visiting El Tule district.

This work has been financed by the UNAM PAPIIT projects IN114002, IN114106-3 and IN100707-3, and CONACyT project 49234-F.

REFERENCES


Presence of two Phanerozoic IOCG belts in México: geological framework and general characteristics.

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ABSTRACT: In Mexico, very recently some iron-rich ore bodies were re-classified as belonging to the IOCG type deposits. Their disposition is roughly parallel to the Pacific Coast, but mimic the disposition of Chilean deposits into two distinctive Belts: (1) an older, Mesozoic belt located near the Pacific border, constituted by magnetite-rich bodies with Cu-Au accumulation; (2) a Tertiary belt, located inland Mexico, grossly parallel to the Mesozoic belt, made up by magnetite-haematite or haematite-rich deposits, with many similarities with the Kiruna (Sweden) or El Laco (Chile) types.

KEYWORDS: IOCG deposits, Mesozoic belt, Tertiary Belt, Fe deposits, Cu-Au deposits, Mexico.

1 INTRODUCTION

Iron oxide–copper–gold deposits (IOCG) have been recently recognized as a new type of mineral deposits with high economic interest (Hitzman, 2000). These deposits are mainly composed by magnetite and/or haematite, with variable amounts of Au, Cu, REE, U, Co, Ni, As, Mo, W and Te. Yet, this typology is still controversial, as the geological settings and the source of metals and fluids is not still well constrained due mainly to their occurrence in highly deformed Proterozoic belts or in smaller deposits of Phanerozoic age where geological controls are usually difficult to ascertain.

Usually, this type of deposits are thought to be related with large scale faults and develop intense Na–Ca (albite–actinolite) or potassic (K-feldspar or biotite) alteration zones. IOCG deposits are usually located in continental or cratonic margins during the Proterozoic whereas the Phanerozoic deposits appear primarily related with continental arc ambients as well as extensional environments along subduction-related margins (Hitzman, 2000).

Although iron deposits with problematic affiliation are known in Mexico for quite a long time (Van Allen, 1978; Lyons, 1988; Corona-Equivel, 2000), the presence of IOCG deposits in Mexico was only very recently formally recognized by Tritlla et al. (2003).

2 IOCG DEPOSITS IN NORTH AMERICA.

In North America (US and Mexico), iron-oxide rich deposits are widespread and located mainly in a belt parallel to the Pacific border of the continent. These deposits share an association with saline fluids, voluminous alkaline (Na and/or K-rich) alterations, low sulphur contents and variable enrichments in REE, Cu, Au, Ag, Co and U (Barton et al., 2000).

3 IOCG DEPOSITS IN MÉXICO.

In Mexico, this disposition is reproduced but, as in the Chilean deposits, two distinctive sub-belts can be recognized: (1) an older, Mesozoic belt located near the Pacific border, constituted by magnetite-rich bodies usually with several mineralized bodies within a discrete zone (Tritlla et al., 2003); (2) a Tertiary belt, located inland Mexico, grossly parallel to the Mesozoic belt, made up by magnetite-haematite or haematite-rich deposits of tertiary age, with many similarities with the Kiruna (Sweden) or El Laco (Chile) types (Corona-Equivel, 2000).
Traditionally, magnetite-dominated Mesozoic deposits have been classified mainly as skarns (Peña Colorada, El Encino, El Encino, Aquila, Las Truchas). However, our revision indicates that truly skarns (Cerro Nahuatl) coexist with well characterized IOCG's (Peña Colorada, Tritlla et al., 2003) in similar geological scenarios. This coexistence has been already recognized in other IOCG provinces worldwide (i.e., Ossa Morena Zone, Spain; Tornos & Casquet, 2005).

Tertiary deposits (La Perla, Chihuaha; Cerro de Mercado, Durango), on the contrary, were proposed to form after the upflow of iron rich magmas (Van Allen, 1978; Lyons, 1988), based mainly on textural evidences and field relationships. This origin has been recently claimed after their comparison with El Laco deposit (Corona-Esquível et al., 2007a and 2007b).

3.1 Pacific Coast (Mesozoic) belt.

This IOCG belt is defined by deposits located, from South to North, within the Guerrero, Michoacán (Aquila, Las Truchas), Jalisco (El Encino, Chanquehahuil) and Colima (Peña Colorada, Las Pesadas) States (Corona-Esquível, 2000; 2007b; Tritlla et al., 2003) as well as in the Baja California Peninsula (Alisitos Belt, López et al., 2006). These deposits are mainly composed by magnetite, with minor quantities of sulphides (chalcopyrite, pyrite, pyrrhotite) and fluorapatite. They have been mined exclusively for iron ore, where no real exploration has been performed to look for other substances.

3.1.1 Peña Colorada (Colima).

The iron ore bodies are hosted by the middle Cretaceous Tepalcatepec formation, that is represented in the mine by a sequence of sedimentary units (lower clays and marls unit; limestone unit) with an overlying volcanioclastic unit, both of Albian age, and an upper conglomerate formation of Cenomanian age (Corona-Esquível, 2000). The lower clay and marl unit is locally intruded in the mine area by a granodiorite and by an aplite dike complex.

The Peña Colorada iron deposit is made up by three different mineralized bodies: (1) an upper massive magnetite body, up to 20 meters thick, sub-concordant with the regional stratification, that contains decimetric to metric fragments of an older garnet-bearing rock (grossular-andradite) completely replaced by plumeose K-feldspar; (2) a lower disseminated magnetite body, also sub-concordant with the regional stratification, with a maximum thickness of 150 meters and made up by pyrite-magnetite-pyroxene rhythmic alternations with poiquilitic K-feldspar crystals, forming a sub-concordant mass resembling an episyenite sensu lato, that has been mistaken with an endoskarn by Zurcher et al. (2001); and (3) a mineralized polymictic breccia, with evidences of hydraulic fracturing, with an overall diatreme morphology, cutting the whole sequence and the other ore bodies at Peña Colorada (Tritlla et al., 2003). The diatreme includes xenoliths of a rock made up by the intergrowth of centimetric, squelctic to euhedral magnetite, pyroxene andapatite crystals, floating in a groundmass of minute magnetite crystals.

The disposition of the different mineralized bodies, their textural characteristics and the difference in ages among them suggest that the Peña Colorada iron deposit formed due to recurrent mineralizing events in a discrete cortical volume and within a relatively wide time lapse (>4 Ma; Tritlla et al., 2003).

3.1.2 Alisitos Belt (Baja California Norte).

The Alisitos Belt represents the prolongation of the Mexican Pacific Coast IOCG Belt into the Baja California Peninsula, that broke up and separated during the Miocene.

Among the other deposits in mainland Mexico, the Alisitos Lower Cretaceous Arc in Baja California Norte stands out due to the presence of comparable magnetite-bearing IOCG deposits with economic concentrations of Cu and Au, now under exploration by Cardero Resource Corporation.

Ore deposits appear enclosed within the Alisitos Group, of Aptian-Albian Age, composed by a sequence of volcanioclastic andesitic to dacitic flows and a intermediate to mafic volcanioclastics and tuffs (López et al., 2006). This sequence is intruded by a granodioritic pluton and a swarm of felsic dikes. This geological scenario is comparable with the local geology found to enclose mainland IOCG deposits.

Alteration around the ore bodies is widespread. This consists in a sequence of sodic (albite) to calcic-sodic (scapolite, actinolite, magnetite, albite), potassic (K-feldspar, biotite), tourmalinization (quartz, tourmaline), albitionization (albite, calcite). Cu mineralization appears related with both potassic and tourmaline alterations (chalcopyrite), with formation of bornite-chalcocite rims around chalcopyrite during
the last alteration phase (albite-calcite).

3.2 Meseta (Tertiary) Belt.

This IOCG belt is defined by deposits located in the Mexican Central Meseta, at the states of Durango (Cerro de Mercado; Lyons, 1988; Corona-Esquivel et al., 2007a), Coahuila (Hércules; Corona-Esquivel, 2000) and Chihuahua (La Perla; Van Allen, 1978; Corona-Esquivel et al., 2007c). These ore deposits are located at the contact between the Sierra Madre Occidental volcanic province, one of the world's largest accumulations of felsic volcanic rocks at W, and the Laramide thrust and fold belt, at E, constituted by Mesozoic sedimentary materials.

These deposits are mainly composed by magnetite, martite and haematite (Cerro de Mercado) or dominant haematite (Hércules, La Perla), with minor quantities of fluorapatite, and both the presence of abundant haematite, their textures coupled with episodes of argillic alteration suggest that they formed in more surficial conditions than their older (Mesozoic) counterparts. They have been also mined exclusively for iron ore, where no real exploration has been performed to look for other substances.

As Cerro de Mercado is the more studied and representative deposit of this kind, we are going to base this discussion mainly on this location, although this is extensible to La Perla and Hércules ore deposits.

3.2.1 Cerro de Mercado (Durango).

Cerro de Mercado ore deposit is located in the City of Durango (Durango State, Mexico). Lyons (1998) and Labarthe et al. (1990) indicate that this deposit is located within the Chupaderos Caldera, a large rhyolitic volcanic center of Oligocene age (30.8-30.1 Ma, Swanson et al., 1978). The caldera consists of a series of units, beginning ash-flow tuffs (Aguila Formation) that filled the caldera. The last volcanic Cacaria Formation (rhyolitic domes, intrusions, and airfall tuffs) host the iron-rich bodies of Cerro de Mercado (Lyons, 1988).

The iron masses appear as massive lenses and breccias within the upper Members of the Cacaria Formation (Lyons 1988). At the present time, the mine workings allow to see that the emplacement of the deposit is controlled by the intersection of two faults of N-S and NE-SW directions that also host part of the breccia ore bodies. The massive bodies were conformable with the surrounding rhyolitic rocks, even though in some places they clearly cut and are cut by silicate-altered rocks. Elsewhere within the Chupaderos caldera, other iron oxide deposits occur within the same general stratigraphic interval and have been correlated by Lyons (1988) as part of the "Mercado Iron Member" of the Cacaria Formation. Megaw & Barton (1999), based upon Lyons (in op cit) comments and their own field observations, that some of the other occurrences represent distinct centers of iron oxide mineralization and thus may not be strictly correlated with the deposit at Cerro de Mercado. The different ore bodies present a fairly simple mineralogy, made up by magnetite, haematite, martite after magnetite, pyroxene and apatite with minor quartz and clays, and is surrounded by an aureole of argillic alteration (Megaw & Barton, 1999).

Two different origins have been proposed for this deposit. Lyons (1988) and Corona-Esquivel (2007a), among others, suggest an iron oxide-rich igneous melt that separated from a parental "oxide magma" in close relationship with the extrusion of silicic magmas, in a similar way as in El Laco deposit (Naslund et al., 2002). Others Labarthe-Hernandez et al., 1987; Barton & Johnson 1996), suggested a combination of the replacement of older volcanic rocks by massive oxide bodies where hydrothermal fluids vented onto the surface.

4 DISCUSSION AND CONCLUSIONS

All these deposits clearly present characteristics that can be found in other IOCG type deposits worldwide. It is noticeable that, as in Chilean deposits, two different IOCG belts can also be distinguished in Mexico not only separated by their age and relative position, but also by their characteristics.

The deposits located within the Pacific Belt present characteristics of a deeper system with clear metasomatic bodies, no extrusive textures and, in Peña Colorada, episodes of reworking due to the formation of late explosive dikes. These deposits just started very recently to be considered as possible targets for Cu-Au resources. The ages found by Tritlla et al. (2003) suggest some sort or relationship with scarce mafic intrusive bodies of the same age.

The deposits that form the Meseta Belt represent a more “surficial”, distal and younger equivalents of the Pacific Belt. Indeed, these Tertiary deposits present characteristics that
suggest their formation in or near the surface, in close relationship with the latest magmatic pulses of the Sierra Madre Occidental Volcanic Province. No other commodities but iron have been found so far related with this ore deposits. This can be due to their “surficial” character, perhaps representing the apical part of an evolving IOCG system, where other metals than iron could be found accumulated in deeper parts of the feeder structures.

ACKNOWLEDGEMENTS

We would like to acknowledge Consorcio Minero Benito Juárez–Peña Colorada S.A. de C.V. and Grupo Acerero del Norte (GAN) and specially Ingenieros Roberto Villalobos Zavala José de la Luz Portugal, Juana Meza, Manuel López, Jesús Manuel Bueno-Rocha and Oswaldo Delgado for the permission, help and the geological discussions.

This work has been financed by the UNAM PAPIIT projects IN-123202-2 and IN115706-3.

REFERENCES


Iron oxide-copper-gold deposits in Turkish Tethyan collage

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ABSTRACT: Iron oxide-copper-gold (IOCG) deposits define a group of diverse, epigenetic Cu-Au deposits to which several economically important deposits belong, and these are very limited in Tethyan-Eurasian metallogenic belt. As a part of this belt, Turkey is a host to several IOCG deposits formed in post-collisional settings related to subduction of NeoTethyan ocean beneath the Eurasian plate. The present work evaluates the IOCG potential of Turkey by studying three iron oxide-rich deposits from two different regions: (1) central Anatolian post-collisional setting and (2) western Anatolian extensional province. The study covers alteration, mineralogy, geochemistry, fluid inclusion characteristics, and geochronology of these deposits. The geological features of the deposits in Hasancelebi, Divrigi and Samli regions are comparable to the IOCG deposits elsewhere. The investigations in Turkey revealed that some of the iron-oxide mineralizations occur in metasomatized magmatic rocks that underwent a pervasive alkaline metasomatism. Early-distal alteration is typically characterized by extensive sodic ± calcic mineral assemblages, chiefly scapolite ±albite-garnet-diopside-actinolite. The potassic alteration products are K-feldspar and phlogopite/biotite or sericite, and the calcic alteration assemblages are dominated by diopside-hedenbergite, and garnet. The magnetite mineralization is commonly associated with potassic zones, while the copper-gold mineralization is associated with late stage sericitic alterations and carbonated rocks mainly along structural discontinuities. The host rocks and alterations are confined to crustal scale regional strike-slip and normal faults. The deposits were formed in post-collisional, late orogenic extensional settings related to subduction of Southern NeoTethyan ocean beneath Eurasian plate during late Cretaceous to Miocene period.

KEYWORDS: sodic-calcic alteration, IOCG deposits, magnetite, gold-copper, Hasancelebi, Divrigi, Samli, post-collision, Turkey

1 INTRODUCTION

Iron oxide-copper-gold (IOCG) deposits, as the name implies, are grouped together chiefly because they contain hydrothermal magnetite and/or specular hematite as major constituents to chalcopyrite±bornite. Nevertheless, there appear to be features that are characteristic for all deposits, although none of them alone is diagnostic by itself. IOCG include world class deposits very large in size (e.g. Olympic Dam, about 3,000Mt) and their origins controversial, hence their discovery has captured the attention of exploration companies and academics, and the number of deposits classified into the IOCG category has drastically increased as is the understanding of the genesis of this enigmatic deposit class during the past 15 years.

The present state of knowledge regarding the IOCG deposits in Turkey is related only to recent studies by Kuscu et al. (2002; 2005) and Yilmazer et al. (2003). Kuscu et al. (2005) compared and correlated the regional sodic-calcic alteration styles of iron-oxide deposits in Central and western Anatolia with well-known IOCG deposits elsewhere, and suggested that these deposits should be investigated in terms of IOCG potential, particularly for copper and gold(?). This paper reviews the geological and metallogenic settings of the IOCG deposits in the western Anatolian extensional province (Samli deposit) and central Anatolian post-collisional setting (Hasancelebi and Divrigi deposits) of Turkey (Figure 1) and then the styles and salient features of the IOCG deposits themselves, with particular emphasis on their altera-
tion styles, temporal and spatial relationships between mineralization and alteration. The ultimate goal is to promote mineral exploration by providing information on host rocks and genetic models of IOCG.

2 GEOLOGICAL SETTING

2.1 General features

In the western and central Anatolia major Mesozoic-Tertiary magmatic complexes are emplaced into broadly sequential arc to post-collisional volcano-plutonic products and underlying deformed metasedimentary, ophiolitic and sedimentary units of Palaeozoic-Mesozoic age. Extensive E-W to NE-SW oriented brittle fault systems including NE-SW trending Malatya-ovacik (MOFZ), Goksu-Sariz (GSFZ) and Kangal-Cetinkaya and Central Anatolian fault zone (CAFZ) fault zones in central Anatolia, and/or ductile/brittle shear zones and deeply penetrating detachment faults trending in E-W to NE-SW in western Anatolia appear to control the spatial association of sodic alteration zones and emplacement/exposure of the causative magmatic rocks. Latest Cretaceous (75-71 Ma) magmatism throughout the easternmost central Anatolia and immediately adjoining regions are generally considered to have taken place under variably extensional conditions in response to retreating subduction boundaries (slab roll-back) along Bitlis-Zagros subduction zone (Kuscu et al., 2007). Oligocene-Miocene magmatism (23-22.3 to 16 Ma; Watanabe et al., 2003; Isik et al., 2004; Ring and Collins, 2005, Innocenti et al., 2005) in the western Anatolia, however, is generally accepted to have been formed during orogenic collapse to slab pull (Innocenti et al., 2005) along the Helenic subduction system.

2.2 Structural controls

The IOCG deposits and associated host rocks are located and/or confined to structural elements along CAFZ, GSFZ and CAFZ in central Anatolia. These follow a oblique NE-SW trend from southeastern coast of Turkey to Erzincan-Sivas where it is made up of a series NE-, and NNE-striking brittle faults which underwent variable sinistral strike-slip motion. NE-SW directed normal to strike slip faults transient ductile to brittle deformation charted by foliation planes of the metamorphosed magmatic and sedimentary rocks in western Anatolia, are the main structural elements that control alteration and emplacement of magmatic rocks. Generalized spatial and temporal distributions of magmatic rocks and IOCG deposits in Turkey shows a systematic southward migration of arc and associated mineralizations, from the latest Cretaceous to Palaeocene in central, and Oligocene to Middle Miocene in western Anatolia. The brittle faults tend to be localized by orogen-parallel extension (central) zones or slab-pull tectonics (western) of Anatolia due to N-S compression caused by collision of Eurasia with Afro-Arabian plates.

2.3 Alteration and mineralization styles-age of alteration-mineralization

The deposits have a distinct sodic-calcic alteration overprinted later by potassic alteration. The wall and host rocks are intensely altered and display a deposit-scale zonation at Divrigi and Samli, and region-scale zonation at Hasancelebi, and the structural control is the most prominent in Hasancelebi and Divrigi. The outer distal alteration zone is characterized by scapolite-diopside-garnet-actinolite in Hasancelebi; scapolite-garnet-diopside in Divrigi; and albite-garnet-pyroxene in Samli deposits. The inner distal alteration zone is characterized by phlogopite-K-feldspar-biotite-sericite in Divrigi and Hasancelebi; garnet-pyroxene-epidote in Samli, while the proximal alteration zone by sericite-K-feldspar-magnetite, calcite, sulphides in Divrigi and Hasancelebi; and epidote-hematite-magnetite and sulphides in Samli deposits. The alteration products and style of mineralization are well comparable to IOCG deposits elsewhere; hence the deposits long known as pyrometasomatic and skarn are of IOCG type. The mineralizations occur as massive magnetite bodies hosted within a K-feldspar and biotite-epidote and/or phlogopite-rich zone superimposing scapolite-garnet or albite-garnet zones. Martitized magnetite, limonitization, silicification, and sulphide mineralizations occur as distal to the main magnetite bodies, and are regarded as late-stage alteration products.

The deposits contain distinct element associations of Fe-Cu-Au ± Ag, Bi, Ba, Co, Th, U, LREE. The concentration of copper and gold is as high as 5.7-8.8 ppm, and Cu as high as 5% (ore grade samples) in Samli; <1 ppm Au, as high as %1.5-2 % Cu in Divrigi, 0.7 (maximum) ppm Au, about 1% in Hasancelebi deposit. Among these, the Samli deposit contains Cu and Au in grades typical for IOCG deposits and thus they best fit to the IOCG category. Al-
though at least Cu was mobile during the mineralization and alteration events related to magnetite deposits in the Hasancelebi and Divrugi deposits, only anomalous values of Cu and Au have been detected. However, the alteration style, fluid inclusion composition and the proposed genetic model of the magnetite deposits at Hasancelebi are consistent with what has been described with IOCG deposits. Therefore, the magnetite deposits in the Hasancelebi and Divrugi region are considered to be representatives of iron oxide-rich type of IOCG deposits.

Fluid inclusion data from Hasancelebi deposit suggest that fluids that circulated in the rocks during the main mineralization event and the subsequent brittle stage(s) were complex medium to low-salinity (25-10 wt.% NaCl eq.) fluids. The temperature during the mineralization event was between 320° and 700°C which is consistent with the high-temperature mineral assemblages.

The age limits for the alteration and ore formation are 73.5-73.40 Ma in Divrugi, 70.4-69 Ma in Hasancelebi, and 23-22.3 Ma in Samli deposit. The data presented is inconsistent with the previous models which suggested that the deposits either are epigenetic iron formations or skarn deposits formed under contact-metasomatic conditions. Instead, the alternative model presented here is that the iron oxide deposits with elevated Cu and Au contents and regional-pervasive sodic-calcic alteration are epigenetic deposits structurally controlled by the crustal scale faults and shear zones. The present data suggest that the deposits best fit into the category of the iron oxide-copper-gold deposits.

2.4 Metallogeny and metallogenic setting of IOCG deposits in Turkey

Based on the age data on the studied deposits and regional compilation, favorable time periods for IOCG mineralization in central Anatolia is 74-69 Ma, and in western Anatolia is 22.3-16 Ma. These periods represent the crustal-scale extension due to post-collisional roll-back of the subducting slab beneath Malatya-Keban platform within Bitlis-Zagros subduction system. The most prospective locations for IOCG deposits in Turkey are post-collisional, late-orogenic settings where latest Cretaceous-Palaeocene (central Anatolia) to Oligocene (western Anatolia) lacustrine to deep marine sedimentary sequences are intruded by alkaline to calc-alkaline magmas formed by orogenic collapse and/or slab roll back in an evolving orogen. The orogenic collapse and consequent detachment driven magmatism is likely mechanism producing the IOCG related magmatism in western Anatolia while late-orogenic events such as roll back appears to be driving mechanism and resultant continental to marine basin evolution and alkaline to calc-alkaline magmatism. The western Anatolian IOCG deposits are related to Hellenic subduction system whereas the central Anatolian IOCG deposits are related to Bitlis-Zagros subduction systems.

3 CONCLUSIONS

The pervasive alkaline metasomatism and relationships between mineralizing events and alkaline metasomatism, the oxide and sulphide mineralogy in and around the Divrugi (Sivas), Hasancelebi (Malatya) and Samli (Balikesir) are inconsistent with the models which suggested that these deposits either are epigenetic iron formations or skarn deposits formed under contact-metasomatic conditions. Instead, the alternative model presented here is that the iron oxide deposits with elevated Cu and Au contents and regional-pervasive sodic-calcic alteration are epigenetic deposits structurally controlled by the crustal scale faults and shear zones. The present data suggest that the deposits best fit into the category of the iron oxide-copper-gold deposits.

ACKNOWLEDGEMENTS

This work is a part of an on-going research project carried out by the authors. The work is generously granted by TUBITAK (YDABCAG 103Y023).

REFERENCES


Mining and current problems of Turkish Iron Deposits, 181-206 (in Turkish with English abstract)


Figure 1. Simplified geological map of western (1) and central-eastern (2) Anatolia with individual deposits of (a) Samli, (b) Hasancelebi-Karakuz and (c) Divrigi deposits.
Complex structural and hydrothermal evolution of the Cala magnetite deposit, SW Iberia – an ICOG deposit?

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ABSTRACT: The Cala deposit is traditionally regarded as a classic calcic iron skarn, formed at the contact between Cambrian limestone and a Variscan monzogranitic stock. Ongoing studies show that the deposit is more complex and the mineralization consists of several stratabound, structurally controlled, lenses replacing calc-silicate and pelitic hornfels and marbles. Although skarn is part of the hydrothermal assemblage, most of the ore appears to be related to a quartz-ankerite-biotite-chlorite assemblage, sharing many features with shallow IOCG deposits. The mineralization formed in a multiply-reactivated pull-apart structure. Re-Os dating shows that most of the magnetite-sulphide ore predated by some 20 Ma the intrusion of the adjacent monzogranite.

KEYWORDS: Ossa Morena Zone, Cala, replacement, magnetite, IOCG, skarn.

1 INTRODUCTION

The Cala deposit is located in SW Iberia (Huelva province). It was one of the most important iron producers in Spain during the 20th century. Nowadays, the mine extracts a small tonnage of high quality magnetite but most of the production consists of granite and skarn for aggregate. Estimated reserves are more than 60Mt @ 39% Fe and 0.27% Cu but the deposit is open at depth. Currently, there is growing interest in the Cala deposit and systematic exploration is taking place.

Previously, this deposit was considered to be a classic calcic iron skarn directly associated with intrusion of an adjacent intermediate stock (Casquet & Velasco 1978, Velasco & Amigó 1981, Casquet & Tornos 1991). However, recent work suggests that the situation is more complex and the intrusion-related skarn is only a part of a larger IOCG-style mineralization.

2 GEOLOGIC SETTING

The Ossa Morena Zone (OMZ) is an accretionary terrane against the autochthonous Iberian Massif. Both are characterized by a complex geodynamic history (Eguíluz et al 2000). The presence of two orogenic cycles, Cadomian and Variscan, has superimposed several magmatic and tectonic events (Quesada 1990; Eguíluz et al 2000).

The Cala mine is located in the southernmost Olivenza-Monesterio belt (Fig. 1), a NW-SE trending kilometre-scale antiformal structure. Exposed in the core are Proterozoic schist, dark slate and quartzite (Serie Negra). Both limbs host a complex sequence of late Neoproterozoic-Cambrian synorogenic and rift-related rocks, including felsic and mafic volcanites, shale, sandstone, calc-silicate rocks and limestone. The region is host to widespread calc-alkaline Variscan magmatism. This includes several composite kilometre-size plutons made up of granodiorite, monzogranite and tonalite, with variably accompanying gabbro, diorite and granite.

Most iron deposits in the OMZ occur in the late Neoproterozoic-Cambrian sequence. Some deposits are interbedded with volcanic rocks and show exhalative features. Other deposits are clearly younger (presumably Variscan), replacing the same sequence. The exact relationship between both exhalative and replacements styles of mineralization is poorly understood.
with banded to massive diopside-hedenbergite (Hd$_{50}$ Di$_{48}$ Jo$_2$) and grandite (Ad$_{50}$ Gr$_{39}$ Sps-Al$_{11}$) is exposed. Subsequent replacement by minor late andradite and actinolite, quartz, epidote, calcite, pyrite and magnetite is followed by vugh-filling quartz, epidote, calcite and magnetite. The retrograde component of the skarn is volumetrically small and includes massive ferroactinolite and magnetite.

Stage II thrusting produced only potassic alteration and greisenization in the monzogranite.

4 MINERALIZATION

Iron oxide ore at Cala is primarily magnetite with far subordinate to rare hematite. The earliest magnetite occurs as structurally-controlled massive replacement bodies related to Stage I (Fig. 2). The later magnetite associated with the retrograde skarn is always massive. While the early magnetite records evidence of deformation, the late skarn-associated magnetite is post-tectonic.

Cu-Au mineralization occurs within massive pyrite-chalcopyrite replacements, usually controlled by extensional, tension-gash structures (Fig. 2). The Cu-Au mineral assemblage includes some other sulphides such as pyrrhotite, nickelite, skutterudite, arsenopyrite, molybdenite and native gold. The proportion of sulphides is much more abundant in Stage I magnetite ores; however, Cu and Au grades are also high in the eastern part of the mine, where the retrograde skarn dominates.

5 GEOCHRONOLOGY

Because the field relationship between massive magnetite and the Cala stock could not be unequivocally determined in the field, a Re-Os study of Stage I mineralization was undertaken. Re-Os dating of magnetite and pyrite in the Stage I assemblage yields a well-constrained age of 373.5 ± 3.2 Ma (Stein et al. 2006). The initial $^{187}$Os/$^{188}$Os ratio is 0.592 ± 0.043, indicating that metals are of crustal derivation. These data together with the recent U-Pb age for the Cala stock (352 ± 4 Ma, Romeo et al. 2006) constrain previously ambiguous Stage I field relations destroyed by Stage II thrusting. Further field work affirms that the Cala stock is undeformed and hosts enclaves of banded magnetite. In addition, there is no associated endoskarn and, where visible, the Cala stock transects prograde skarn zonation suggesting that the monzogranite postdated even the prograde skarn.

Given the Re-Os and U-Pb geochronologic data, the tectonic-hydrothermal evolution of the Cala area is complex and spans at least 20 Ma (Fig. 3). Hypothetically, the skarn could be related to an unexposed intrusion located below the eastern part of the deposit, where the skarn dominates and where the Cu and Au grades are higher. In fact, in this eastern area we report some small outcrops of diorite-like intrusions affected by pervasive endoskarn that could correspond to shallow expressions of a deeper intrusion.

6 STABLE ISOTOPE GEOCHEMISTRY

Sulphur isotope data for pyrite ($\delta^{34}$S, 14.3-16.5‰) shows that most of the sulphur in the sulphides is of crustal derivation, probably derived from underlying shales and homogenized during hydrothermal transport.
Preliminary oxygen isotopic data show that fluids involved in both Stage I and skarn assemblages are of deep derivation. Calculated δ\(^{18}\)O values range from 9.9 to 11.1‰. If fluids forming the skarn and the Stage I magnetite were isotopically similar, then this magnetite precipitated at temperatures higher than those of the skarn, probably in the 500-600ºC range. δ\(^{18}\)O values of clinoamphibole and magnetite of the retrograde skarn record the influx of modified surficial fluids (δ\(^{18}\)O\(_{fl}\), 5.1-5.6‰; δD, -17 to -13‰). These results confirm different stable isotope histories for the two ore types.

Fluid inclusion data suggest that fluid circulation at the Cala deposit was complex and may have involved several events with CO\(_2\)-rich fluids and brines.

7 IOCG MINERALIZATION?

On the whole, the Cala deposit shares many features with epizonal IOCG deposits (Tornos and Casquet 2005). Stage I magnetite (Cu-Au) mineralization occurs as massive replacement of calcic-rich rocks. The mineral assemblage of Stage I is consistent with a K-Ca-Fe alteration event that overprinted an earlier (minor?) Na-rich alteration. Cala mineralization exhibits major structural control and hydrothermal fluids were most likely hot CO\(_2\)-bearing brines of deep origin. Compared to other iron oxide deposits of the OMZ, Cala has less pronounced Na alteration and no associated magmatic albite, but exhibits higher Cu and Au grades. We suggest that Cala represents the shallow levels of a vertically extensive hydrothermal system. Other nearby Fe oxide deposits such as Monchi, Colmenar and La Berrona may represent deeper equivalents.

8 CONCLUSIONS

The iron oxide (Cu-Au) mineralization of the Cala mine shows a complex polyphase tectonic, magmatic and hydrothermal evolution, probably reflecting several tectonic and magmatic pulses. The Cala ore is concentrated in a small pull-apart structure. In the OMZ, small extensional structures in an overall transpressional orogen efficiently focussed fluids and magmatism in the crust (Tornos et al 2005). Although some of the ore is related to classic skarn processes, most of it seems to predate the skarn and magmatism. This earlier mineralization, associated with shear deformation, probably corresponds to the shallow portion of a hydrothermal system that shares many features with IOCG-style mineralization.

ACKNOWLEDGEMENTS

Support for this study comes from the IGME (Instituto Geológico y Minero de España) and the Spanish DGI-FEDER project 2003-0290. We acknowledge help from JL Canto (PRESUR), LR Pevida, A Terrón, C Maldonado (RNGM) and C Conde (IGME). The Re-Os analytical work was carried out under the AIRIE Program (Colorado State University) through the generous support of Edward M. Warner. Richard Markey performed the Re-Os analyses.

REFERENCES


In more detail, the Cala deposit is located in the southern limb of the Olivenza-Monesterio antiform, close to the major strike-slip faults that separate the OMZ from the South Portuguese Zone. The deposit itself is located within a major structural boundary and is directly adjacent to a small ellipsoidal monzogranitic stock. The stock was intruded at about 3km depth and produced an aureole of contact metamorphism (Velasco et al 1981). Recent U-Pb zircon dating yields an age of 352 ± 4 Ma for the Cala stock (Romeo et al 2006).

Detailed mapping has shown that both the orebody and the plutonic rocks were emplaced in a pull-apart structure formed during sinistral Variscan transpression. In detail, there are two major tectonic events:

Stage I – early sinistral brittle-ductile deformation was channeled along several 10 m-thick subvertical shear zones subparallel to the sedimentary layering; related to this event are abundant microgabbro dikes suggesting that these structures are deep regional ones.

Stage II – later N-S compression produced a system of low angle imbricated thrusts with a significant dextral component; these thrusts are mostly located along monzogranite contacts, obscuring the field relationship between igneous and metamorphic rocks.

3 HYDROTHERMAL ALTERATION

The area shows widespread hydrothermal alteration. Stage I has produced a pervasive alteration of limestone and calc-silicate and metapelitic rocks to a banded assemblage of quartz, ankerite, green biotite, phengite, ferroactinolite and chlorite along with massive magnetite. Locally, these rocks replace previous albitic and dolomitic alteration.

Most of the skarn postdates Stage I but predates Stage II; however, the presence of some skarnified boudins within the shear zone suggests that some skarn could be late Stage I. The more prominent skarn is mostly calcic, dominated by garnet, and occurs in the southeastern part of the mine. Here, a prograde event
Searching for In-carrier minerals in polymetallic sulphide deposits: digging deeper into the crystal chemistry of indium chalcogenides

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ABSTRACT: A review is presented on the crystal chemistry of indium chalcogenides as a contribution to enhance the smart search for the metal and improve its exploitation from massive polymetallic sulphides. Data on trace element concentrations concerning Neves-Corvo and Aljustrel ores from the Iberian Pyrite Belt (IPB) are commented. Suggestions are put forward to improve the search for indium in plausible carrier minerals.

KEYWORDS: Indium; crystal-chemistry; carrier minerals; Iberian Pyrite Belt.

1 INTRODUCTION

Discovered quite accidentally in 1863 and isolated four years later as a metallic element, indium has been widely used since the middle of past century in various technologic fields, namely, in low melting-temperature alloys, solders and electronics.

In the last decades, it became one of the most relevant scarce metals used in the production of new “high-tech devices” based on innovative nanotechnologies. Suggestive examples of indium incorporation - along with other rare metals like gallium and tin - are nowadays liquid crystal displays, LCDs, and organic light emitting diodes, OLEDs, as well as the recently introduced transparent flexible thin-films (e.g., Fortunato et al., 2005) manufactured with ionic amorphous oxide semiconductors (IAOSs) from the systems In-Sn-O (ITO, Koh et al., 2006) and In-Ga-Zn-O (Nomura et al., 2004; Hosono, 2006).

Consumption of indium is therefore expected to increase in the next years, keeping the trend registered in the nineties. Improvements in primary recovery and recycling technologies are then most advantageous. Simultaneously, enhancing the search for the metal and its exploitation expertise are overwhelming purposes.

Once the Iberian Pyrite Belt (IPB) – an important metallogenic province crossing the south of Portugal and extending to Spain – looks a very promising indium supplier in view of the trace-element concentrations assigned to both Neves-Corvo (Gaspar, 2002; Serranti et al., 2002) and Aljustrel (Gaspar, 1984) polymetallic sulphide ores, an appraisal on the crystal and mineral chemistry of this element is presented, focusing on chalcogenides.

2 CRYSTAL CHEMISTRY OF INDIUM

Like gallium and unlike tin, indium does not form specific minerals; it occurs rather dispersed within polymetallic sulphides. Stable In-compounds range from the hydride (InH) and nitride (InN) configuring the two stable formal valences (1+) and (3+), to the phosphide (InP) and arsenide (InAs) where indium behaves formally as a trivalent ion and which have been extensively applied in semiconductor technologies. Other synthetic In-compounds include halides, oxides and chalcogenides, the latter being worthy of a particular interest for the understanding of indium geochemical behavior.

The average In-content of the Earth’s crust is estimated at 0.1 parts per million, similarly to silver. Canada is the world main producer, holding the largest indium reserves.

The recovery of the metal stands mostly on the zinc extraction from sphalerite (see e.g., Falconbridge website). This cubic mineral is the
prototype of “tetrahedral sulphides” where cations fill half of the available tetrahedral sites in the cubic closest packing (ccp) of sulphur anions. The crystal-chemical formula of sphalerite can then be written $\text{Zn}^t\{\text{S}^6\}^c$, where $t$ stands for tetrahedral coordination of metal cations and $c$ quotes the ccp of anions (Figueiredo & Basto, 1986).

Indium is also carried in trace (but noteworthy) contents by excess-metal copper sulphides like bornite, also a tetrahedral compound with formula $\text{Cu}_t\{\text{Fe}^t\}\{\text{S}^4\}^c$, and by the rare mineral sakuraiite, $(\text{Cu,Ag})_t\{\text{Zn,Fe}^t\}\{\text{In,Sn}^t\}\{\text{S}^4\}^c$, as well as by more complex sulphides from the series tetrahedrite-tennantite.

Pure In-chalcogenides – $\text{In}_6\text{Se}_7$, $\text{In}_7\text{Te}_{10}$, $\text{InTe}$ and $\text{In}_3\text{Se}_3$ plus $\text{In}_3\text{Te}_3$, with excess metal – are synthetics and contain polynuclear cations: $[\text{In}_2]^{3+}$ dimmers and/or $[\text{In}_3]^{5+}$ trimers (Schwarz et al., 1995; Epple et al., 2000).

3 INDIUM AT THE NANOSCALE IN POLYMETALLIC SULPHIDES

Replacements and recrystallization due to a later copper-rich hydrothermal solution often remove the primary textures in volcanogenic massive sulphides (VMS). Accordingly, remobilization of chalcopyrite and tetrahedrite are common in copper ores from Neves-Corvo deposit (Gaspar & Pinto, 1991) and the resulting paragenesis involves promising indium-carriers (Table 1). Indeed, encouraging results have already been published (Benzaazoua et al., 2003).

Table 1. Selected trace-element concentrations in accessory minerals from bornite-massive copper sulphide Neves-Corvo ore.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Empirical formula</th>
<th>Se ppm</th>
<th>In ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bornite</td>
<td>$(\text{Cu,Ag})<em>{0.93} \text{Fe}</em>{0.97} \text{S}_{4.10}$</td>
<td>4900</td>
<td>n.r.</td>
</tr>
<tr>
<td>Mawsonite</td>
<td>$\text{Cu}<em>{5.95} \text{Fe}</em>{2.01} \text{Sn}<em>{1.0} \text{S}</em>{8.05}$</td>
<td>n.r.</td>
<td>300</td>
</tr>
<tr>
<td>Tennantite</td>
<td>$(\text{Cu,Fe,Zn,Ag})<em>{11.8} {\text{As,Bi}^t}</em>{2.1} {\text{S}^3_{1.2}}$</td>
<td>n.r.</td>
<td>27400</td>
</tr>
<tr>
<td>Galena</td>
<td>$\text{Pb}<em>{0.95} {\text{S,Se}}</em>{1.0}$</td>
<td>72500</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

(From Gaspar, 2002; n.r., not reported)

Mastering nano-scale complexity in minerals is gaining well turned-out solutions through the use of highly focused microbeam techniques making use, not only of particle beams (electrons in EPMA or protons in micro-PIXE), but also of photon beams in synchrotrons of the third generation - like the European Synchrotron Research Facility (ESRF in Grenoble/France) and many national facilities being now under installation in Europe. These large-scale installations provide very suitable instrumental means of research at the nanoscale and the assessment to the binding situation of both metal and chalcogen components in mixed-valent solids containing indium (Epplle et al., 2000).

4 FINAL COMMENTS

It is worth noticing that the ccp anionic array configured by sulphur anions in chalcopyrite, bornite, mawsonite, tetrahedrite-tennantite and galena is particularly suitable to accommodate polynuclear cations by filling closely located tetrahedral sites. Furthermore, once indium selenides and tellurides are stable synthetics containing indium polycations, it is expectable that Se and Te can favorably be hosted by such anionic packing in the presence of indium.

Such crystal chemical guesses suggest that it is worthwhile searching for indium, selenium and tellurium in sulphide paragenesis assigned at the Neves-Corvo and Aljustrel deposits from IPB. Accordingly, it is foreseen to undertake a nanoscale analysis of selected ore samples and pursue an X-ray absorption spectroscopy study on indium binding in assigned carrier minerals.

REFERENCES


Porphyry type mineralizations in Sardinia (Italy)

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ABSTRACT: Hydrothermal ore-forming activity associated with Tertiary volcanism occurred at different times and places in the western part of Sardinia, producing orebodies of different types and sizes, including porphyry deposits and epithermal base and precious metal occurrences. Following a list of the main porphyry-type occurrences, the general features and the alteration zones are discussed for the well known Calabona copper mine and for the recently discovered porphyry copper system in the Siliqua-Decimoputzu district.

KEYWORDS: porphyry-Cu, epithermal, gold, molybdenum, Sardinia

1 INTRODUCTION

In western Sardinia (Italy), sparse ore occurrences are associated with the regional calc-alkaline magmatic activity that took place from Oligocene to middle Miocene in the course of the early drift of the Sardinian microplate, interpreted as a late manifestation of the underthrusting of the African plate beneath the European plate. Corsica and Sardinia separated from Europe moving away from Iberia; the movement occurred as a counterclockwise rotation of approx. 45° of the entire block.

Hydrothermal ore-forming activity associated with Tertiary volcanism occurred at different times and places in the western part of the island producing orebodies of different types and sizes, including porphyry deposits and epithermal base and precious metal occurrences.

2 INVESTIGATED MINERALIZATIONS

The porphyry stock of the Calabona copper mine, south of Alghero on the north-western coast of the island (Fig. 1), exhibits an isotopic age of 34Ma and may be considered to be the first phase of the Tertiary calc-alkaline magmatism evolved during the orogenic event following a continent-continent collision. The mineralization is hosted in a sub-volcanic intrusion formed by dacite and andesite porphyries of calc-alkaline affinity. They were emplaced at very shallow depth near the contact between the Hercynian basement and the Permo-Triassic sedimentary cover. The porphyry stock exhibits an elongated shape, extending at least 4km in length and more than 1.5km in width. The exploited orebodies produced more than 25,000 tonnes of 8-9% Cu-rich ores and some 40,000 tonnes of cupferiferous pyrite from small lenses. They were mainly composed of massive pyrite supergene-enriched with secondary copper minerals (mainly chalcostite and covellite) and extended approximately 50-60m in depth within the Triassic limestone. The alteration pattern and assemblages reflect the style of several porphyry copper deposits. The mineralization is present in two forms: disseminated, and as stockwork veins. Hydrothermal alteration and brecciation is well developed, in sharp contrast to the overlying unaltered volcanics. The observed alteration zones are propylitic and quartz-sericitic zones, spotty argillic alteration and, only at depth, trace of potassic-silicate alteration. Three major generations of veins were distinguished: early, intermediate, and late (Frezzotti et al., 1992). The early veins are short and discontinuous and are thought to represent an early fracturing episode in the complex. The intermediate veins are more continuous and thicker containing pyrite, chalcopirite and bornite. Sphalerite is present in a few places and molybdenite occurs only in areas of intense quartz injections. Chalcocite is fairly
common and usually coats pyrite as a thin film. A low grade, supergene-enrichment blanket also is developed above the sericite zone. Fluids associated with late stages of hydrothermal circulation have significantly lower salinities and are characterized by a progressive cooling (500°- 90° C) and dilution throughout the shallow and peripheral zones of the intrusions and with late quartz-pyrite veins. The Calabona porphyry stock appears to be a fairly typical porphyry type development, located in the upper part of a porphyry system. However, the lack of the Cu-Mo-rich K-silicate core strongly reduces the economic potential of this deposit.

There are other indications of porphyry-type mineralizations in three areas of the SW corner of the island (Fig. 1):

Tratalias, where a concealed mineralization evidently is associated with a strong magnetic anomaly, related to a potassic alteration;

San Simplicio, an extensive andesite dike swarm exhibits propylitic and argillic alteration, accompanied by disseminated pyrite and minor chalcopyrite at the skarn formation in the Cambrian carbonate host rocks.

A porphyry-copper district has recently been discovered in the Siliqua-Decimoputzu volcanic complex formed in the southwestern part of Sardinia during the Tertiary calc-alkaline magmatism. At Siliqua the rocks are usually porphyritic and holocrystalline in domes, dikes and sub-volcanic bodies; the facies range from basaltic through dacitic, to rhyolitic with local tholeiitic and peralkaline occurrences. In this area several sub-volcanic calc-alkaline bodies show strong alteration phenomena and indications of mineralization. This mineralization was discovered in the course of road construction when a trench was cut into a propylitic halo, containing a dissemination of pyrite and minor chalcopyrite. This broad halo surrounds the Monte Accas hill (Fig. 2), which proved to be a K-alteration core.

A more important mineralized area occurs and an exploration drilling campaign was carried out along the Monte Idda-Monte Silixianu ridge. Mineralization comprises disseminated pyrite and chalcopyrite, with minor molybdenite. Samples collected from these outcrops show copper, molybdenum and gold contents close to an economic grade. The alteration zone sequence and distribution of copper mineralization in the Siliqua sub-volcanic complex roughly fits in a “diorite model” of porphyry copper systems. Recent field observations suggest that there is also an outcropping epithermal mineralization, possibly exposed due to differential offsets caused by the Campidano faults (Fadda et al., 2006 and references therein).

Silicification and pyritization, along with the occurrence of calcite-barite veinlets mineralized with pyrite, marcasite and arsenopyrite with Au contents from some tens of ppb up to a few ppm, points to the existence of a low-sulphidation epithermal system, probably re-
lated to the latter phases of emplacement of the porphyry system. Hydrothermal breccias occur in the south of the area and appear to be associated with this epithermal activity. They may be considered as first indications of “explosive” hydrothermal activity in the Siliqua area. Whether or not there is a direct genetic link between the porphyry and the epithermal regimes, the magmatic event may have been important for the introduction of metals, which were then available for later remobilisation and concentration by circulating fluids of non-magmatic origin.

2.1 Alteration characteristics at Siliqua

In the Monte Accas area the different alteration facies of the porphyry system are arranged in a concentric array. The potassic alteration, characterized by abundant magnetite, shows irregular distribution and intensity. It appears at the rims of the Monte Accas, Monte Silixianu, and Monte Idda bodies as a pervasive biotite alteration associated with quartz veinlets containing magnetite and sulphides. In the core of the Monte Silixianu and Monte Idda bodies the alteration appears as veinlets and decimetre-thick veins of quartz, K-feldspar, and magnetite (Fiori et al. 1998). The most common alteration facies is a propylitic alteration, affecting mainly the andesites with varying intensity. In general, the propylitic and potassic alteration zones gradually merge into each other, without interposition of other forms of alteration. The only exception was observed in the exposed outcrops on the northern flank of Monte Idda, where, between these two types of alteration, a third type was recognised. This major facies is formed of an actinolite-sphene-hematite association with abundant chalcopyrite. This form of alteration totally obliterates the former rock texture. As this type of alteration is confined to the contact between diorites and younger andesites, it is most probably the result of a thermo-metamorphic process.

Lastly, a supergene alteration facies could also be observed. This facies has been formed by deep leaching of the andesites, along with their Palaeozoic roof, cropping out in the small valley between Monte Idda and Monte Sa Pipionada. The leaching completely argilised the volcanic rock resulting in a quartz-kaolinite association with minor montmorillonite and crusts and veinlets formed of jarosite and hematite, with abundant alunite and barite. This mineral assemblage suggests that the original rock hosted abundant sulphide dissemination, composed mainly of pyrite.

3 THE ORE MINERALIZATION STYLES

Hypogenic sulphides, including pyrite, chalcopyrite, and minor molybdenite form the mineralizations. They occur at the fringe of the K-alteration zone, where there is a gradual transition to propylitic alteration and a sharp contact with Palaeozoic rocks. In the latter case pyrite is disseminated throughout these rocks. The sulphides occur usually as veinlets composed of quartz, pyrite, and chalcopyrite – and to a lesser extent as disseminations. The molybdenite generally occurs in the disseminated portion. The average Cu content is 0.15–0.2 wt%, locally reaching 0.4 wt%. The maximum Mo content is 160 ppm. In the actinolite-sphene-hematite alteration zone the sulphides form aggregates that concentrate in the actinolite veinlets. The highest Cu-concentrations (up to 0.6 wt%) were observed in this zone. All the above values refer to samples collected at the surface. In the core of the K-alteration zone a very irregularly distributed mineralization occurs and is associated with the magnetite and the quartz-K-feldspar veinlets. The samples contain up to more than 2 ppm gold.

Another very important aspect concerns the strong structural control on sulphide enrichment, along the main Campidano faults and their conjugate fractures. This control is due to the extremely low permeability of the Palaeozoic host rocks, confining the circulation of the hydrothermal fluids to the open channels created by these extensive faults, as can easily be observed at Monte Idda and Monte Niu de Crobu.

There are also indications of a quartz-marcasite-pyrite-arsenopyrite mineralization, with significant traces of gold (Mitza Purdia spring), suggesting subsequent circulation of lower temperature fluids along the same confined channel-ways. The Mitza Purdia mineralization is characterised by the presence of polyphase quartz-pyritic crustiform veinified silicifed intrusive rocks. In the layered pyrite veins large sphalerite grains (containing up to 1wt % As) and small grains of bismuth sulphosalts occur. Samples collected from the spring yielded 2 g/t Au. These features, together with the strong affinity with a magmatic source of the veins, suggest an epithermal origin for this occurrence.
4 PRELIMINARY EXPLORATION RESULTS AND PERSPECTIVES

A preliminary exploration programme focused on the Mitza Purdia corridor by a preliminary RC drilling campaign. A 50m intercept of strong silicification and 5-10% pyrite mineralization was intersected from 40m downhole in the first RC drill hole which showed anomalous gold contents. The epithermal silica-pyrite alteration is hosted in andesitic volcanics and is similar to that expressed in the Mitza Purdia exposure 400m to the north. This result confirms the continuity of the mineralization concealed beneath the thin alluvial cover along the whole corridor. However, the alteration pattern only includes K-alteration at the core, and a broad propylitic halo, usually with no trace of an intermediate sericitic zone. Where andesites and diorites are in contact the absence of a quartz-sericite alteration is observed. In a “classic” American Cordillera-type porphyry, this would imply a deep erosion level, and consequently a comparative scarcity mineralization. The diorite model actually exhibits a mineralization and an alteration pattern quite comparable with the situation described. The main criticism as to the validity of this interpretation concerns the fact that the diorite model was established in an alkaline rocks context, while the occurrence described here includes typically calc-alkaline rocks. On the other hand, the drilling campaign on the Calabona porphyry-Cu mineralization, also hosted in calc-alkaline rocks, showed a similar alteration pattern. However, as far as the occurrence of gold is concerned, it is demonstrated that the area underwent a second epithermal mineralizing phase whose significance has yet to be investigated. The occurrence studied at Siliqua exhibits individual characteristics concerning depth of emplacement of the plutons, type of host rock, type and thickness of continental crust, characteristics of the subducted oceanic crust, etc. Perhaps the best geotectonic conditions for the formations of porphyry ore systems that would permit the rapid and easy access of magmas to the shallow crust were limited in time and space. However excellent exposure relationships provides a good opportunity to study spatial, temporal and possibly genetic links between porphyry and epithermal stages of the development of a complex contemporaneous magmatic-hydrothermal-epithermal activity. The epithermal occurrences in the study area may be considered to represent the upper parts of the porphyry systems buried at depth. The existence of a magmatic contribution is till now only speculation. Alternatively, the close space and time relationship between multiple and/or successive intrusion phases and different epithermal fluids along the same or different plumbing systems may support a genetic connection if erosion and tectonism in the province are taken into account. Systematic exploration will provide data for a correct interpretation in addition to detailed fieldwork and petrographic study, which may form the basis to reconstruct the chemical, spatial and temporal evolution of the events. Microthermometric investigations and chemical analyses of fluid inclusions from the porphyry and the epithermal parts of the system combined with electron microprobe analyses of magmatic phenocrysts and hydrothermal minerals are currently in progress and will be of primary interest in understanding magmatic factors controlling the mineralization. Additionally, isotope geochemistry, as well as high-precision (U-Pb and Ar-Ar) dating of the different magmatic and hydrothermal regimes will help to elucidate the connection between these two styles of mineralization.

Besides the interesting scientific aspects of this question a sound explanation of the relation between the porphyry systems and the possibly cogenetic epithermal mineralizations will evidently have a big impact on gold exploration related to these systems.

ACKNOWLEDGEMENTS

The research was also supported by CNR-Cagliari (Italy)

REFERENCES


1362 "Digging Deeper" C.J. Andrew et al (editors)
A comparison of hydrothermal fluids in barren versus mineralized breccia pipes, Cloncurry district, Australia

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ABSTRACT: Iron oxide-copper-gold mineralized breccia systems (e.g., Ernest Henry) have been studied in detail in the Cloncurry district, however, barren systems are more common but to date have lacked extensive research. This research has studied fluid inclusions in the barren Suicide Ridge breccia pipe in order to identify differences from mineralized systems. Two dominant types of fluid inclusions are observed: (1) pure CO₂-rich primary to pseudosecondary fluid inclusions that occur exclusively in granite breccia clasts and (2) abundant secondary sodic-calcic brine inclusions that occur in all samples. The brine inclusions are paragenetically linked to albitic alteration and therefore represent the fluid that caused the albitization. These inclusions have lower homogenization temperatures (110 to 360°C) and salinity (22 to 45 wt% NaCl+CaCl₂ equiv.) than the high temperature, ultrasaline multisolid fluid inclusions that are abundant in IOCG deposits. The absence of these fluids in the barren systems suggests they were critical for the formation of IOCG deposits.

KEYWORDS: IOCG deposits, barren breccia pipe, fluid inclusions

1 INTRODUCTION

The occurrence of breccia in close association with a wide variety of hydrothermal ore deposits has been well documented (Meinert, 1982; Sillitoe, 1985; Sillitoe & Sawkins, 1971). Breccia commonly occurs as host for the mineralization, but it also plays an important role as pathways for mineralizing fluids. In the Cloncurry District of the Mt Isa Inlier, Australia, brecciation is widespread particularly in the proximity of the Cloncurry fault and granitic intrusions and is commonly developed within calc-silicate rocks of the Corella Formation (Marshall, 2003 unpublished data). Previous work in the Cloncurry District has focused mainly on breccia directly linked to known iron oxide-copper-gold (IOCG) deposits (Adshead, 1995 unpublished data; Adshead-Bell, 1998; Mark, 2006; Pollard et al., 1997), and research on regional breccias has dealt mostly with mechanical aspects of breccia formation (Marshall and Oliver, 2006; unpublished data Oliver et al., 2006). Few studies have addressed the chemistry of fluids related to these systems (de Jong, 1995; Marshall, 2006). The aim of the present work is to determine the characteristics of fluid associated with a barren breccia system, the Suicide Ridge breccia pipe, in the Snake Creek Anticline area. The results will shed light on our understanding of the key differences between barren and mineralized systems.

2 GEOLOGICAL BACKGROUND

The area of study is located in the Snake Creek Anticline, approximately 30 km southeast of Cloncurry in the Eastern Succession. The Eastern Succession comprises rocks of two cover sequences: Cover Sequence 2 (ca 1800-1725 Ma) that consists mostly of calc-silicate rocks of the Mary Kathleen Group and Cover Sequence 3 (ca 1680-1610 Ma) which contains pelitic and psammitic rocks of the Soldiers Cap Group (Foster & Austin, 2006). Rocks of the two cover sequences were deformed during the 1600-1500 Ma Isan Orogeny and was accompanied by variable grade metamorphism from lower greenschist to upper amphibolite facies.
(Foster & Rubenach, 2006). The waning stages of the orogeny are characterized by the emplacement of the Williams-Naraku Batholith (ca 1550-1500 Ma) that was accompanied by widespread sodic (-calcic) alteration. The region is characterized by extensive brecciation that developed predominantly within the calc-silicate rocks of the Corella Formation (Marshall, 2003 unpublished data). Bodies of breccia of different sizes and shapes are commonly widespread around and along the Cloncurry Fault and appear to be closely associated with 1550 to 1500 Ma granitoids (Oliver et al., 2006).

The Suicide Ridge breccia pipe crops out within rocks of the Soldiers Cap Group that contains schist and quartzite of the Mount Norna Quartzite (Fig.1). The breccia forms a pipe-like body about 1000m long and 25m wide and strikes SW-NE, cutting the foliation of the schist almost perpendicularly. The pipe is found in close proximity to, and extends from, an intrusion located at its southwestern end. The pipe contains several granitic bodies (up to 10m in size) and magnetite-hematite-rich rocks and is characterized by very intense albite alteration which affects breccia throughout the whole pipe and host rocks adjacent to the pipe.

Breccia is characterized by clasts of variable composition including dominant calc-silicate of the Corella Formation and lesser abundant albrite and granite clasts. Fragments are rarely angular and dominantly sub-round to round in shape with variable dimensions that range from millimetre to metre-scale.

3 SAMPLE SELECTION AND ANALYTICAL METHOD

Samples for the fluid inclusion include granite clasts and Fe-rich rocks. Granite samples are representative of early stages of breccia formation and dominantly consist of albite and quartz and display textures that collectively have been interpreted as characteristic of the magmatic-hydrothermal transition. The matrix and infill component of the breccia were also examined for fluid inclusions but fluid inclusions were scarce and too small to be analyzed.

Analytical techniques include microthermometry, laser Raman and LA ICP MS analysis. Microthermometric measurements of fluid inclusions was undertaken on fluid inclusion wafers using a Linkam MDS600 heating/freezing stage at the School of Earth and

![Fig. 1 Map of the breccia locality showing the breccia pipe and its relationship with the host of the Soldiers Cap Group and the granitoids that outcrop in the southwestern part of the area.](image)

4 FLUID INCLUSIONS

4.1 Fluid inclusion types and microthermometry

Five main types of inclusions have been identified from the study of polished thin sections and fluid inclusion sections.

Type I fluid inclusions are primary (type Ia) and pseudosecondary (type Ib) monophase CO$_2$-rich fluid inclusions containing only liquid at room temperature, with a bubble developing upon freezing. These inclusions were observed only in granite clast samples and occur within quartz related to the magmatic-hydrothermal transition.

Type II fluid inclusions are mixed aqueous-carbonic (type IIa) and mixed brine-carbonic (type IIb) fluid inclusions. At room temperature type IIa inclusions contain an aqueous phase, liquid CO$_2$ and halite. These small (≤10µm), inclusions are exclusively observed in pegmatite clast samples commonly in association with type Ia and type IIb. Their origin is unclear, although their association with type Ia may suggest a primary origin.

First melting values of type I and type II
fluid inclusions indicate composition close to that of pure CO₂ confirmed by laser raman analysis that did not detect other gas species a part from CO₂. Type Ia and Ib display different range of homogenization temperatures, between -17.1 and -0.5°C for primary type Ia, and between -1.1 and 30.5°C for pseudosecondary type Ib fluid inclusions, implying generally higher densities for type Ia fluid inclusions. CO₂ homogenization temperatures ranged between -0.7 and 25.4°C for type II fluid inclusions, whereas total homogenization was only observed once (276.4°C) due to the tendency of these inclusions to decrepitate before total homogenization.

Type III inclusions are the most abundant inclusions and occur in every sample considered in the study. Type III fluid inclusions are three phase liquid-rich inclusions with a vapour bubble and a small halite crystal (type IIIa), and two-phase liquid-rich inclusions without daughter phases (type IIIb). These inclusions are interpreted to be secondary and in particular to be linked to albite alteration that affects rock within and adjacent to the pipe (Fig.2). These inclusions display temperatures of first melting mostly below -49°C indicating the presence in the fluid of CaCl₂ and likely other salts in addition to Na. Salinities range from 22.4 to 45.4 wt% NaCl +CaCl₂ equivalents.

4.2 Fluid chemistry

LA ICP MS analysis of type III fluid inclusions revealed that the fluid contains similar average concentrations K (~19500ppm) and Ca (~20500ppm), but single inclusions display variable K/Ca ratios. The inclusions also contain Fe (average ~2000 ppm), Ba (average ~800 ppm), and Sr (average ~300 ppm). Among the metals Zn is the most abundant (average ~ 700 ppm) followed by Cu (average ~300 ppm) and Pb (~150 ppm). Type IV fluid inclusions are similarly dominated by K and Ca with Ca (~30000 ppm) on average more abundant than K (~24000 ppm). These inclusions generally display similar average concentrations of Fe (~2000 ppm), Ba (~1000 ppm) and Sr (~200 ppm) compared to type III fluid inclusions but contain more Cu (~800 ppm) and Zn (~2000 ppm) than type III fluid inclusions. Concentrations of Cu, Zn and Pb are expected to be lower considering that these elements are often below detection. Manganese was below detection limit in the majority of type III and IV inclusions analyzed.

5 DISCUSSION AND CONCLUSIONS

The Suicide Ridge barren breccia pipe is characterized by two dominant types of inclusions. CO₂ fluid inclusions are abundant and exclusively observed in granite clasts and represent fluid exsolved from the crystallizing magma prior to, and perhaps leading to, brecciation. Sodic-calcic fluid inclusions are similar to those documented elsewhere in regional albite alteration (de Jong, 1995; Fu, 2003) and to the late lower salinity and lower temperature inclusions observed in IOCG (e.g Baker, 1998; Rotherham 1998). The barren breccia pipe is characterized by the absence of high temperature, multiphase, high salinity fluid inclusions commonly observed in IOCG. This observation suggests that hot hypersaline brine were critical for the formation of IOCG deposits whereas moderate salinity sodic-calcic fluids were primarily responsible for barren regional albitisation.

ACKNOWLEDGEMENTS

This research is supported by the Predictive Mineral Discovery Cooperative Research Cen-
REFERENCES


Pb stepwise leaching of epidote from Mount Isa, northern Australia: implications for dating mineral phases from poly-deformed terranes

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ABSTRACT: Epidote metasomatism has affected large areas of tholeiitic metabasalts that comprise the ca 1780 Ma Eastern Creek Volcanics of the Western Fold Belt of the Mount Isa Inlier. Epidote generally occurs in quartz veins that are parallel to the dominant S2 fabric, and in some cases the veins are boudinaged by it, indicating that epidote crystallisation was largely synchronous with the D2 metamorphic event during the ca 1590-1500 Ma Isan Orogeny. An attempt to date epidote formation using the Pb stepwise leaching technique recovered only a small range in radiogenic Pb (206Pb/204Pb from 16.0 to 20.5). The bulk of the epidote Pb is unradiogenic and the method, in this case, failed to efficiently isolate the small amount (<1% of total Pb) of radiogenic Pb present in the crystals (Pb4+), from common Pb, that is present as Pb2+. Age regressions of the PbSL data yield apparent ages that are 150 to 1500 myr older that the host rocks, and over 450 myr older than the accepted metamorphic ages of ~1575 Ma. The most likely reason for the old ages is the presence of volumetrically small mineral surface coatings that are relatively rich in radiogenic Pb and are easily dissolved during the leaching experiments, thus radiogenic Pb is released in early leach steps that involve weak acids. This finding has implications for the application of the Pb stepwise leaching technique to geochronological problems in regions that have undergone a protracted fluid flow history that may allow Pb-rich mineral surface coatings to accumulate.

KEYWORDS: Proterozoic; Mount Isa Inlier; Pb stepwise leaching; Epidote; Hydrothermal fluids

1 INTRODUCTION

The metallogenuically important Proterozoic Mount Isa Inlier of north-west Queensland, Australia, consists of several poly-deformed supra-crustal sequences that have been affected by numerous metasomatic events between 1740 and 1100 Ma (e.g., Oliver 1995; Mark et al. 2004; Oliver et al. 2004). The main aim of this study was to provide absolute timing constraints on epidote alteration that is common within the tholeiitic metabasalts of the Eastern Creek Volcanics around Mount Isa [dated at 1779±4 Ma using U-Pb zircon data from an interbedded quartzite member (Neumann et al. 2006)]. Epidote alteration at Mount Isa is thought to have coincided with the (D2) peak metamorphic event that occurred during the Isan Orogeny around 1575 Ma (Hannan et al. 1993; Heinrich et al. 1993; Duncan et al. 2006; Gregory 2006).

The epidote metasomatic event is considered important in the hydrothermal evolution of the Mount Isa region as epidote-rich zones delineate zones of high fluid flow that have been enriched in copper that was released via the metamorphic decomposition of titanomagnetite in the Eastern Creek Volcanics during metamorphism (Gregory 2006). Therefore, improved geochemical and geochronological constraints on epidote formation would further help to refine the nature and timing of hydrothermal activity and metal mobility during the Isan Orogeny.

2 EPIDOTE VEINING CHARACTERISTICS

Epidote alteration is most pronounced to the east of Mount Isa (Haslingden area), where up to 10% of the outcrop area exhibits epidote enrichment (Heinrich et al. 1995). Epidote is also present to a lesser extent on a more regional scale to the west of the Mount Isa Fault Zone (Hazeldene area) and ~120km to the north of Mount Isa, close to the Gunpowder copper deposit. Figure 1 shows the typical occurrence of
epidote around Mount Isa. The vein mineral assemblage consists of 25 to 50% epidote (by volume), and is usually intergrown with quartz and/or calcite. Other phases usually include titanite, K-feldspar, actinolite, chlorite, magnetite, pyrite and chalcopyrite. Epidote typically occurs as euhedral, fibrous crystals, but may also occur as fine-grained crystalline aggregates. The most striking epidote occurrences are 5 to 10 cm wide vein segregations (<50 cm wide) and are generally restricted to the Hazeldene area. Swarms of epidote-dominated veinlets (over a decimetre scale) are typical in both the Haslingden and Gunpowder regions (Figure 1).

The majority of epidote-bearing veins are parallel to the near-vertical S₂ cleavage that formed during peak metamorphism (Hannan et al. 1993). In the Hazeldene area, some of the epidote-quartz veins appear to have been boudinaged by the S₂ fabric, suggesting a pre-to early syn-D₂ timing for epidote alteration. Epidote has been replaced by chlorite-albite alteration that is intensive along north-west trending fault that were active during late stage orogenic wrenching (Hannan et al. 1993).

CaCl₂-rich (up to 38 wt % NaCl + CaCl₂ eq.), high salinity fluid inclusions of unknown relative timing are found in quartz associated with epidote alteration and yield homogenisation temperature of 130 to 160°C (Heinrich et al. 1995). Epidote stable isotopic data (δ¹⁸O and δD) and Br/Cl ratios from veins in the Haslingden region are most compatible with formation from a fluid that was released as a result of metamorphic dehydration (or a fluid that equilibrated with metamorphic rocks at depth), along with an evaporitic component.

3 ANALYTICAL METHODS

The PbSL technique was carried out at the University of Melbourne on epidote heavy mineral separates (200 to 300 µm grain size fraction) that had been handpicked to select grains that were free of visible inclusions. The separates were then repeatedly cleaned in an ultrasonic bath with distilled water and then sequentially leached with a series of acids according to the method use by Buick et al. (1999). The last step involved total residue dissolution in HF. Pb was extracted on 0.1 ml (12 mm x 4 mm) columns of EiChrom™ Sr resin (50 to 100 µm) using the method of Thériault & Davies (1999). The EiChrom™ Sr resin technique provides Pb fractions of adequate purity from difficult matrices in a single pass, with acceptable blanks and reasonable Pb yields (e.g., Gale 1996).

Acid blanks were <1 pg/g Pb (<3 pg/g Pb for HF). Distilled water produced in an ELGA water purification system had blanks <0.5 pg/g Pb. Total procedural blanks for this study were <30 pg/g Pb. Lead isotopic ratios were measured by multi-collector ICP-MS, using a Nu Plasma MC-ICP-MS equipped with a CETAC-Adrius desolvating nebulizer and Glass Expansion Opalmist nebulizer, providing a sensitivity of ~100 V/ppm Pb at 30 µl/min uptake (Woodhead 2002).

Figure 1 Field photographs of epidote occurrences around Mount Isa. a Epidote-quartz vein boudinaged by S₂ foliation from east of Mount Isa. b Folded epidote-calcite segregation from west of Mount Isa. c Network of epidote veins from the Gunpowder area, north of Mount Isa.
Table 1: Pb isotopic data for epidote from Mount Isa derived by the stepwise leaching technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>Acid</th>
<th>Time</th>
<th>Code</th>
<th>Pb (ng)</th>
<th>207Pb/206Pb</th>
<th>206Pb/207Pb</th>
<th>208Pb/206Pb</th>
<th>Age (Ma) ±2σ (Ma)</th>
<th>MSWD</th>
<th>Steps</th>
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</thead>
<tbody>
<tr>
<td>1.5 N HBr-2 N HCl</td>
<td>15m</td>
<td>[1]</td>
<td>4.7</td>
<td>32.058</td>
<td>0.110</td>
<td>17.096</td>
<td>0.004</td>
<td>48.001</td>
<td>0.112</td>
<td>1223</td>
</tr>
<tr>
<td>4 N HBr</td>
<td>3h</td>
<td>[2]</td>
<td>137.6</td>
<td>0.003</td>
<td>18.181</td>
<td>0.008</td>
<td>41.947</td>
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<tr>
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<td>0h</td>
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<td>55.6</td>
<td>0.020</td>
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<td>1223</td>
<td>33</td>
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<td>[4]</td>
<td>18.7</td>
<td>10.952</td>
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<td>36.128</td>
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<td>0.003</td>
<td>15.998</td>
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<td>0.019</td>
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<tr>
<td>15 N HNO3</td>
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</table>

Table 1: Pb isotopic data for epidote from Mount Isa derived by the stepwise leaching technique.

4 RESULTS

The Pb isotopic results from the PbSL experiments are given in Table 1. Pb isotopic data were blank-corrected using a 50 pg blank of Broken Hill galena isotopic composition (Cuming & Richards 1975); actual blank isotopic compositions scatter around the Broken Hill mean. Blank correction is possible during ICP-MS work, as the actual Pb quantities can be estimated accurately using the signal intensities and dilution factors. Error propagations were applied using Monte Carlo techniques and isochron calculations were undertaken in ISOPLOT v.3.00 (Ludwig 2003). To account for the uncertainty due to mass bias correction of the data where the in-run 2σ error was <0.03%, a minimum 0.03% 2σ error was applied. The results demonstrate that Pb isotopic signatures are dominated by common Pb, which is especially prevalent in the total residue dissolution step involving HF (over 95% of the total Pb content). In this study the PbSL technique cannot efficiently extract radiogenic Pb preferentially over common Pb. Isochrons have been constructed, however, they probably represent mixing lines with no geochronological significance (see below; Table 1), so the terms isochron is avoided.

5 INTERPRETATION

The radiogenic Pb leach steps are invariably found in the first leach step, which accounts for only 0.01 to 0.2% of the total Pb extracted. Leach steps 1 to 4 contain between 1.4 and 14.4% of the total Pb. Approximately 90% of the Pb held in the epidote lattice is not released until final dissolution of the sample in HF. This Pb release behaviour contrasts with that found in many other PbSL studies on silicates minerals, including epidote studied by Buick et al. (1999); silicates usually release more radiogenic Pb in strong HNO3, after removal of much of the common Pb in the preceding HBr steps (e.g., Frei & Kamber 1995). Early release of mildly radiogenic Pb, coupled with a very large common Pb component, may be related to soluble uraniferous impurities or U-rich surface coatings; alternatively a loosely-bound radiogenic component (without parental U) may be present on mineral surfaces (see below).

The epidote PbSL data demonstrate that as the acid strength and leach time increases the Pb isotopic ratios change towards a lattice-bound unradiogenic Pb component, that accounts for the majority of Pb released during the leaching experiments. The involvement of radiogenic Pb derived from micro-inclusions (e.g., zircon or monazite) is not favoured given that the time integrated Th/U epidote values (calculated from 208Pb/206Pb) are within a narrow range and are typical of silicates. Furthermore, back-scattered electron imagery of epidote grains has not identified any such inclusions.
The mineral surface contamination does not mean that all mineral phases around Mount Isa, or indeed those from other terranes that have been overprinted by (hydro-)thermal or tectonic events, cannot yield geochronologically significant data (see Frei & Pettke 1996; Buick et al. 1999; Duncan et al. 2006). The early release of radiogenic Pb has been documented before in chalcopyrite and magnetite separates from the Mount Isa copper deposit and garnets from the Eastern Fold Belt of the Mount Isa Inlier (Bassano unpublished data and this volume; Mark & Mass unpublished data). Garnets from the Proterozoic Broken Hill Pb-Zn-Ag orebodies in Australia are coated with intergranular amorphous phases, which include K and Na chlorides, chlorite and an un-named Ti phase that are all enriched in light rare-earth elements (Schwandt 1993). Contributions from such phases would obviously dominate the Pb isotopic composition of the first leach steps and would influence the feasibility of applying the PbSL technique to solve geological problems in areas that have undergone multiple episodes and hydrothermal fluid flow and/or tectonism that characterise many ore-forming systems. Chalcopyrite, pyrite and pyrrhotite from the post-peak metamorphic copper orebodies at Mount Isa yield an apparent Pb-Pb age of ~1900 Ma, although this age has no apparent geochronological significance (Gulson et al. 1999). Thus, the post depositional impregnation of ore minerals in the Mount Isa orebodies by fluids that deposit radiogenic Pb fracture coatings may provide an explanation for this old age.

ACKNOWLEDGEMENTS

We are grateful to J. Hergt and J. Woodhead (University of Melbourne) for their support of this work, and for sharing their knowledge of Pb step-leaching. Work here forms part of RJD’s PhD within the pmd*CRC with support from Xstrata Copper, and this paper is published with permission. We acknowledge the help of S. McKnight (University of Ballarat) for his generous help with imaging the epidote grains.

REFERENCES


Hannan KW, Golding SD, Herbert HK, Krouse HR (1993) Contrasting alteration assemblages in metabasites from Mount Isa, Queensland: implications for copper ore genesis. Econ Geol 8:1135-1175


SUPERGENE FORMATION AND UPGRADING
OF ORE DEPOSITS

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ABSTRACT: Important European ore deposits, which are directly related to palaeo-weathering include bauxites, nickel laterites and supergene deposits of both copper and zinc. Current dating information for these deposits is incomplete but there is strong evidence of a clustering of all deposit types in distinct time periods with two major periods being the Cretaceous and Eocene-Miocene. Current palaeoclimate models further suggest that some of the bauxite and nickel laterite deposits may relate to warm temperate weathering periods rather than tropical conditions as is traditionally thought. A more holistic study of these diverse ore deposits linked to a better geochronology of the weathering process integrated into palaeoclimatic interpretations is needed to provide better models for their formation.

KEYWORDS: Palaeoclimate, weathering, nickel laterite, bauxite, supergene, non-sulphide, zinc, copper

1 INTRODUCTION

Weathering is a major ore-forming process for a number of mineral deposit types, specifically for commodities such as Al, Fe, Ni, Cu, Au and Zn. In the case of metals such as Al, Fe, Ni and Au, lateritic weathering, processes of bulk rock mineralogical change and mass transfer are invoked whereas in the case of supergene Cu and Zn deposits, key processes are sulphide oxidation and redeposition with concomitant enrichment of the metal of interest (Hitzman et al. 2003; Sillitoe 2005). Whilst specific controls to formation of these diverse deposit types show a similar diversity, there are key features critical in all cases, notably the need for a degree of stability to suitable formation conditions for a period of time long enough for deposit formation, a consistent supply of suitable meteoric water for necessary dissolution-precipitation reactions, probably elevated temperatures and the necessity to preserve the formed weathering profile post-formation.

The bulk of commercial bauxite and Ni-laterites known worldwide have formed since Lower Cretaceous times. Palaeozoic bauxites are known but are uncommon. It is generally accepted that for most bauxites, the most extreme leaching of silica with concomitant residual upgrade of Al is needed to form the deposits and this likely demands protracted tropical weathering conditions (Bardossy & Aleva 1990). These authors concluded from studies of modern environments that the optimum conditions for bauxite formation correspond to humid tropical conditions, with rainfalls in excess of 1.2m during 9-11 wet months per year with an annual mean temperature in excess of 22°. Similarly, many Ni-laterites are largely interpreted to have formed under humid tropical conditions (Budel 1982), since they are also regolith materials, again largely interpreted as having formed in humid tropical regions where the important current producers of New Caledonia, Indonesia, Philippines, Caribbean and South America occur. Many deposits are known from the ancient geological record, where the past climatic conditions are less well documented. However, there is evidence that in many circumstances alternating wet-dry conditions, more common in savannah-type settings, are more favorable rather than a truly
humid-tropical environment. In fact, it is clear that many nickel laterite deposits are currently located in climatic zones quite different to those described as tropical. Even some bauxites appear to have formed in more arid and temperate conditions, when their positions are corrected for latitude using published palaeogeographic models. This suggests that either our knowledge of palaeoclimate control to these deposits is flawed or that the models themselves may need some revisiting.

Climatic conditions for the formation of supergene zones over weathered sulphide bodies of Zn and Cu are possibly less proscriptive. The region best known for supergene enrichment to Cu sulphide ores in the world is Chile where warm conditions in semi-arid to pluvial conditions imposed on pedeplain topography were ideal environments to form these deposits (Sil-litoe 2005, Hartley & Rice, 2005). Similar conditions would appear to favour locally the formation of secondary Zn deposits (Reichert & Borg, in prep), although for the important class of replacement and cavity fillings in carbonate rocks, the necessity for an available carbonate trap rock subjected to strong karstic dissolution where re-precipitate the metals mainly as carbonates is evident.

2 WEATHERING HISTORY OF EUROPE

In Europe, weathering as a process for ore formation has been recognized not only at lower latitudes (Italy, Southern France, Greece), but also in several areas of Northern Europe, i.e. Scandinavia, the British Isles, Belgium, France, Germany and Poland. In some of these countries the weathered profiles are covered by glacial till, such as in Ireland and Sweden, in others the visible occurrences represent only the non-eroded remnants of much thicker residual saprolites, which are preserved beneath the glacial deposits. Only part of these weathering profiles have been dated either with isotopic methods, by palaeomagnetism or more directly, following the stratigraphic principle of superposition of well-dated sediments on top of the residual deposits. Though several intense palaeoweathering periods have been recorded in Europe from Upper Palaeozoic to Mesozoic, two main age intervals are considered as most favorable: Cretaceous-Eocene and Middle Miocene, when the deep weathering was controlled by strong uplift episodes and enhanced by warm and humid climate. Many of the Mediterranean bauxites are Cretaceous in age, as well as several kaolinite deposits in central and Western Europe. Also the nickel laterite deposits in Southeastern Europe mark the occurrence of both Cretaceous and Eocene periods of tropical weathering.

3 PALAEOGEOGRAPHY AND PALAEOCLIMATE

Palaeogeographic maps with climate data derived from the web-based publications of Scotese and Boucot (Fig. 1) are plotted for these ‘peak’ periods of deposit formation.

![Palaeogeographical maps after Scotese (1990) for Miocene and Mid-Cretaceous with palaeoclimate zones (after Boucot unpubl.) and specific ore types plotted.](image)

It is apparent that there are broad correlations between climatic data and deposit types in many cases. It is clear however that there are many anomalies in the data, which need clarification. Bauxites and Ni-laterites do not seem to be restricted to tropical zones since in the Mid Cretaceous the southern European and Urals bauxites and Ni-laterites are clearly developed in temperate zones. This agrees with similar settings for these deposit types in Australia developed at the same time. Bauxite and Ni-laterite deposits formed in the Miocene fit the tropical climate zones much better although again many examples of Ni-laterite are found in more temperate climatic zones.

The map for the Cretaceous is also somewhat problematic. Much of Africa is consid-
ered to be arid at this time until the breakup of Pangea in the Upper Cretaceous yet at this time significant deep weathering was responsible for profiles in parts of Africa. It appears that better palaeoclimatic data is needed for this time period coupled with more precise age dates for the actual weathering history before a clearer picture can be built.

4 DEPOSITS AND GEOLOGICAL TIME

Despite many individual studies, scientific attention has in each case focused on single deposit types with no coherent analysis of weathering cycles through geological history for Europe. An exception to this attitude, are the bauxites and the clay deposits. In Fig 2 we show a simple representation of compiled data for the various deposit types formed as a result of weathering with respect to geological time.

From this diagram it is evident that there are clearly favorable geological periods for the development of weathering, which when examined together, point to the two periods of the Cretaceous and Eocene-Miocene in the Tertiary. Both these periods are responsible for important bauxites, Ni-laterites, kaolinitic clays and supergene sulphide-derived Zn and Cu deposits. The surprise here might be the generally common ages for deposits regardless of type, suggesting that these periods of geological history many have common formation parameters, which controlled the formation of diverse deposit types.

5 DISCUSSION

The palaeoclimatic plots may well reflect the largely poor age constraint to the formation of the deposits. Direct dating of these deposits is problematic with age controls largely stratigraphic, particularly for the bauxites. Bauxites are generally poorly age-constrained but there are possibilities to date K-bearing phases in many of the Ni, Zn and Cu deposits which is ongoing (e.g. Vasconcelos et al. 1994). Another interpretation of these data may indicate that there is a much broader range of climate conditions suitable for the formation of these deposit types than currently proposed. Some deposits apparently formed in what the paleoclimate maps indicate as arid zones, which may actually suggest that there is some degree of mis-interpretation. However, the clusters of ages, if correct, may indicate that features such as tectonic evolution and erosion rates may actually be more important features than climate. Periods characterised by progressive uplift with only moderate erosion would be favoured for most deposit types. The possibility of erosion of a formed deposit is possibly the largest threat to whether a deposit may be preserved at a particular stratigraphic level and thus it is possible that either periods of low erosion rates or alternatively rapid cover by effusive volcanic suites may favour preservation of formed profiles.

In Europe the Cretaceous marked one distinctive period of closure of part of the Tethys ocean accompanied by collision, uplift, exhum-
Fig. 3 Idealised profiles for 1 – Diverse lateritic Ni deposits developed in ophiolite-limestone terrain. 2 – Supergene Zn deposits in limestone terrain (adapted from Boev & Jankovic 1996, Hitzman et al. 2003)

...ation of both ophiolites, arc volcanics and carbonates. The Miocene marked the final closure of the Tethys with formation of the Alpine-Balkan chain. It is notable that bauxites, Ni-laterites and supergene Zn deposits can all form in karstic environments. Fig. 3 shows the broad features described for these deposit types, which clearly show the common characteristic of a weathered limestone as both a physical and possibly chemical trap. It may be no coincidence that during much of the Mesozoic, Europe and its adjacent regions was formed of large regions of exhumed and eroding carbonates at this time (many of the Carboniferous and Triassic limestones were in fact mineralised with Pb-Zn sulphides), forming a suitable scenery for karstic weathering. In the Urals, the Triassic marked the end of the Uralide orogenic events with a period of stability and gentle uplift. Ophiolites from the Urals palaeocean became exposed at this time and karsting developed in Palaeozoic carbonates. Uplifted ultramafics in both the Urals and along the line of the former Tethys underwent deep weathering through both the Cretaceous and periods of the Tertiary, principally the Eocene-Miocene. Many of the bauxites were developed in karstified terranes and deeply weathered ultramafics yielded nickel laterites. It is clear that it is important to further link these phenomena to the development of non-sulphide zinc and copper deposits formed by supergene processes, which would have major exploration implications in the region and contribute to the understanding of palaeoclimatic at these times.

REFERENCES


Boey B. and Jankovic, S., 1996, Nickel and nickeliferous iron deposits of the Vardar zone (SE Europe). University 'St Kiril and Metodij' Stip Geological Department, Special Issue No. 3 273pp.


Non-sulphide Zn-Pb mineralization in the Irish Midlands (Tynagh, Silvermines and Galmoy)

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ABSTRACT: Non-sulphide zinc-lead mineralization in the Irish Midlands represents an example of surface oxidation of primary sulphide ores, with local redeposition and preservation under glacial till. The dominant composition of oxidised ores is relatively simple: smithsonite-hemimorphite prevails at Silvermines and smithsonite at Galmoy. Smithsonite, cerussite and Cu carbonates occur at Tynagh. The lack of rhombohedral smithsonite, which commonly characterizes the upper phreatic sulphide oxidation zone, points to a relative immaturity of the weathering profiles. Owing to the absence of a well-developed karstic network, non-sulphide concentrations are considered of poor economic value. Time constraints for the deposition of the non-sulphide ores are still unclear. Oxygen isotope values of base metal carbonates are fairly high and cannot discriminate between Palaeogene (one of the most likely weathering periods in Ireland) and Plio-Pleistocene age models.

KEYWORDS: Non-sulphide ores, Ireland, Zn-Pb carbonates, supergene

1 INTRODUCTION

Ireland is renowned for its zinc-lead sulphide mineralization. Also non-sulphide ores have been located in Ireland, where they are generally associated with primary sulphide deposits. The most important occur at Tynagh, Silvermines and Galmoy (Morrissey & Whitehead 1971; Clifford et al. 1986; Boland et al. 1992; Lowther et al. 2003) (Fig. 1).

We report here on mineralogy, petrography, and isotope geochemistry of non-sulphide ores at Silvermines, Tynagh and Galmoy, in order to decipher the supergene evolution of the primary deposits. At Silvermines, the analyses were carried out on lithotypes from two drill cores (drill holes 302/3 and 303/3) located in Knockanroe Townland, at the periphery of the main orebody. At Silvermines, the analyses were carried out on lithotypes from two drill cores (drill holes 302/3 and 303/3) located in Knockanroe Townland, at the periphery of the main orebody. At Silvermines, the analyses were carried out on lithotypes from two drill cores (drill holes 302/3 and 303/3) located in Knockanroe Townland, at the periphery of the main orebody. At Galmoy, the non-sulphides were sampled from the G-orebody between 77 and 93m below the surface. We could not access any part of the old Tynagh supergene deposit, but have been able to obtain a few samples from the mineral collections of the Natural History Museum and the Imperial College in London (coll. Morrissey).

2 GEOLOGICAL SETTING AND SULPHIDE ORES

There are several excellent summaries of the regional geological setting of the Irish Orefield including Philips & Sevastopulo (1986) and Andrew (1993). The commonly dolomitised Ballysteen Limestone and Waulsortian facies (Lower Carboniferous) represent the main host
for both sulphide and non-sulphide Zn-Pb deposits, which occur in Courceyan carbonates in the Irish Midlands. Irish deposits share the characteristics of both Mississippi Valley-type and Sedimentary Exhalative ores. Two competing genetic models have been proposed: a deep convection model, firstly proposed by Russell (1978) and a topographically driven fluid flow model (Hitzman & Beaty 1996).

Ireland was, between the end of Variscan orogeny and the Tertiary, largely a continental area subject to weathering. One of the better known weathering periods was early Tertiary in age. During the Palaeogene the basalts of Antrim, Northern Ireland, were transformed to laterites and even bauxites (Hill et al. 2001). This weathering phase might have extended also to other areas of the country. Further weathering phases, especially during Upper Tertiary and within the warm interglacial periods of the Quaternary, cannot be excluded.

3 NON-SULPHIDE ZINC DEPOSITS

The only economically significant non-sulphide resource in Ireland occurred at Tynagh (Morrissey & Whitehead 1971; Clifford et al. 1986). A zinc “oxide” deposit was also known in Silvermines (Boland et al. 1992). In both localities the secondary orebodies were preserved below glacial overburden, deposited during the Midlandian Cold stage.

The mineralization of the “Residual Orebody” of Tynagh consisted of a mixture of detrital and supergene sulphides, together with smithsonite, hemimorphite, cerussite and minor Cu carbonates. (Morrissey & Whitehead 1971; Boni & Large 2003). The original resource of the non-sulphide Zn ore was 1.2 Mt @ 4.7% Zn and 9.9% Pb (Clifford et al. 1986).

Four small non-sulphide deposits were exploited intermittently until 1953 at Silvermines. An evaluation of non-sulphide ore in the early 1980’s determined a minimum resource of at least 1Mt grading 21% Zn and minor lead (Boland et al. 1992). The residual mineralization is unconsolidated or semi-consolidated, developed in weathered-out, steep-sided troughs. The main oxidized bodies were delimited by karstified and digitated margins, and by irregular fractures. The ore grades ranged from 3% Pb and 2-3% Zn in the gossan area, up to maximum values of 8% Pb and 15 to 20% Zn in the deeper orebodies.

Non-sulphide ore at Galmoy was never exploited. It occurs mainly in the G orebody (Lowther et al., 2003). The oxidation is particularly evident at depths between 77m and 93m below surface.

4 MINERALOGY AND PETROGRAPHY

Non-sulphide zinc phases in the drill holes at Silvermines are fine-grained and dominated by smithsonite and hemimorphite (Balassone et al. in press). In 302/03 both minerals are distributed equally throughout the entire section, whilst in drill hole 303/03 smithsonite is more common than hemimorphite, but the latter becomes abundant at depth. Cerussite and rare anglesite also occur. Smithsonite at Silvermines shows an evolution from early encrustations and botryoidal aggregates to late “rice grain” shaped crystals, and a systematic decrease of Fe content with time in the paragenetic sequence. Early smithsonite replacing dolomite host rocks can be Fe- and Mn-rich. This evolution points to slightly more reducing conditions during deposition of the early Zn carbonates, compared to late smithsonites, which coexist with Mn- and Fe-(hydr)oxides.

The main non-sulphide Zn-Fe-Pb phases at Galmoy are smithsonite, cerussite and Fe-(hydr)oxides (Balassone et al. in press). The smithsonite-rich samples are virtually hemimorphite-free, in contrast to Silvermines. A complex association of at least three different, often intergrown types of smithsonite aggregates was observed at Galmoy, where replacement of sulphides and vugh-infilling are predominant. Early globular or crustiform Pb- and Ca-rich smithsonite is followed by tiny rounded (Fe-poor) to clusters (Fe-rich) and again by late “rice grain” types.

5 STABLE ISOTOPES GEOCHEMISTRY

We could not isolate enough pure carbonates for isotopic geochemistry from the Silvermines drill cores. The smithsonites from Galmoy and Tynagh have similar, but unusually high $\delta^{18}O_{VSMOW}$ values ranging from 29.2 to 31.2 ‰ (n = 12; Fig. 2) as compared to other supergene non-sulphide Zn-Pb deposits, e.g., SW Sardinia, E Belgium, Broken Hill-NSW, or Skorpion (Gilg et al. in press). Oxygen isotope values of cerussites (16.6 to 18.6 ‰, n=5) are about 13 ‰ lower than those of smithsonite,
broadly consistent with observations in other deposits (Gilg et al. in press).

The $\delta^{13}C_{VPDB}$ values of smithsonites scatter mostly between -10.9 and -5.7 ‰ with samples from Galmoy being heavier than those from Tynagh. We note an individual outlier (+1.3 ‰) from Tynagh. The few studied cerussites also show a remarkably large carbon isotopic variation from -16.4 to -0.1 ‰, again with samples from Galmoy heavier than those from Tynagh.

6 DISCUSSION AND CONCLUSION

The Irish non-sulphide Zn-Pb mineralization shows all the characteristics of supergene deposition, related to limited (palaeo-)weathering processes of the primary sulphide orebodies. The oxidation minerals at Silvermines are confined, even in the fringe of the main orebody, to the upper parts of the oxidation zone (between 40 and 50m below the present day surface), as already mentioned by Boland et al. (1992) for the top zone of the sulphide deposit. At Galmoy, sulphide oxidation has been encountered at deeper levels, down to between 70 and 90m below today’s surface. At both sites, but also at Tynagh (Morrissey & Whitehead 1971), the oxidation was particularly enhanced along the structural features, which controlled the emplacement of the primary sulphides and probably acted also as conduits for oxidizing meteoric waters.

We detected a direct correspondence between some morphological types of the smithsonite crystals and their content of minor and trace elements. At both Silvermines and Galmoy, “rice grain” smithsonite, remarkably depleted in Fe and other trace elements, represents the latest Zn carbonate generation, which was precipitated in open cavities. Other smithsonites types (Balassone et al. in press) are locally rich in Pb, Fe and Mn. In the Silvermines drill cores, smithsonite generally replaces the dolomite host rocks, whereas at Galmoy smithsonite seem to replace primary sulphides or precipitate in cavities derived from their dissolution. The lack of rhombohedral smithsonite, which characterizes the upper phreatic zone in the oxidation zones of SW Sardinia and E Belgium, may indicate the relative immaturity of the weathering profiles in Ireland.

Carbon isotope values of the Zn and Pb carbonates indicate a predominant organic carbon source, most probably from soils with C3 plant vegetation, and only a limited contribution of wall-rock carbonate. Oxygen isotope data are not conclusive with respect to the timing of oxidation and can be interpreted in two ways. The carbonates are either in isotope equilibrium with waters of $\delta^{18}O = -6.5 \pm 0.5$ ‰ similar to the present-day meteoric waters (Diefendorf & Patterson, 2005) at temperatures of 8 to 9 °C, similar to today’s mean annual air temperatures. Alternatively, if oxidation occurred in the Early Tertiary at temperatures of about 15 to 20°C, the oxygen isotope composition of palaeometeoric waters can be calculated at about -4 ‰ using the fractionation factors of Gilg et al. (in press). Such isotopically heavy waters would be expected in a hot and humid climate at low altitudes and latitudes. Stable carbon isotope studies on goethite, gibbsite, and organic matter in the Palaeogene laterites at Antrim (Northern Ireland) also suggest an interval of hot and humid climate at high latitudes, associated to elevated atmospheric CO$_2$ concentration (Tabor & Yapp, 2005).

Nevertheless, these considerations leave the time constraints for the deposition of the non-sulphide ores in Ireland still unclear, because we cannot discriminate between Palaeogene...
(one of the most likely weathering periods in Ireland) and Plio-Pleistocene age models.

ACKNOWLEDGEMENTS

We wish to thank P. McDermott and the staff of Galmoy Mines for the support during the sampling. Thanks are due also to J. Wilkinson of Imperial College and to the staff of Natural History Museum, London, for allowing the sampling of Tynagh from their collections. Isotope analyses were performed by U. Struck, Museum für Naturkunde, Humboldt-Universität Berlin, and Ch. Mayr, GeoBioCentre LMU, Munich.

REFERENCES


The formation of hemimorphite as a characteristic late-stage mineral of carbonate-hosted non-sulphide zinc deposits

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ABSTRACT: The formation of hemimorphite is commonly assumed to be related to late stages of the formation of non-sulphide zinc deposits. The oxidation of sulphide protore generates metal-bearing fluids, from which zinc precipitates predominantly as Zn-(hydro-) carbonates. The \( \text{H}_4\text{SiO}_4(\text{aq}) \) concentrations within these fluids are commonly too low for a quantitative precipitation of the available zinc as Zn-silicates. However, the formation of zinc silicates becomes an important process at the post-oxidation stage. The successive contact with \( \text{H}_4\text{SiO}_4(\text{aq}) \)-bearing fluids leads to the formation of zinc silicates over time. The amount of hemimorphite within the studied deposits correlates with the availability of \( \text{H}_4\text{SiO}_4(\text{aq}) \). The zinc silicate precipitates in open spaces and pores as a result of changing mineral stabilities and is intimately associated with the red- or white zinc ore (smithsonite/hydrozincite).

KEYWORDS: Hemimorphite, Mehdi-Abad, Iran-Kuh, non-sulphide zinc, Iran

1 INTRODUCTION

This study is based on observations from the carbonate-hosted non-sulphide zinc deposits Mehdi-Abad, Iran-Kuh, and Kuh-e-Surmeh in Iran. Here, hemimorphite occurs as the most common zinc silicate mineral. Other secondary zinc silicates, such as sauconite or willemite are rare or absent. In most cases, hemimorphite occurs in open spaces of ‘white-’ and ‘red zinc-ore’, within fault zones and -breccias and in the matrix of fault breccias as euhedral crystals, which have grown perpendicular to the underlying surface along fractures and spaces (Fig. 1 and 2). A late-stage origin of hemimorphite has been observed at Mehdi-Abad, Iran-Kuh, and Kuh-e-Surmeh, but has been also detected in samples from Sierra Mojada (Mexico), and is also reported from other authors such as Hayl & Bozion (1962), Heyl (1963), and Takahashi (1960). These authors have shown that hemimorphite is related to late or even the final stages of non-sulphide mineralization processes, growing within fractures and open spaces of ‘white-’ and ‘red zinc-ore’ over long periods. However, the mass-relationship between zinc (hydro-) silicates and zinc (hydro-) carbonates varies considerably between several deposits.

2 GEOLOGICAL OVERVIEW AND MINERALOGY OF THE NON-SULPHIDE MINERALIZATION

The model for hemimorphite precipitation presented here, applies to carbonate-hosted (limestone or dolomite) non-sulphide zinc deposits, which represent the majority of the known non-sulphide zinc deposits (Large, 2001; Hitzman et al., 2003). The studied non-sulphide zinc deposits share similar features. The occurrence of sulphide- and non-sulphide ore is controlled and limited by faults. Most economic quantities of non-sulphide zinc minerals occur as cement of karst breccias. The non-sulphide zinc ore can be classified into two different types: the red zinc ore and the white zinc ore (Reichert & Borg in press). Both are mainly determined by the Fe- and Pb concentrations within and occur spatial separated. The ‘red zinc ore’ occurs mainly residually in the place of the former sulphide ore and shows high amounts of Fe-oxyhydroxides, lead carbonates and some non-sulphide zinc minerals. Fe-oxyhydroxides precipitated and remained within the oxidation zone due to their low solubility.

The white zinc ore occurs commonly within karst breccias of the carbonate host rock. Here,
the non-sulphide zinc minerals occur as cement and as partial replacement of dissolution-collapse breccia clasts. White zinc ore occurs typically at a distance of some 10’s to several 100’s of metres from the sulphide protore and its oxidation zone. White zinc ore commonly underlies the former oxidation zone and the red zinc ore. The most common non-sulphide Zn-Pb minerals in the studied area are hydrated zinc-silicates (*e.g.* hemimorphite: $\text{Zn}_3\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$ and zinc (hydro-) carbonates, such as hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) and smithsonite ($\text{ZnCO}_3$).

3 HEMIMORPHITE, OCCURRENCE AND MECHANISMS OF FORMATION

In most cases the occurrence of hemimorphite is associated with other non-sulphide zinc minerals such as smithsonite or hydrozincite. Hemimorphite occurs commonly in veins and open spaces of fault-zones and -breccias, and in the matrix of fault breccias as euhedral crystals, which have grown perpendicular to the underlying surface of fractures and spaces (Fig. 3). The size of the hemimorphite crystals ranges from sub-mm up to several millimetres. In some cases, several generations of hemimorphite can be distinguished. This phenomenon of several stages of hemimorphite precipitation is common, especially at the Mountain Ore Body (MOB) of Mehdi-Abad (Reichert *et al.*, 2003).

The occurrence of hemimorphite is mainly limited to the red- and white zinc ore. The barren host rock shows no or only subordinate amounts of hemimorphite. The formation of hemimorphite is closely linked with different stages of the non-sulphide ore forming processes. The formation of carbonate-hosted non-sulphide zinc deposits can be subdivided into two geochemical different stages that influence the stability and the effectiveness of both zinc (hydro-) carbonates and zinc (hydro-) silicate minerals. These main stages are the oxidation stage and the post-oxidation stage (Reichert & Borg, in press).

The first stage is characterised by acidic conditions in the oxidation zone and the vicinity of the sulphide protore. The oxidation process of the sulphide protore (mainly oxidation of pyrite) lead to the formation of sulphuric acid and stable low pH-values. The products of this oxidation influence the geochemical behaviour of the oxidation system in several important ways: The gypsum- and hydrous ferric oxide armour the carbonates of the host rock and inhibit the host-rock from a fast neutralization reaction with the acidic solution (Humicki, 2004; Huminicki & Rimstidt, 2004). This armouring establishes and stabilises an acidic low pH value within the oxidation zone and the adjacent strata in spite of the carbonate host rock, which usually provides high capabilities to neutralise acidic solutions.

At this oxidation stage, the most portions of the zinc precipitates as smithsonite and other
zinc carbonate minerals as soon as their stability is reached mostly trapped in karst breccias. Zinc silicate minerals will form if H$_4$SiO$_4$(aq) is available and the partial pressure of CO$_2$(g) (P$_{CO2(g)}$) is low (log$_{PCO2}$ < -0.5 kPa). Higher values of P$_{CO2}$ (log$_{PCO2}$ > -0.5 kPa) support the precipitation of hydrozincite or smithsonite. These low P$_{CO2}$ occur preferentially in arid climates with low biological activities within the soil and deep groundwater tables. High P$_{CO2}$ values are most probable present at the oxidation stage of the sulphide ore due to acid neutralisation reaction with the carbonate rock (Reichert & Borg, in press, Germain et al. 1994).

At the oxidation stage of the sulphide ore the zinc concentration can be assumed to be relatively high. Comparable fluids from acid mine drainage (AMD) waters reach zinc concentrations of up to 2.41·10$^{-2}$ mol·l$^{-1}$ and pH values ranges from pH 1.7 to 7.9 (Gazea et al., 1996). A concentration of at least 1.2·10$^{-2}$ mol·l$^{-1}$ of H$_4$SiO$_4$(aq) is necessary for the precipitation of 2.41·10$^{-2}$ mol·l$^{-1}$ Zn$^{2+}$ as hemimorphite. H$_4$SiO$_4$(aq) is a weak acid and dissociates appreciably about two pH units above neutrality (Dove & Rimstidt, 1994). The availability of dissolved silica is limited by the solubility of SiO$_2$ in water and the slow dissolution rate of SiO$_2$. Solubility calculations show that the H$_4$SiO$_4$(aq) concentration in carbonate-buffered solutions reaches 9.6·10$^{-4}$ mol·l$^{-1}$ for crystalline quartz and up to 2.0·10$^{-3}$ mol·l$^{-1}$ for amorphous SiO$_2$. The solubility of silica phases increases drastically from crystalline quartz to amorphous silica (Dove & Rimstidt, 1994).

However, silica concentrations are to low at the oxidation stage for a quantitative precipitation of zinc as silicate minerals at the oxidation stage.

After the oxidation of the sulphide ore the geochemical system changes drastically. At the post-oxidation stage the pH values increase and the concentration of Zn$^{2+}$ and other metal ions drop to low values according to the solubility of hydrozincite/smithsonite and other non-sulphide zinc minerals. Thus, the concentration of Zn$^{2+}$ drops down to 1,1·10$^{-6}$ mol·l$^{-1}$ (e.g. according to the solubility of hydrozincite). At this stage the metal transport of Zn with aqueous solutions is limited.

The data and calculations presented by Takahashi (1960), McPhail et al. (2003) and Ingwersen (1990) indicate that the zinc silicates hemimorphite and willemite are the least soluble and most stable Zn-minerals at pH around 7 (at atmospheric P$_{CO2(g)}$) compared with zinc carbonates. Under these conditions, hemimorphite is more stable than hydrozincite or smithsonite and should precipitate and replace these zinc (hydro-) carbonates (Fig. 3). At this post-oxidation stage, the successive contact with H$_4$SiO$_4$(aq)-bearing descending fluids leads to the formation of zinc silicates over the time.

4 CONCLUSIONS

In most cases, the formation of large quantities of zinc silicates is not associated with the oxidation stage of sulphide ores. As long as the oxidation process is still active, only subordinate amounts of zinc silicates will precipitate.

The formation of zinc silicates becomes an important process at the post-oxidation stage. During the post-oxidation stage zinc silicates, such as hemimorphite precipitate in open spaces and pores and are commonly intimately associated with the red- or white zinc ore (smithsonite/hydrozincite) replacing Zn-carbonate minerals.

Hemimorphite is common and forms quantitative amounts in systems, which are able to provide sufficient concentrations of silica. The amount of hemimorphite within carbonate-hosted non-sulphide zinc deposits correlate with the availability of H$_4$SiO$_4$(aq), which is mainly controlled by the chemistry of the host rock and the strata that are in contact with the aqueous solution. The occurrence of high quantities of late-stage related hemimorphite in the non-sulphide ore of Mehdi-Abad corresponds.
with the chert-rich limestone, which hosts the non-sulphide ore. In contrast, hemimorphite is less common at Iran-Kuh, since the SiO\(_2\)(s) content of host rock and the overlying strata is much lower.

ACKNOWLEDGEMENTS

The author would like to thank PARS KANI Mineral Industries Research and Development Co, Iran and especially Zaker Salehi, A. Houshmand-Zadeh, and Rashidi Bahman for the hospitality, logistical support, and stimulating scientific discussions. Furthermore, the author is grateful to the management and staff of BAMA Mining Co. Esfahan, and management of the Mehdi Abad project, and Kuh-e-Surmeh mine for their hospitality and support. Anglo American has generously sponsored logistical and analytical work.

REFERENCES


Huminiki, D.M.C. & Rimstidt, J.D. (2004): The Effect of Secondary Precipitates on the Dissolution Rate of Calcite in Acid Mine Drainage Solutions. Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg


Numerical modeling of oxide-type Ni-laterite deposits: preliminary results

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ABSTRACT: The eastern Cuba Ni-laterite deposits are classified as oxide-type. In these deposits, Ni and Co occur mainly in the limonite zone, composed of Fe oxyhydroxides as the dominant minerals in the upper part of the profile. The quantitative mineralogical composition along the laterite profile, together with a structural characterization of the main crystalline phases present, are obtained by X-ray diffraction full profile matching (Rietveld method). On the basis of these results and on chemical and hydrological data, we try to build a quantitative reactive transport model to explain the formation of the laterite profile. One important difficulty encountered in these initial attempts is the present lack of understanding of the stability field of lizardite.

KEYWORDS: Nickel, Ni-Laterite, Reactive transport, Cuba

1 INTRODUCTION

Ni laterite deposits are currently producing about the 40% of the world's annual Ni (Dalvi et al. 2004). Three main types of deposits can be distinguished based on the mineralogy of the dominant mineral carrier of Ni (Brand et al. 1998, Gleeson et al. 2003). In the oxide-type deposits, the upper limonite is the main ore horizon, and the ore minerals are Fe oxyhydroxides (mainly goethite).

The studied profile (Fig. 1) come from the Punta Gorda Ni-Co laterite deposit, located in the Moa mining district (northeast of Cuba). This deposit can be classified as oxide-type (Oliveira et al. 2003) and, as many Cuban deposits, the typical section through the profile consists of four principal horizons, from bottom to top: (1) serpentinized peridotite, (2) saprolite, (3) limonite and (4) ferricrete (Lewis et al. 2006). Occasionally the profile may contain gabbro bodies altered to bauxite. The Ni and Co is contained mainly in the limonite zone but doubts about the detailed location of metals (adsorbed onto the surface or in solid solution) still remain.

This particular profile has been characterized mineralogically by qualitative and quantitative powder X-ray diffraction and by whole rock analyses (ICP-MS, 43 elements). In addition, ground waters from similar profiles in the Moa district were also sampled and analyzed.

In this work, we present the mineralogical...
composition along the laterite profile obtained by quantitative diffraction and try to reproduce by reactive transport modeling this observed profile, on the basis of different hypotheses regarding parent rock, uplift rate, climate and other intrinsic parameters as porosity, hydraulic conductivity and others.

2 QUANTITATIVE XRD

Representative fractions of the samples were powdered below 30µm and back mounted in the holder to avoid preferential orientation. Quantitative analyses were achieved by full diffraction profile matching method (Rietveld method), using the TOPAS V2.1 software. Results are given in Fig. 2. The detailed crystallographic characterization of the phases may afford relevant information regarding the genesis of the profile.

Goethite, which contains most of the Ni, is the major phase. The refined parameters were: cell parameters, atomic occupation factors and crystal size. The cell volume is always smaller than the accepted value for goethite, indicating some substitution (2-17%) of Fe by Al, in agreement with the atomic occupation factors encountered. Crystallite domain size is rather small (11-23 nm), indicating a large specific surface estimated in 65-30 m²/g. This value suggests the importance of the goethite surface in the retention of metals, and plays an important role in the kinetics of dissolution-precipitation. In most samples, goethite coexists with maghemite and haematite. In only one sample, goethite coexists with lizardite (M8, 33m), and is absent in deeper samples (M9 and M10).

Maghemite, appears in all the profile beneath the first 10 m. The refined cell parameter is very similar to the accepted value of 8.3505 Å, indicating a composition near the ideal Fe₂O₃. Magnetite, which is considered a precursor of maghemite, has not been found.

Haematite, the second most important Fe-bearing mineral, has almost an ideal composition and structure. However it presents a rather low crystallite size (30 to 40 nm). In several samples enriched in Mn (M3 and M6), haematite is completely absent.

Gibbsite, is a less soluble alteration product of plagioclase from the gabbro bodies in the parent rock. The cell volume suggests some degree of substitution of Al by Fe. Gibbsite is more abundant in the top of the limonitic horizon and in ferricrete.

Serpentine minerals present are the lizardite polotypes 1T and 2H1, the former being dominant, and the latter minor, less crystalline, with many stacking faults. The cell volume is slightly bigger than that corresponding to the ideal end member Mg₃Si₂O₅(OH)₄, due to substitution of some Mg by Fe and minor Ni and Mn, as confirmed by chemical analyses. In the deeper sample M10, lizardite appears together with olivine, enstatite and maghemite as the only iron oxide. It is apparent that magnetite formed by the hydration of olivine is quickly transformed to maghemite in atmospheric conditions, and later on, in goethite.

The insufficient data available for a realistic evaluation of the stability field of serpentine polymorphs, as well as their equilibrium constants and dissolution rates, poses the main problem when trying to approximate the real observed profile by reactive transport modeling (Evans 2004).

Other minor phases encountered are asbolane, appears only in sample M3 corresponding to the altered gabbro body, pyrochroite (1.5 wt.% in M6), and quartz, (1.6 wt.% in sample M8, coexisting with lizardite).

3 HYDROGEOCHEMICAL MODEL

The geochemical calculations were performed with the simulator RETRASO (Saaltink et al. 2004), in two steps. In the first simulation, the equilibrium between the minerals forming the parent rock and pore water is attained as a function of the equilibrium constants, dissolution-precipitation rates and time. This simulation allows to find the approximate composition of the initial water pore solution. In the second step, this pore water will mix with percolating water from rain, and a column of downwards reactive transport is numerically simulated in isothermal conditions. Along the column, pos-

Figure 2. Quantification of mineral species.
sible reactions include aqueous complexation, gas dissolution and dissolution/precipitation of minerals (Figs. 3 and 4).

The modeled parent rock consists of a harzburgite impregnated by plagioclase according to the following modal proportions and compositions: olivine 70% (Fo0.9-Fa0.1); pyroxene 16% (En0.9-Fe0.1); anortite 14%. A fraction of serpentine, could also be included. However, given the great instability of olivine and pyroxene in presence of water, serpentine appears immediately, and its introduction as mineral forming the parent rock would not change significantly the final results. Nickel is still not included in the model, which considers only major components. Nevertheless, in oxide laterite profiles, Ni concentrates mainly in goethite.

The new precipitating minerals resulting from alteration are lizardite, goethite and gibbsite. The reason for excluding maghemite and haematite as iron bearing minerals is the very small Gibbs free energy of the reactions relating these minerals with goethite, that makes their presence rather contingent, depending on small climatic variations. As a rule, maghemite changes its structure to haematite, and is absent in the top of the profile, which samples the most ancient altered parent rock not eliminated by erosion. In addition, haematite may result from dehydraion of goethite produced in drier levels, located in the top of the profile as well.

Table 1. Conditions used for the reactive transport simulations.

<table>
<thead>
<tr>
<th>Geometry and length of the initial rocks</th>
<th>A column of 200 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>25° C</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.05</td>
</tr>
<tr>
<td>Permeability</td>
<td>$10^{-15}$ m$^2$</td>
</tr>
<tr>
<td>Molecular diffusion</td>
<td>$10^{-9}$ m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Dispersivity</td>
<td>0.5 m</td>
</tr>
<tr>
<td>Flux</td>
<td>$3\cdot10^{-9}$ m$^3$ m$^{-2}$ s$^{-1}$, which corresponds to one tenth of the annual precipitation in tropical to subtropical climate</td>
</tr>
<tr>
<td>Saturated zone</td>
<td>the whole column</td>
</tr>
<tr>
<td>Initial pore water</td>
<td>in equilibrium with lizardite, goethite and gibbsite, and a partial pressure of oxygen of 0.05</td>
</tr>
<tr>
<td>Rain water</td>
<td>distilled water in equilibrium with atmospheric oxygen (pH=5.65)</td>
</tr>
<tr>
<td>Duration of the simulated process</td>
<td>10 Ma</td>
</tr>
</tbody>
</table>

In these preliminary attempts, the reactive transport simulations have been performed in simplified conditions (Table 1); these will become more complete in future work, that will include a better evaluation of equilibrium and kinetic constants for the phases involved, the possible influence of minor, but important elements like Ni, (adsorption effects), and flow velocities.

4 RESULTS AND DISCUSSION

In Fig. 3 the calculated volume fractions of minerals as a function of depth, at time 10 Ma are shown. The same results recalculated on the basis of the exclusion of lizardite, given in Fig. 4, would be a better approximation to real existing laterite profile. It is noteworthy that, once all hydrated magnesium silicates is eliminated, there is a big volume contraction: oxide laterites represent only 7% volume of the parent rock.
The main trends of the mass balance for iron and aluminium, and the corresponding simulated chemical profiles are coincident with real observations. In particular, it is shown that all iron contained in olivine and pyroxene would remain in the laterite profile. However, in the conditions of the present simulation, a great deal of magnesium and silicon forming lizardite, that is considered to precipitate in equilibrium, is not leached, and remain in the altered rock. The pre-eminence of lizardite and other hydrated magnesium silicates (talc, chlorites) makes the difference between two main typologies of lateritic profiles, and poses the main problem to be solved by numerical simulation. We envisage several hypotheses to be proven in future work: a) lizardite does not precipitate in the higher horizons, due to kinetic factors (i.e. high supersaturation needed); b) equilibrium constant used for lizardite is not correct; c) pH of rain water is lower than the values introduced (i.e. due to organic matter influence and/or atmospheric CO2); d) more than one rock zone has to be taken into account (i.e. saturated versus not saturated zone). In summary, the model is still too simplistic and future attempts should include a revision of the chemical and kinetic constants for lizardite, the inclusion of nickel as a component, a more realistic geometrical model formed by two or more rock zones, the possible influence of the uplift and erosion rates, and a complete characterization of the percolating water.

ACKNOWLEDGEMENTS

This research has been funded by the Spanish Project CGL2006-07384/BTE and the by SGR00589 of the Catalonian Government. The authors thank Prof. Carles Ayora for his useful help and advise.

REFERENCES


TOPAS, General Profile and Structure Software for Powder Diffraction Data, V2.1 Bruker AXS GmbH, Karlsruhe, Germany.

Mineralogy of oxide and hydrous silicate Ni laterite profiles in Moa Bay area, northeast Cuba

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ABSTRACT: The nickel laterite deposits of Moa Bay area are part of a large province of nickel laterites in eastern Cuba. The mineralogy of principal ore-bearing phases indicates that both oxide- and hydrous silicate-type profiles are present. The former weathering profile (e.g. the Yagrumaje deposit) comprises a thick limonitic horizon that overlies a thin saprolite, and the Ni and Co occur mainly in the limonite zone associated with goethite (∼1.4 wt.% Ni), maghemite (up to 8 wt.% Ni), lithiophorite (∼8.1 wt.% Ni, ∼4.5 wt.% Co). The later Ni laterite profile (e.g. the Yamanigüey deposit) comprises a zone of saprolite and saprolitized harzburgite, capped by a thin limonite horizon, and the ore minerals are Ni-rich lizardite (up to 3.7 wt.% Ni) and hydrous Mg-Ni silicates (“garnierites”, up to 32 wt% Ni) occurring deeper in the profile.

KEYWORDS: Nickel, Oxide, Hydrous silicates, Ni-Laterite, Moa, Cuba

1 INTRODUCTION

Nickel laterite profiles have been classified into three types on the basis of the dominant mineralogy developed in the profile (Brand et al. 1998). In general, based on mineralogy of principal ore-bearing phases (silicated or oxidized), northeast Cuba Ni-laterite deposits are classified as oxide-type. In this case, the upper part (limonite zone) is the main ore horizon. According to Gleeson et al. (2003) the best known example of Ni-laterite deposits of oxide-type, in commercial production, are those of Moa Bay area in northeast Cuba. However, these deposits contain oxide and hydrous silicate ores in varied proportion. In some cases, silicate ore dominates the laterite profiles forming typical hydrous silicate-type deposits. Despite their economic importance, relatively little has been published on the Cuban laterite deposits.

Here, we report new data on the mineralogical composition and mineral chemistry of two Ni-laterite profiles in northeast Cuba (Fig. 1). These profiles come from Yagrumaje Norte and Yamanigüey economic deposits, located in the Moa mining district (Moa Bay in the English literature). Laterite mineralogy was investigated using X-ray diffraction, optical microscopy, scanning electron microscopy and electron probe microanalysis. The primary aim of this study is to identify the major Ni-bearing phases.

2 GEOLOGICAL SETTING

The largest area of exposed serpentinitized peridotites in the whole Caribbean occurs in northeast Cuba in the Mayari-Baracoa Ophiolite Belt. The eastern part of this belt is constituted by the Moa-Baracoa massif (Fig. 1, Proença et al. 1999, Lewis et al. 2006). The Moa-Baracoa massif is comprised of mantle tectonites (> 2.2km thick) topped by a thin crustal section made up of lower gabbros (ca. 300 meter thick) and discordant basaltic rocks with back arc basin affinity (Marchesi et al. 2005). The ultramafic rocks correspond mainly to harzburgites (more than 70%) and to a lesser extent to dunites and impregnated peridotites with clinopyroxene and plagioclase. They have a variable degree of serpentinization that in shear or fracture zones can reach up to 95% of the whole rock (typical serpentinite). The peri-
dotites are cut by dikes of gabbro and pegmatite gabbro (Proenza et al. 1999, Marchesi et al. 2006). The emplacement of the ophiolite took place in the Maastrichtian to early Danian.

The Moa laterite deposits are part of a larger province of nickel laterites in northeast Cuba. The deposits were developed over serpentinized harzburgite with weathering and laterization commencing during the Miocene (Lewis et al. 2006). The elevation above sea level of the peneplain surface of the deposits varies from 60 to 360 m, and the weathering mantle attained a considerable thickness (10-50 m, Linchenat & Shirakova, 1964).

3 THE LATERITE PROFILES AND MINERALOGY

The Ni laterite profile of the eastern Cuban deposits has been divided into various zones and sub-zones by mine personnel and Cuban geologists. The nomenclature of these zones does not follow the recommended classification of Ni laterite deposits (e.g. Lavaut 1998). However, in general terms one can recognize, in eastern Cuba, the same horizons that have been described in other Ni laterite deposits of the world (e.g. Brand et al. 1981, Gleeson et al., 2003), the laterite profile is composed of four principal horizons (Lewis et al. 2006), from bottom to top these are: (i) serpentinized peridotite, (ii) saprolite, (iii) limonite, (iv) ferricrete. The studied laterite profiles from Yagrumaje and Yamanigüey deposits exhibit variation in total thickness and the thickness of individual horizons (Fig. 1).

3.1 The lateritic profile at Yagrumaje

The lowest part of the profile is represented by non-weathered serpentinized harzburgite. This horizon is overlain by a saprolite zone (4 m thick), which is characterized by the preservation of the primary fabric. This horizon is fine grained, and contains remnants of the protolith. The mineralogical composition is dominated by lizardite, which replaces original serpentinized olivine grains. Small amounts of goethite and chromite are also present. The saprolitic zone passes upwards in the section to a limonite zone (19 m thick), which is the horizon of economic interest. This zone consists mainly of goethite (> 50 wt.%), and minor maghemite, haematite and gibbsite (Fig. 2). Goethite grains are locally replaced by haematite. The ground mass is very fine grained, and evidence of the original texture of the protolith has been destroyed. Maghemite is more abundant towards the lowest part of the limonite horizon (11 wt.% at 18 m deep; 1 wt.% at 8 m deep), while haematite is dominant in its upper part. Finally, a concentration of Mn-Co-Ni oxide minerals (cryptomelane and lithiophorite) occur at the limonite horizon, particularly at the lowest part. These Mn oxides occur as veins and coatings or concretions along fractures.

3.2 The lateritic profile at Yamanigüey

Unweathered serpentinized harzburgite (parent rock) in this section is similar to that in the Yagrumaje profile. The profile is characterized by a thick saprolite horizon (9 m thick), followed by a thin limonite horizon (3 m thick). The horizon of economic interest is the lower saprolite. This zone consists of variably altered serpentinized harzburgite in which most of the original structure and textures in the peridotite are preserved.
The saprolitized harzburgite is usually pale green, and in the upper part the material is more soft and has a wide colour range from yellow to reddish-brown. Lizardite and second generation of Ni-rich lizardite are the major crystalline phases occurring with minor magnetite, chromite and goethite. Ni-rich lizardite replaces and pseudomorph former serpentinized olivine and orthopyroxene, and is locally transformed into goethite. In addition, the saprolite zone contains hydrous Ni-Mg silicate veining, follow fractures and grain boundaries (Fig. 3A).

4 MINERAL CHEMISTRY OF THE NICKEL-BEARING PHASES

The average Ni content of olivine in basal harzburgites of both studied profiles is 0.4 wt.%, whereas the Ni content of orthopyroxene is very low (Ni < 0.1 wt.%).

4.1 Yagrumaje deposit: oxidized lateritic ore

The principal minerals that contain Ni in the limonite horizon of the studied profile are goethite, maghemite and lithiophorite (Fig. 2). In contrast, haematite, chromite and gibbsite have low Ni contents.

The nickel content in goethite varies from 0.3 to 4.5 wt.% (average value = 1.4 wt.%), whilst cobalt content ranges between 0.1 and 1.7 wt.% (average value = 0.27 wt.%). Goethite exhibits variable proportions of Al (substitution of Al$^{3+}$ for Fe$^{3+}$). Al/Fe ration increases toward the top of the profiles (up to 8.2 wt.% Al$_2$O$_3$). Minor amounts of Cr$_2$O$_3$ (< 2.5 wt%) and MnO (<1.9 wt%) also were detected.

Maghemite shows Ni contents range from 0.5 to 8 wt.%, and up to 1.1 wt.% of Co$_2$O$_3$ (Fig. 2B).

The analyzed lithiophorite grains may contain up to 6.0 wt.% Co and up to 12 wt.% Ni. These Mn phases are the main hosts to Co mineralization.

4.2 Yamanigüey deposit: hydrous silicate ore

The second generation of lizardite and the hydrous Mg-Ni silicates are the major Ni-bearing silicate phases. Nickel content in Ni-rich lizardite ranges from 1.7 to 3.7 wt.%, in contrast with primary lizardite, which is no more enriched in Ni than the olivine (~0.4 wt.%).

Figure 2. Back scattered electron images showing Ni-rich maghemite in Yagrumaje deposit (oxide type Ni laterite profile)

Figure 3. Back scattered electron images showing hydrous Mg-Ni silicate in Yamaniguey deposit (hydrous silicate type Ni laterite profile).

5 DISCUSSION AND CONCLUSION

In the Yagrumaje Ni-laterite profile, a significant fraction of nickel is associated with goethite and maghemite in the limonite zone, and can be classified as an oxide-type profile.

The analyzed goethite contains up to 4.5 wt. % of Ni, but it is not clear if all Ni occur in solid solution, or as a separated phase. However, isomorphous substitution for Fe$^{3+}$ by Ni within natural goethite has been confirmed with EXAFS data (Carvalho-e-Silva et al. 2003). The charge balance from Ni$^{2+}$ for Fe$^{3+}$ substitution in goethite structure are likely to be locally charge-balanced by the substitution of OH for O$^-$. On the other hand, Ni-rich maghemite may has been produced by oxidation of magnetite, but this mineral has not been found. Other mechanism suggested is maghemite formation by dehydroxylation of Fe oxyhydroxides (Anand & Gilkes 1987).
In contrast, in the Yamanigüey Ni-laterite profile most of the nickel occurs in the saprolite zone and can be classified as a silicate-type profile (highest-grade Ni laterites). In this case, Ni is leached from the limonite horizon and moves downwards through the profile, forming concentration, with Si and Mg, within the saprolite horizon. Nickel is mainly derived by the recrystallization of goethite to haematite, which cannot incorporate the Ni formerly contained in the goethite.

Mineralogical composition suggests that the two laterite profiles studied had different weathering histories. This difference may be the result of different serpentinization of the protolith, drainage and position of the water table.

ACKNOWLEDGEMENTS

This research has been funded by the Spanish Project CGL2006-07384/BTE and the by SGR00589 of the Catalonian Government.

REFERENCES


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"Digging Deeper" C.J. Andrew et al (editors)
Geology and mineralogy of the Shevchenko lateritic Ni-Co deposit, Kazakhstan

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ABSTRACT: The Shevchenko deposit in western Kazakhstan, discovered by Soviet geologists and now controlled by Oriel Resources plc, contains a total resource of 104Mt @ 0.79% Ni. The deposit developed on ophiolites located in the Trans-Uralian Zone of the Urals, obducted onto the Kazakh continent during the Uralide Orogeny and deeply weathered in a number of stages up to the Tertiary. The deposit is dominated by nickeliferous smectites with subordinate nickel-bearing iron oxides and hydroxides. Weathering was variably developed on the serpentinites with deeper weathering controlled by distinct structural trends.

KEYWORDS: Nickel laterite, smectite, Urals, structure

1 REGIONAL GEOLOGY

The Shevchenko lateritic nickel deposit developed on ophiolitic ultramafic rocks of the Pzitobolsko-Akkarginski Complex (PAC) and lies in the Trans-Uralian zone (TUZ) of the Urals (Fig.1). The geology and evolution of the TUZ is not well understood due to poor exposure since it only crops out in the South Urals. It has been traced northward by its aeromagnetic signature and is correlated with parts of the Altaiid collage (Herrington et al. 2005a). The best-known part of the TUZ is the Andean-type Valerianovka arc, which is thought to have formed by subduction under the Kazakh craton margin. Ophiolite units and high-pressure rocks are reported at the western margin of the TUZ (Puchkov, 2000) and these include the PAC and a similar complex hosting the Buruktal nickel deposit farther to the south. These ultramafic complexes are likely to represent obducted fragments of oceanic crust relating to the Urals palaeo-ocean and are therefore interpreted to be Silurian or Devonian in age (Fig. 1).

The ultramafic complex on which the Shevchenko nickel mineralization is developed now forms a series of low, rounded, hills that stand some 35-60m above the surrounding flat steppe, which forms a plain at around 330m asl. In addition to the Shevchenko deposit, the Zhitiqara region immediately to the north is...
host to a giant asbestos (chrysotile) deposit, currently accounting for some 20% of world production.

The host ultramafic complex extends for 36km along the long axis and is 5-6km wide. It has been largely altered to serpentineite, although rare unaltered sections suggest that the parent material was primarily dunite, with orthopyroxene (enstatite) forming less than 10% of the rock, by volume. The serpentinites are cut by sub-horizontal sills and dykes of fine to coarse-grained gabbros and pyroxenites. These bodies are typically only a few centimetres thick, but have lateral extents of several metres.

The serpentinites of the PAC are surrounded by Proterozoic gneisses and subordinate schists intruded by granodiorite and diorite of the Milutinski Complex and diorites and gabbros of the Sokolovsko-Sarbaiski Complex, which together form part of the Valerianovka arc sequence. This arc sequence hosts the giant Kachar and Sarbai magnetite deposits (Herrington et al. 2005). Fault-bounded outcrops of Devonian marble and Silurian basalt lie adjacent to the eastern flank of the ultramafic complex and further to the east, thrust slices carry a variety of Upper to Lower Proterozoic, Silurian, Devonian and Carboniferous metasediments.

2 DISCOVERY AND PROJECT HISTORY

The Shevchenko deposit was discovered in 1952, using a combination of regional mapping, which identified the ultramafic host rocks and then by geophysical and geochemical exploration, which identified the individual nickel-cobalt ore bodies. Soviet reserve statement was approved in 1967 of 101.7Mt of ore containing 730,700t of Ni and 51,208t Co.

Wardell Armstrong International undertook a preliminary evaluation of the project in September 2003 as part of a due diligence study, conducted on behalf of Oriel Resources plc. In November 2003 an exclusive option for Shevchenko was signed by Oriel and in May 2004 Oriel increased its stake in the Shevchenko project to its current holding of 90%. The local Kazakhstan partner Muzbel LLP holds the remaining 10%.

3 UPLIFT AND WEATHERING

Three distinct periods of lateritisation are recorded since the Palaeozoic in the Urals, responsible for both bauxites and nickel laterites. These events occurred broadly in the Upper Triassic, Lower-Upper Cretaceous and Oligocene-Miocene (Mordberg 2005). At Shevchenko, the age constraint on the weathering is poor but both the Cretaceous and Tertiary weathering events are likely to have affected the region.

The Ni silicate and oxide mineralization occurs in broad flat steppe terrain where residual weathered near-surface material lies directly over - and hence is largely directly derived from - the underlying serpentinite. However, differential erosion has resulted in a partly variable weathered layer, giving rise to a variable spatial distribution of the laterite and a fluctuation in its thickness.

4 GEOLOGY AT THE DEPOSIT SCALE:

There are eight individual zones that make up the Shevchenko deposit called Shevchenko, Tarasov, Grigoriev, Blizhny, Jubilee, Uzhny (see Fig. 2).

These individual zones are up to 4 km long and 1.5 km wide and are separated from each other by barren areas.

Individual ore bodies such as Shevchenko are in the order of 4km long and 1.5km wide. Mineralization in these broad areas is generally relatively thin of the order of 10-15 metres. In
addition to the broad thin areas of mineralization there are locally thicker zones of mineralization, up to 50 metres thick or more. Grade distribution can be locally quite variable but does show quite good continuation at the scale of the individual ore body, particularly within the thicker, central parts of ore bodies.

The ore consists of the weathering products that are classified into three major groups. An ideal profile extends from surface to unaltered rock and contains something of each of the zones:

1. Limonite zone: This is an area dominated by iron oxides and residual clays. The iron oxides include limonite, hematite and goethite and manganese oxides are also locally present. The primary serpentine texture has virtually been completely destroyed.

2. Nontronite clays: The nontronites are a grey/buff clay group, replacing serpentinites. The primary texture is mostly destroyed but this zone may carry clasts of saprolite and weakly weathered serpentinite.

3. Saprolite: The saprolite zone is very strongly weathered but generally competent. It shows well-developed relict textures of the primary serpentinite and grades into fresh rock at the base. Some sections have undergone extensive silicification and partial replacement by siliceous limonite. This zone commonly contains considerable amounts of magnesite (MgCO₃) in seams up to 10 cm thick, generally close to the transition from saprolite to relatively unaltered serpentinite.

The above description is of an idealized profile, however, there is considerable horizontal variation across individual deposits and it is possible to pass from any member of the sequence to any other and parts of the sequence may be repeated. For example limonite-rich laterites have been found below fresh serpentinites, suggesting that some sub-horizontal structure may have acted as channel for enhanced fluid flow leading to more aggressive weathering along its length.

The areas of greatest deposit thickness are also commonly associated with areas of highest contoured Ni and Co grades and are the most economically significant parts of the deposits. They have preferred orientations and the two predominant structural trends at the deposit scale are NNE (020°) and ENE (070°). At the regional scale, the ultramafic belt is cut by a series of major faults, trending NNE, NE and ENE and it seems likely that these regional scale faults are influencing the distribution of mineralization at the deposit scale. These elongated ellipsoidal zones of significant mineralization are of the order of 200 metres by 50 metres and are often twinned with similar nearby parallel or offset zones, suggesting fault control in close-set arrays.

Abrupt changes in the mineralized zone occur, probably as a result of these fracture systems, represented by changes from zones of thin sub-continuous mineralization into the localized deeper structurally controlled zones. Locally joint planes that have been filled by silica are also features marking abrupt changes in lithology as well as original internal magmatic contacts and dykes which seem to have had a role in controlling the subsequent weathering process.

Within the limonite zone, there are also small-scale zones associated with intense iron and manganese enrichment, probably controlled geochemically (Eh, pH).

5 MINERALOGY

The mineralogy of the protolith is dominated by the serpentine minerals antigorite and berthierine. The mineralogy of the nickeliferous zones is dominated by weathered serpentine products, comprising clay minerals iron oxide-hydroxides, and ubiquitous silica. The upper ochre-rich zones are principally made up of admixtures of limonite (Fe₂O₃·nH₂O), haematite (Fe₂O₃) and goethite (FeO(OH)), which in the limonite zone generally form the bulk of the laterite and of these limonite is by far the most common iron species. Smectite group clays (forming from the breakdown of pre-existing serpentinite group minerals) are dominant in the iron-poor, parts of the laterite and are represented by grey to green clays, which have previously described as nontronites.

A generalized formula for the smectite group is \( A₀₃D₂₋₃\left[T₄O₁₀\right]Z₂·nH₂O \) where usually \( A = \) Ca, Na; \( D = \) Mg, Fe²⁺, Fe³⁺, Li; \( T = Si, Al; Z = OH, F. \) In the case of nickel laterites, Ni substitutes into the D site, replacing Mg directly. In the older Soviet reports for the deposit, phases identified have been variously described as cerolite (stevensite), saponite or nontronite but these are all smectites, so it is likely that using such precise names is not helpful.

Preliminary XRD data collected at the Natural History Museum has identified a poorly crystalline smectite to be present in all the sam-

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ples from the ‘nontronite zone’. Preliminary SEM data confirms the presence of a phyllosilicate, which is consistent with being classified as a Ni-rich trioctohedral smectite (Dana nomenclature) or ‘Talc’ (Stunz nomenclature) with an approximate formula of Ca\((0-0.1)\)Fe\(0.25\)Mg\(0.75\)Ni\(2\)Si\(4\)Al\(0.1\)O\(10\)[OH]\(2\).nH\(2\)O.

This composition lies in the range of compositions quoted for willemite (formula \((\text{Ni,Mg})_3\text{Si}_4\text{O}_{10}[\text{OH}]_2.4\text{H}_2\text{O}\)), close to the Ni end member nickel smectite (or ‘talc’) called pimelite. SEM studies indicate a complete range of Ni-bearing smectite compositions from this to a composition, which approximates to the mineral formula: Ca\(0.1\)(Fe\(1.8\)Mg\(0.3\)Al\(0.2\)Ni\(0.2\))Si\(4\)O\(10\)[OH]\(2\).nH\(2\)O. Further detailed XRD studies are ongoing to refine the structures of the Ni-silicate phases present. Other mineral species present include manganese oxides (most likely one or more of the isochemical MnO\(_2\) series) and additionally poorly crystalline asbolane \((\text{Co,Ni})_{1-y}\text{Mn}_{2-y}\text{O}_2\cdot x\text{H}_2\text{O}\) is common, forming coatings on parting plane surfaces and as aggregates within clay zones. These manganese oxides are important hosts for both Ni (up to 11 wt%) and Co (up to 3 wt%).

Magnesite (MgCO\(_3\)) is also very common, in the deeper parts of the saprolite, as dense white amorphous nodules and occasional veins.

Selenite (CaSO\(_4\).2H\(_2\)O), is present as coarse aggregates of crystals typically at the interface of the subsoil with clay-rich laterites. Less common in the profile is opal and its rare apple green nickel-bearing analogue, chrysoprase. XRD confirms that much of the silica is present as quartz. Another rare mineral species present in the laterite profile is stichtite \((\text{Mg}_6\text{Cr}_2(\text{CO}_3)(\text{OH})_{16}.4\text{H}_2\text{O})\) which is a pale purple chromium-bearing secondary mineral.

6 RESOURCE ESTIMATE

Table 1 summarizes the geological resource calculated for Shevchenko for each of the individual deposits and ore type.

7 COMPARISONS TO OTHER NICKEL LATERITE DEPOSITS

Based on their relatively high clay contents the laterite deposits at Shevchenko more closely resemble the clay-dominated nickel laterite profiles that are extensively developed in Australia (e.g. Murrin Murrin). These contrast with the iron oxide dominated nickel laterites such as Goro in New Caledonia and Moa Bay in Cuba.

The Fe contents in the limonites at Shevchenko are lower than those for laterites such as Goro in New Caledonia that were developed in tropical weathering conditions which attain grades of up to 45-50% Fe. This suggests that limonite zone at Shevchenko has a significant clay content. Shevchenko was probably formed under more temperate weathering conditions with a less well drained weathering profile, perhaps characterized by a static water table.

ACKNOWLEDGEMENTS

Oriel Resources Plc is thanked for permission to publish this abstract.

REFERENCES


Supergene Co-Ni-Mn mineralization in Ni-laterite deposits from northeast Cuba

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ABSTRACT: The Mn-Co-Ni oxide minerals in northeast Cuba Ni-laterite deposits occur particularly at the transition zone between saprolite and limonite horizons, as surface coatings on minerals and in fractures. The mineralogical composition is dominated by lithiophorite (up to 8.7 wt. % Ni and up to 12.8 wt. % Co) and asbolane and phases with compositions between those of lithiophorite and asbolane “lithiophorite-asbolane intermediates” (up to 21.7 wt. % Ni and up to 10 wt. % Co). Microprobe analyses suggest the existence of continuous series between lithiophorite and asbolane.


1 INTRODUCTION

In Ni-laterite deposits, Ni and Co may be incorporated in Mn oxides and hydroxides where they have been precipitated by redox reactions (Elias et al. 1981). In addition to asbolane (Ni- and Co-rich), there are other Co minerals as heterogenite and lithiophorite (Chukhrov et al. 1983, Manceau et al. 1987, Llorca and Monchoux 1991). Generally, in these laterite deposits all black Mn- and Co-rich products, essentially amorphous or with a low degree of crystallinity, have been named “asbolane”. These black products constitute an excellent guide for mineralization.

Here, we report the mineralogical results of the study of a Co-Ni-Mn mineralization in northeast Cuba Ni-laterite deposits (Fig. 1), no detailed studies have been previously published on such mineralization. Mineralogy was investigated using X-ray Diffraction (XRD), Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Electron Microprobe (EMPA), Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction (SAED) and Electron Energy Loss Spectrometry (EELS).

2 GEOLOGICAL OCCURRENCE AND SAMPLING

The nickel laterite deposits of northeast Cuba were developed on serpentinitised harzbur-
Ni-Co-Mn mineralization occurs as veins and surface coatings on minerals and in fractures as those described by Llorca and Monchoux (1991) in New Caledonia. The samples were obtained from a lateritic profile located 5 km far from the city of Moa, where the black Co-rich horizon occurs (Fig. 1).

3 RESULTS

3.1 XRD

Figure 2 shows the powder X-ray patterns obtained from the different analyzed fractions. Previously to the XRD analysis the samples were submitted to a magnetic and density separation using both diiodomethane and bromoform as dense liquids. As a result four fractions were obtained, three of them from diiodomethane (1) heavy magnetic fraction (IHM); (2) heavy non magnetic fraction (IHNM); (3) light non magnetic fraction (ILNM) and one from bromoform: (4) lighter non-magnetic fraction (BLNM). X-ray powder diffraction measurements were performed in a Bragg-Brentano 0/20 Siemens D-500 diffractometer (radius = 215.5 mm) with Cu Kα radiation, selected by means of a secondary graphite monochromator. The divergence and receiving slits were of 1° and 0.15° respectively. The starting and the final 2θ angles were 4° and 80° respectively. The step size was 0.03° 2θ and the measuring time of 18 seconds per step. Mineral identification was made with the Diffract (Bruker) software.

Magnetite and maghemite are the dominant phases in the heavy magnetic fraction; furthermore some signs for haematite, asbolane and lithiophorite are presents.

For the rest of samples, lithiophorite is the main phase and it is the only mineral, together with some indications for asbolane, in the heavy non-magnetic fraction.

For lighter fractions also lizardite, Mg-Ni-chlorite, Ni-smectite and goethite have been identified.
3.2 TEM

TEM studies were performed for ILNM fraction. It has been used a Philips CM30 electron microscope working at an accelerating voltage of 300 kV and a field emission JEOL JEM 2010F electron microscope at an accelerating voltage of 200 kV equipped with an EELS device. Both lithiophorite and asbolane have been observed (Fig. 3, 4). EELS analyses of the asbolane reveal higher contents of Ni and Co than in lithiophorite.

3.3 SEM-EMPA

SEM observations were made by a JEOL JSM-840 Microscope while EMPA analyses were performed with a CAMECA SX-50 microprobe. Lithiophorite (Fig. 5) shows high Co content (between 5.32 and 12.82 wt. %), and Ni (4.77 and 8.68 wt. %). MnO2 content varies between 37.15 and 52.58 wt. % and Al2O3 between 14.86 and 20.95 wt. % (Fig. 6).

These compositions point out that lithiophorite from laterite deposits of Moa is Co- and Ni-richer than those from New Caledonia (Llorca & Monchoux 1991).

The other predominant Mn-Ni-Co phases analyzed show chemical compositions which are intermediate between lithiophorite and true asbolane (Fig. 6). These phases have high Ni contents (up to 21.65 wt. %) and Co (up to 9.60 wt. %), MnO2 between 39.32 and 46.29 wt. %, and low contents of Al2O3 (<7 wt. %).

Finally a Mn-rich phase has been analyzed showing MnO2 contents about 80 wt. % and a very low Co content (< 2 wt. %) and Ni (1< wt. %).

4 CONCLUSIONS

The main Mn phases containing Ni and Co in the studied samples are lithiophorite, asbolane and intermediate products between lithiophorite and asbolane (Al-rich asbolane). These results suggest the existence of continuous series between lithiophorite and asbolane. Other-
wise, heterogenite [(Co, Ni), OOH]), a characteristic mineral from laterites of New Caledonia (Llorca et al. 1991) has not been detected. These results confirm that ones obtained by Chukhrov et al. (1983). The presence of lithiophorite implies the availability of Al in the environment which is consistent with the presence of impregnate peridotites (with plagioclase and clinopyroxene) and sills of gabbro in the peridotitic substrate from which the lateritic crust were developed (Proenza et al. 2003). On the other hand the lithiophorite crystal structure does not allow having a great Co and Ni content (Chukhrov et al. 1983). This implies that the main Ni and Co in Mn-phases from the meteoric crust developed on ultramaphic rocks is the asbolane. On the contrary to Ni, Co does not form secondary silicate therefore asbolane and lithiophorite are the main Co phases in the laterites from northeast Cuba.

Figure 6. Cationic composition in terms of Mn-Al-Co of analyzed lithiophorite from eastern Cuba laterite.

ACKNOWLEDGEMENTS

This research has been funded by to the Spanish Project CGL2006-07384/BTE and the by SGR00589 of the Catalonian Government.

REFERENCES


Non-sulphide zinc deposits in Upper Silesia, Southern Poland

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ABSTRACT: Two types of non-sulphide zinc ores, red and white galman, occur in the Ore Bearing Dolomite (Middle Muschelkalk) of the Upper Silesian Zn-Pb district, Southern Poland. The predominant red galman ore comprises Fe oxides, smithsonite, cerussite, Zn silicates, and Ca carbonates. Smithsonites from red galman ore show variable oxygen isotopic compositions from 25.3 to 28.5 ‰ (VSMOW) and constant δ¹³C values of about -10‰ (VPDB). These ores formed by weathering of primary Zn-Pb sulphide ores at least before the Neogene, as evidenced by karst morphology filled with non-sulphides and covered by Tortonian sediments. A different type of non-sulphide ore (white galman) is characterized by the presence of ferrous smithsonite (“monheimite”) and zincian dolomite, and the absence of Fe oxides. These ores occurred at the fringes of some unoxidised sulphide orebodies. Smithsonites from white galman have uniform δ¹⁸O values, but more positive and more variable δ¹³C values (-2.9 to -7.4‰) as red galman. White galman ores may have been deposited by hydrothermal fluids at the same time as sulphide mineralization.

KEYWORDS: Non-sulphide ores, Poland, Zn-Pb carbonates, hypogene, supergene

1 INTRODUCTION

At the beginning of 19th century, Poland was world leader of Zn production (40% of the world production), due to the non-sulphide calamine ores (galman in Polish). These ores occur in several districts of the Upper Silesian province. In 2005, the Zn-Pb ore resources of Poland are estimated at ~170.7Mt of sulphides (3.88% wt Zn and 1.78% wt Pb), and 57Mt of non-sulphide ores (5.6% wt Zn and 1.4% wt Pb).

2 GEOLOGICAL SETTING

The Upper Silesian Zn-Pb district is located north of the Carpathian thrust front, across the boundary between the Upper Silesian Coal Basin in the south and the Cracow-Silesia Mesozoic monocline to the northeast (Fig.1). The deposits occur in the Mesozoic cover of the Cracow-Silesia Mesozoic monocline. Both sulphide and non-sulphide ores are mainly hosted by epigenetic dolomite replacing Middle Muschelkalk (Mid-Triassic) limestone.

Figure 1. Localization of Polish Zn –Pb ore deposits.
The Silesia-Cracow area was peripherally affected by the Alpine orogeny (Mid-Cretaceous to Recent), which was responsible of the deformation and uplift of the Carpathian chain.

The late Alpine (Tertiary) vertical movements established a N-S and E-W fault network, which controlled the onset of horst-and-graben structures. These dislocations were followed by short periods of emersion, erosion and weathering of the Triassic carbonate lithotypes, alternated with local ingresses. During at least part of the Tertiary, both outcropping lithologies and climate were very favourable to erosion, thus facilitating the removal of Mesozoic and Palaeogene successions. Erosion surfaces, paired by deep karst morphology, were very common. The effects of these phenomena were the formation of sinkholes in Triassic carbonates, deposition and cementation of collapse breccias, and oxidation through percolating meteoric waters. The Tertiary or even older morphological surfaces were buried under marine clastic sediments of Tortonian age.

3 SULPHIDE ORE DEPOSITS

Primary Zn-Pb sulphide ores are hosted by the OBD. This lithology represents the product of several phases of hydrothermal dolomitization: the first and more widespread phase (OBD I, possibly of Triassic age) is not related to the genesis of sulphide ores. The main deposition of sulphides is associated to a second generation of hydrothermal dolomitization (OBD II), crystallising also Zn- and Fe-rich dolomites. Two kinds of sulphide bodies were recognized in Upper Silesia: (a) tabular and/or stratabound replacement bodies, (b) open-space infilling fractures and breccias. The mineralogical association consists of sphalerite, galena, marcasite and pyrite. The ores show colloform and banded textures in collapse breccia zones, while in the replacement bodies the typical “rhythmite” texture is frequently observed. An epigenetic, low-temperature hydrothermal origin of the Zn-Pb deposits is generally accepted, but their emplacement age is still controversial. Sass-Gustkiewicz et al. (1982) proposed a multistage mineralization event, occurring preferentially between late Triassic and Middle Jurassic. Leach et al. (1996) suggested a Palaeogene age based on palaeomagnetic data (Symons et al., 1996), whereas Heijlen et al. (2003) proposed an early Cretaceous age for the main mineralization event, from Rb-Sr dating of sphalerite.

4 NON-SULPHIDE ORE DEPOSITS

Non-sulphide Zn deposits occur in several mining districts of Upper Silesia: in the Trzebinia-Krzeszowice-Olkusz-Siewierz belt in the Tarnowiskie Gory (Fryderyk mine) and Bytom trough (Nowy Dwor, Orzel Bialy, Warynski, Marchlewski, Dabrowka mines), in the Chrzanow trough (Matylda, Galmany, Trzebionka mines) and in the Olkusz region (Boleslaw, Olkusz, Pomorzany mines) (Fig. 1). The oxidised Zn orebodies occur in form of stratiform bodies, nests and lenses within the whole vertical extension of the Ore Bearing Dolomite, from the lower contact with the Gogolin Limestone beds to the upper contact with the overlying Diplopora Dolomites. The oxide ores in the western part of Upper Silesia were not only exploited for Zn, but also for iron and Ag-rich residual galena.

Figure 2. Generalized paragenesis of the Zn-Pb ores (considering for the sulphides the Cretaceous age data of Heijlen et al., 2003).

The Zn oxide ores show a wide range of morphologies and textures. They occur in earthy masses, crystalline aggregates and concretions in cavities. Breccia and replacement textures are also very common. The ores comprise an association of smithsonite, cerussite, Zn-rich dolomite, the hydrous carbonates hydrozincite and hydrocerussite, hemimorphite, goethite, plumbian aragonite and relics of sulphides (Fig. 2). Occasionally, phosgenite, pyromorphite, greenockite and several base metal sulphates are part of the oxide assemblage. In the northern deposits (Bibiela, Bytom) Fe-oxides and galena are dominant, while in the
southern area (Chzranow) non-sulphide Zn minerals prevail. In the Boleslaw mine near Olkusz and in the Bytom trough, the oxidised ores were developed on the horst structures, generally linked with fault zones, whereas the Boleslaw graben was filled with unweathered sulphide ores, covered by Keuper clays and Diplopora dolomites (Middle Muschelkalk). The non-sulphide bodies had more irregular geometries than primary sulphide ores; disaggregated dolomites, reddish smithsonites and Fe-(hydr)oxides were common. In the Boleslaw deposit, as in the Trzebionka mine, a halo of Zn-rich dolomite and Fe-rich, white smithsonite occurred at the periphery of the sulphide bodies. At Matylda, near Trzebionka, smithsonite, Fe-rich smithsonite and Zn-rich dolomite instead of Zn sulphides were the prevailing mineral phases. Fe-(hydr)oxides were also commonly absent in these ore types. These two distinct non-sulphide assemblages correspond to the common definition of red galman (with abundant Fe-(hydr)oxides) and white galman by the Polish authors (Zabinski, 1960; Panek & Szuwarzynski, 1974; Kucha, 2005). On the whole, white galman is much rarer than red galman. In the Matylda mine, white galman forms patches within the red galman.

5 STABLE ISOTOPE

Differences between white and red galman are mirrored also by stable isotopes data of Zn carbonates (Fig. 3). Smithsonites from the red galman show a limited range of $\delta^{13}C_{VPDB}$ values (-10.1 to -11.4‰, n= 11), and variable $\delta^{18}O_{VSMOW}$ values (25.3 to 28.5‰, ave. 26.8 ± 0.3‰, 1σ, n=11). The oxygen isotope variation of red galman smithsonites can be related either to a 3‰ change in the isotope composition of the oxidation fluid, or to a temperature variation or a combination of both. We note that such isotope variations in supergene smithsonites are not unusual (Gilg et al. in press). Assuming a constant oxygen isotope value of about -8‰ for the local Tertiary palaeometeoric waters as indicated by kaolinite H-O-isotope data (Gilg, 2003), we calculate formation temperatures of about 6 to 18°C. The uniform and low carbon isotope values of red galman smithsonites are unusual for supergene carbonate-hosted deposits and indicate the predominance of organic soil-derived carbon in the formation of the Zn carbonate (Gilg et al. in press). Smithsonites from white galman have more variable and more positive carbon isotope values than red galman (-2.9 to -7.4‰), but broadly similar oxygen isotope compositions (26.8 to 28.9‰). If we consider white galman as a peripheral hydrothermal alteration product related to fluids that precipitated both OBD II and sulphides, we calculate temperatures of 35 to 50°C using an isotopic value of about 0‰ for the hydrothermal fluid as reported by Heijlen et al. (2003).

Figure 3. Plot of $\delta^{13}C$ vs. $\delta^{18}O$ of Zn, Pb and Ca carbonates from non-sulphide ores, Upper Silesia. Calcites are syn- and post red galman.

The C isotope variation of white galman smithsonites indicates a mixed contribution between carbon from OBD host rock and organic carbon: a range commonly reported in supergene smithsonites (Gilg et al. in press). Late meteoric calcites deposited with and after Zn carbonates in red galman, have very uniform $\delta^{18}O$ values of 21.3 to 23.9‰ (ave. 22.8 ±0.2‰, 1σ, n=12) about 4‰ lower than smithsonites. The C-isotope compositions of these calcites range between -4.4 and -10.1‰.

Proceedings of the Ninth Biennial SGA Meeting, Dublin 2007 1403
CONCLUSION

Though non-sulphide Zn ores have currently no economic significance in Poland, they are still an interesting subject for scientific research. The majority of galman ores are considered as supergene (red galman), derived from weathering of primary sulphides. White galman (containing Fe-smithsonite and Zn-rich dolomite) may represent a peripheral facies of the sulphide ores (Kucha & Czajka 1984; Kucha 2005).

The nature and age of the non-sulphide ores in Poland are of great importance also to determine the emplacement age of the primary sulphide deposits, a subject which is still highly debated (Sass-Gustkiewicz et al. 1982; Leach et al. 1996; Heijlen et al. 2003). However, the age of the weathering processes in Silesia-Cracow ore province is still ambiguous, having been probably developed in different geological periods. The most important paleoweathering stage took place during Palaeogene or early Neogene. It was surely pre-Tortonian, as evidenced by the karst morphology filled with detrital sulphide and oxide minerals, associated to Palaeogene continental and Tortonian marine sediments.

ACKNOWLEDGEMENTS

We wish to thank R. Herrington and the staff of EMMA division at the Natural History Museum, London, for the support to V. Coppola during an ACCORD project. Isotope analyses were performed by Ch. Mayr, GeoBioCentreLMU, Munich.

REFERENCES


FROM MINERAL SYSTEMS TO
PREDICTIVE MINERAL DISCOVERY

EDITED BY:
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ABSTRACT: Why giant ore deposits form is a critical question for mineral exploration. An answer can be found using the concept of Mineral Systems - ‘all geological factors that control the generation and preservation of mineral deposits’. Such an analysis is, however, still essentially empirical in nature and it is hard to evaluate why giant systems develop. It is possible to derive a relationship describing the critical factors necessary for the formation of a (giant) hydrothermal ore body, yielding a rigorous underpinning of the analysis of mineral systems. Most of these parameters translate readily to mappable features that have concerned exploration geologists for many years. Identifying practical expressions of these terms allows exploration to be based on firm scientific foundations. This link between fundamental scientific understanding, the mappable expression of the key parameters and exploration forms Exploration Science.

KEYWORDS: Mineral Systems, exploration, hydrothermal

1 INTRODUCTION

The questions as to why giant ore deposits form is a critical one for mineral exploration. Partial answers to this question can be gained by using the concept of Mineral Systems - ‘all geological factors that control the generation and preservation of mineral deposits... stressing the processes that are involved in mobilising ore components from a source, transporting and accumulating them...’ (Wyborn et al., 1994). In the Predictive Mineral Discovery Cooperative Research Centre (pmd*CRC), we have adapted an approach, initiated in the Australian Geodynamics Cooperative Research Centre (a predecessor of the pmd*CRC), called the ‘Five Questions’ (Price & Stoker, 2002). These questions are:

1) What are the geodynamic and P-T histories of the mineral system?
2) What is its architecture?
3) What fluid reservoirs were involved?
4) What were the fluid pathways and driving forces?
5) What processes were responsible for metal and sulphur transport and deposition?

This approach ensures that the context of an ore body across a range of scales is considered, and avoids issues of omission and/or confusion that arise from what is often a casual use of the source-transport-trap paradigm. This paper explores how we can look more deeply at controls on ore formation and link them to the exploration process.

2 THE BASIC RELATIONSHIP

While the Mineral System concept and its application via the Five Questions ensures a systematic consideration of the necessary conditions for ore formation, it is still essentially empirical in nature and it is hard to evaluate why giant systems develop. In general, the rate of precipitation of a mineral is given by the product of the fluid flow velocity and the gradient in concentration of the element of interest (Walsh et al., 1984; Helgeson & Lichtner, 1987). A specific expression for this relationship in hydrothermal systems can be created by combining an equation given by Philips (1990, 1991) and Hobbs & Ord (1997), together with Darcy’s Law for fluid flow in a porous medium. This allows the fundamental controls on
hydrothermal ore formation to be clearly identified. The basic relationship is:

\[
A = -\int \frac{\kappa \rho T}{\mu} \left( \frac{\partial c}{\partial T} \nabla T + \frac{\partial c}{\partial P} \nabla P + \sum_r \frac{\partial c_r}{\partial c_r} \nabla c_r \right) dt \tag{1}
\]

where \( A \) is the amount of material deposited at a particular point, \( \kappa \) the permeability, \( \rho \) the fluid density, \( g \) the acceleration due to gravity, \( \mu \) fluid viscosity and \( \nabla P \) the gradient in non-hydrostatic pressure. \( \frac{\partial c}{\partial T}, \frac{\partial c}{\partial P} \) and \( \frac{\partial c_r}{\partial c_r} \) are the equilibrium solubility sensitivities with respect to temperature, pressure and concentration of other species respectively, \( \nabla T, \nabla p \) and \( \nabla c_r \) the spatial gradients in \( T, p \) and \( c_r \), and \( t \) is the time the system operates for. The minus sign is because the amount mineral precipitated is the opposite of the change in the amount in solution. There are thus five independent factors (permeability, the gradient in non-hydrostatic pressure, the solubility sensitivities, spatial gradients and duration of flow). For \( A \) to be maximised (in other words for the formation of a giant ore body), all the terms in the equation must be greater than zero and the product of the terms (formally the scalar product of the vectors of \( \nabla P \) and the spatial gradients \( \nabla T, \nabla p \) and \( \nabla c_r \)) maximised. The equation is a scalar product because both the gradient in non-hydrostatic pressure (and hence the fluid flow velocity) and the gradients in \( T, p \) and \( c_r \) are vectors, and the angular relationship between these vectors is crucial. If fluid flow is along isotherms, isobars and isopleths, no change in solubility and hence no deposition will occur. The relationship noted above forms a rigorous underpinning for the analysis of mineral systems. It describes a complex system that may display emergence in the form of the development of (giant) ore bodies.

3 USING THE BASIC RELATIONSHIP

In order to utilise the expression and factors described above, it is necessary to translate the terms into something more tangible. A look at the factors reveals that they can be evaluated if the 5 questions are answered in an appropriate manner (see the left-hand two columns in Figure 1).

For example, the permeability factor will be explored if the question about architecture is answered with a view to outlining where permeable structures and lithologies are distributed. Gradients in \( T, p \) and \( c_r \) will be examined in answering the question on metal transport and deposition.

It is thus possible to link the underlying factors responsible for ore formation and the mineral system via the five questions. It is further possible to link the answers to the five questions to the exploration process, with the information drawn from the ‘Five Questions’ analysis depending on the nature of the exploration issue at hand (Figure 1). When seeking to make large-scale exploration decisions (terrain/province selection), information concerning the geodynamic setting is most appropriate,
whereas when evaluating drill targets, information about controls on ore deposition is relevant. In other words, the information taken from a mineral systems analysis depends on the scale at which exploration decisions are required.

Some of these parameters translate readily to mappable features that have concerned exploration geologists for many years. Permeability is related to the distribution of structures and of permeable sedimentary facies, for example. A preliminary examination of the parameters and what controls them yields the following three sets of geological inputs:

**Palaeogeography:** feeds into most of the critical factors:
- Describes distribution of (emergent) topography and hydrocarbon generation potential, both potential sources of hydraulic gradient (factor A in Figure 1).
- Controls distribution of facies and diagenesis that control permeability distribution in sedimentary sequences (factor C).
- Describes potential source regions for meteoric fluids (emergence again) and brines in marginal marine areas: key controls on solubility sensitivity (factor D).
- Allows identification of stable areas where P & t gradients could have been stable for long periods (factors E and B).

**Magmatism:** also plays a major role in many critical factors:
- Source of fluids and temperature distributions that may create hydraulic gradients (factor A).
- Repetitive magmatism will lead to long-lived hydrothermal systems (factor B).
- Driver for fracture generation and hence a control on permeability (factor C).
- Act as a fluid source the nature of which will depend on the magma’s origin: key control on solubility sensitivity (factor D).
- Creates spatial gradients in temperature and potentially chemistry (factor E).

**(Structural) Architecture:** dominates several of the critical factors
- Controls the distribution of dilation sites that play an important role in de-

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Figure 2. (a) Calculated gold solubility (ppm) at 300°C and 1 kbar in 1m NaCl solution with total sulphur 0.01m. The diagonal white line marks the boundary between sulphate (above) and sulphide (below) predominance (b) the sensitivity of gold solubility with respect to pH (\(\partial \text{Au}/\partial \text{pH}\)), (c) the sensitivity of gold solubility with respect to \(\log f_{\text{O}_2}\) (\(\partial \text{Au}/\partial \log f_{\text{O}_2}\)).
veloping steep hydraulic gradients (factor A).

- Repeated failure on structures (including reactivation of deeper faults and other structures) allows prolonged fluid movement and/or multiple deposition/mixing/etc. events (factor B).
- Defines most of the high-permeability domains in the crust (factor C).
- Defines locally steep pressure gradients, and plays a role in facilitating fluid mixing (factor E).

This list is clearly not complete, but shows how links can be made between the fundamental parameters and detectable (hence practical/usable) features.

One group of parameters, the solubility sensitivities (\(\partial c_e/\partial T\), \(\partial c_e/\partial P\) and \(\partial c_e/\partial c_r\); see Figure 2) have not been explicitly considered in the past. These will all vanish to zero if the hydrothermal fluid is unsaturated in the element of interest, although this is complicated in cases where fluid mixing occurs. In such sites, large gradients in solubility will occur, which is why mixing is such an effective process of ore formation. They are controlled at the most fundamental level by the geodynamic setting which controls \(c_e\).

4 CONCLUSIONS

From equation (1) and the detectable expressions of its key parameters, scale-appropriate information can be fed into the exploration process: for example gradients in \(T\), \(P\) and \(c_r\), which control the actual deposition of ore, are relevant at the scale of drill targets but not normally when considering province selection.

Identifying practical expressions of these terms will allow exploration to rest on firm scientific foundations and will enable the quality of exploration targets to be determined using formal risk analysis. This link between fundamental scientific understanding, the mappable expression of the key parameters and exploration forms Exploration Science.

ACKNOWLEDGEMENTS

I am grateful to many people, but especially Bruce Hobbs and John Walshe, for discussions and to Russell Korsch and Richard Chopping for reviews. The work reported here was conducted as part of the Predictive Mineral Discovery Cooperative Research Centre (pmd*CRC) and is published with the permission of the CEOs of the pmd*CRC and Geoscience Australia.

REFERENCES


ABSTRACT: The Earth’s core is considered the dominant reservoir of hydrogen and the hypothesis of a hydrogen flux from the core provides an explanation for many redox related phenomena through Earth history, including the formation of many giant mineral deposits. The depth of mineral systems may well be 100s to 1000s of kilometres rather than 10s of kilometres commonly assumed. Aqueous fluids and melts will dominate metallogenic processes in the crust and upper mantle but metal transport phenomena at depths greater than 300 to 400 km are much more likely to be controlled by hydridic fluids. Recognition of the nature and role of deep - Earth fluids will aid the construction of genuine mineral system models independent of types /classes of deposits. Scale-integrated models that take account of the deep-Earth fluids should provide a framework for resolving metal sources from metal sinks within mineral systems and development of 4D targeting technologies at all scales.

KEYWORDS: Hydridic fluids, Earth - degassing, Earth-systems, metallogenic models

1 INTRODUCTION: WHY EARTH-SYSTEM METALLOGENIC MODELS?

The rationale for developing whole-of-earth mineral-system models is to better understand the properties of mineral systems at all spatial and temporal scales through Earth history as well as the links between metallogenesis and other Earth processes. Typical length scales of major mineral provinces are of the order of 1000s of kilometres across the earth’s surface. Given that aspect ratios (length to depth) of systems can be expected to be of the order of 1:1 then the depth of mineral systems may well be 100s to 1000s of kilometres rather than 10s of kilometres as commonly assumed. The distance from the surface of the Earth to the core is approximately 3000 km making it conceivable that some components in mineral systems originate in the lower mantle, if not the core of the Earth.

The core is possibly the largest reservoir of H₂ on the Earth (Williams & Hemley, 2001) and arguably degassing of H₂ from the core has controlled many redox sensitive Earth processes that ultimately drive events such as large-volume magma eruptions, global anoxia, green house - ice house cycles, mass extinction events, as well as metallogenic epochs including formation of oil and gas deposits (Walshe, 2006; Walshe et al., 2005a). The history of Earth’s degassing may be reconstructed from redox-sensitive indicators of the hydrosphere and it is possible to differentiate epochs of enhanced diffusive loss of H₂ from epochs of enhanced advection of CH₄ - rich or CO₂ - rich gases that reflect the complex interplay of the relatively oxidized outer layers of the Earth with the hydridic fluid flux from the Earth’s core with ultra reduced fluids, coexisting with metals and silicides rather than silicates and oxides, being derived from depths greater than 600-700 km. (Walshe & Mikucki, in prep).

2 NATURE AND TRANSPORT CAPACITY OF DEEP - EARTH FLUIDS

Hydrogen-rich or hydridic fluids (Larin, 1993) have potential to complex a wide range of elements of metallogenic interest (e.g. Ti, V, Cr, Ni, Co, Cu, Pb, Zn, Mo, W, U, Th, Au, PGEs, REEs) at high temperature and pressure, either as hydrides or S, N, C and/or halogen complexes. Hence there is the possibility of transporting a wide range of elements at high temperature and pressure within the mantle and
crust by fluids other than silicate melts. Aqueous fluids may dominate processes in the crust but metal transport phenomena in the mantle, in fluids other than silicate melts, are much more likely to be controlled by anhydrous fluids and at depths greater than 300 to 400 km these fluids will be dominated by H2 and CH4 rather than CO2. The “deep-earth” fluids are postulated to contain H, N, C, S and halogen (Cl, F) complexes with hydridic complexes such as NaH, MgH2, AlH3 and SiH4 potentially playing a significant role in mobilizing the common rock forming elements. The alkali and most alkali earth elements form ionic hydrides. Group 3 through 7 elements (e.g. Al, Si, N, S, Cl) form covalent hydrides. The decreasing stability of hydrides with increasing atomic number within any Group of the Periodic Table (Mackay and Mackay, 1968) implies Na ± Li metasomatism will be favoured over K metasomatism and Mg over Ca - metasomatism. The stability of the iron hydride is strongly pressure dependent (Antonov et al., 1980; Okuchi, 1997) with FeHx forming at pressures > 5 GPa suggesting that transport of Fe relative to alkali and alkali-earth in hydridic fluids will be low.

3 HYDRIDIC FLUID PATHWAYS IN THE CRUST

How are anhydrous fluids that are far from equilibrium in the crust transported through the crust? Traditional boiling models of mineral deposition invoke phase separation in response to local changes in pressure/temperature or bulk composition at the site of deposit formation. Potentially phase separation occurred over a much larger volume of the system and the dynamics of phase immiscibility may have been the driver to segregate the hydrous and anhydrous parts of the system. The size of the two phase domain, i.e. the PT conditions over which a volatile rich fluid phase exists in addition to an aqueous fluid phase, is poorly constrained for the bulk composition of interest. However, on available data the two-phase domain could have extended through the crust into the mantle, permitting the flow of anhydrous fluids over vertical distances of 10s to 100s of kilometres into environments in which such fluids would normally be highly unstable. The most likely mechanisms of advection through the crust of hydridic fluids are transient, deep-lithospheric blasts of gas, or Verne-shots as proposed by Morgan et al. (2004) that will have characteristics similar to bolide impacts. Such explosive blasts could create shockwaves, cavitation, and mass jet formation within the venting region and potentially transport a large mass of shocked crust and mantle into globally dispersive super-stratospheric trajectories. The occurrence of impact structures in many major mineral provinces raising the possibility that some impact structures at least result from ‘bottom-up’ failure of the lithosphere and that a genetic relationship exists between such events and supply of volatiles ± metals in mineral systems.

4 METSOMATIC/METAMORPHIC REACTIONS IN THE CRUST

The responses to injecting a hydridic fluid, stable at > 600 km within the earth, into crustal rocks ± aqueous crustal fluids will depend on the precise reaction path and P/T conditions. A significant factor will be ratio of alkali and alkali-earth halides to HF and HCl which will control the evolution of acid/base balance of the fluids as they react with crustal fluids and rocks degrading to aqueous fluids of varying acidity, redox state and salinity. Relatively high halogen to alkali ratios should lead to acid production through dissociation of HCl and HF in aqueous crustal fluids; assuming limited degassing of hydrogen. Loss of hydrogen through degassing, or consumption of hydrogen through reaction with oxidised species or rocks (sulfate and carbonate or CO2) could lead to neutral to alkaline, highly saline and sodic brines. These “degraded” hydridic fluids can explain the widespread occurrence of acidic alteration associated with major mineral provinces and within sedimentary basins. They may also explain the common, district-scale albitization associated with many deposit types. With declining pressure hydridic fluids are likely to evolve to H2 ± CH4 ± H2S ± N2 gases that maintain significant reducing capacity with potential to mobilize carbonaceous material in the crust to produce sour gas and petroleum products.

5 CONCLUDING COMMENTS ON METALLOGENIC IMPLICATIONS

Recognition of the nature and role of deep-Earth fluids in formation of mineral deposits will aid the refinement of the concept of the time-bound nature of deposits from a generalized concept related to Earth evolution to a pre-
cise targeting tool. Recognition of the scale of alteration patterns will promote a reexamination of the relationships between and definitions of hydrothermal alteration, metamorphism and metasomatic processes. Recognition of the nature and role of deep-Earth fluids in formation of mineral deposits will aid the construction of genuine mineral system models that are independent of types/classes and are constrained by data at all scales, spatial as well as temporal (Walshe et al., 2005b). Scale-integrated models that take account of the deep-Earth fluids should provide a framework for resolving metal sources from metal sinks within mineral systems: e.g.

1. Determining if black shales in sedimentary basins were sources of metals versus shales acting as sinks for metals derived from much deeper in the system and potentially from the mantle.

2. Determining if silicate magmas (intruded or vented) acted as the transport medium for metals such as Cu, Ni, Cr, Au, PGEs versus silicate magmas acting as sinks/traps for metals transported into the crust by deep-lithospheric blasts of hydridic fluids.

ACKNOWLEDGEMENTS

The study is financially supported by the Predictive Mineral Discovery Cooperative Research Centre (pmd*CRC) and MERIWA (Mineral and Energy Research Institute of Western Australia), Projects 358 and 377. In particular, the support of SIGMC (Gold Fields) and Placer Dome (now part of Barrick Gold Corp) is acknowledged.

REFERENCES


Walshe, JL, Hobbs BE, Ord A, Regenauer-Lieb K, Barnicoat AC (2005a) Mineral systems, hydridic fluids, the Earth’s core, mass extinction events and related phenomena: Mineral deposit research: Meeting the global challenge, v 1, Mao & Bierlein (eds): 65-68

Walshe JL, Cooke DR, Neumayr, P (2005b), Five questions for fun and profit: A mineral systems perspective on metallogenic epochs, provinces and magmatic hydrothermal Cu and Au deposits: Mineral deposit research: Meeting the global challenge, v 1, Mao & Bierlein (eds): 477-480


The architecture of mineral systems in the third dimension: constraints from seismic reflection data

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ABSTRACT: Deep seismic reflection profiles in mineral provinces in Australia constrain the crustal architectures during the building of 3D geological maps of the regions. These profiles identify the main crustal-scale architecture which is the key to determining regional scale controls on mineralisation and possible fluid migration pathways. These new interpretations are challenging our current understanding of the geology, ore deposit models and prospectivity of Australia.

KEYWORDS: mineral systems, architecture, seismic, 3D geology

1 INTRODUCTION

In undertaking a ‘whole of system’ approach to mineralisation, the Predictive Mineral Discovery Cooperative Research Centre has adopted an integrated methodology across all scales using the ‘Five Questions’, as outlined by Price & Stoker (2002) and Barnicoat (2007). In understanding the architecture (Question 2) of a mineral system, the pmd*CRC routinely constructs 3D geological maps in selected mineral provinces in Australia, to examine regional scale controls on mineralisation and possible fluid migration pathways. To help constrain the architecture in the third dimension, the pmd*CRC has been involved, with Geoscience Australia, state government agencies and industry sponsors, in the acquisition and interpretation of a series of deep seismic reflection profiles to provide information on mineral systems at scales ranging from the province to the deposit. Here we examine some of these seismic profiles in terms of their contribution to the understanding of mineral systems in the province.

2 MCARTHUR BASIN (PB-ZN SYSTEM)

The Palaeoproterozoic to Mesoproterozoic (<1850–<1490 Ma) southern McArthur Basin, Northern Territory, Australia, contains an unmetamorphosed, relatively undeformed succession of carbonate, siliciclastic and volcanic rocks that host the McArthur River (HYC) Zn-Pb-Ag deposit. Deep seismic reflection data obtained along a 110 km long east-west profile across this basin were collected in late 2002, in part to examine the fundamental basin architecture of the southern McArthur Basin, particularly the Batten Fault Zone (Rawlings et al. 2004).

The seismic data provides little evidence for pronounced stratigraphic thickening in the seismic section, with no evidence for the Batten “Trough” being a separate depocentre, or for the presence of large asymmetric half graben, because the thick sedimentary succession extends both to the east and west, beyond the inferred boundaries of the “trough”. The western two-thirds of the seismic profile is dominated by a series of west-dipping low-angle faults that form part of a previously unrecognised major thrust belt that has propagated eastward, forming a forward-breaking sequence of thrusts. Displacement on the thrusts tends to be greatest in the west and diminishes to the east, with the frontal thrust of the system having only minor displacement and occurring ~6 km west of the Emu Fault Zone. In the west, the youngest strata of the McArthur Basin, the Roper Group, forms the western limb of the Bauhinia monocline, which developed above the most western thrust ramp in the seismic data, and indicates a post-Roper timing for the thrust system. The thrusts continue at depth beyond the western limit of the seismic section,
and this part of the thrust belt is now hidden beneath younger sedimentary cover.

In the eastern part of the basin, The Emu Fault Zone is interpreted as a near-vertical, braided strike-slip fault system. The seismic data suggest the likelihood of minor stratigraphic thickening adjacent to the Emu Fault during deposition of the McArthur Group, probably in a small pull-apart basin forming a negative flower structure. This interpretation is supported by the rectilinear nature of the fault system in map view. There have been at least two episodes of fault activity. The first involved sinistral movement in middle McArthur Group times, leading to possible thickened strata at transtensional fault bends. The second involved dextral transpression, which inverted earlier transtensional zones to form positive flower structures in post-Roper time.

For the giant McArthur River Zn-Pb-Ag deposit, it has been argued that the Emu Fault provides a conduit for ore forming fluids to move from source to depositional site (Williams 1978). The trap for the base metals is the thick accumulation of carbonaceous deep-water shales and siltstones of the Barney Creek Formation (middle McArthur Group), deposited in a sub-basin adjacent to the Emu Fault.

Numerical fluid flow models for base metal mineralization at McArthur River (e.g. Garven et al. 2001) rely largely on the circulation of metalliferous brines in free convective cells of 20-50 km diameter, which develop within the proposed lateral aquifer system. First order control on ore fluid focussing was discharge to the surface along the active Emu Fault, and recharge along the Tawallah Fault to the west. The subvertical orientation and deep-rooted nature of both the Emu and Tawallah faults and a subhorizontal aquifer is implicit to the initiation and maintenance of west-to-east brine transport and the proposed discharge and recharge points. Although the seismic data suggest that the Emu Fault is subvertical, this is not the case for the Tawallah Fault which is a thrust dipping shallowly to the west. Hence the fluid flow model for the formation of the McArthur River deposit is invalid and needs to be reconsidered.

The new seismic data suggest that the potential for McArthur style base metal deposits is increased within and to the east of the Batten Fault Zone. Given the strike-slip nature of the Emu Fault, segments of it now under cover to the north and south of the McArthur River deposit may also have formed sub-basins (negative flower structures) that would also be prospective for base-metals.

The recognition of a previously unknown major thrust belt enhances the prospectivity of large areas of the McArthur Basin for exploration for younger (post-Roper Group) foreland basin type deposits such as Mississippi Valley types (MVT) as well as equivalent styles to the Century deposit, which possibly formed by topographically driven fluid flow. Also, under cover well to the west of the seismic profile, in the core of the thrust belt (orogen), there may be potential for orogenic gold deposits under younger cover.

3 CURNAMONA PROVINCE (AG-PB-ZN AND CU-AU SYSTEMS)

The Curnamona Province contains the world class Broken Hill Ag-Pb-Zn deposit and consists of the Palaeoproterozoic (~1720-1640 Ma) Willyama Supergroup and coeval magmatic rocks that were deformed and metamorphosed during the ~1600 Ma Olarian Orogeny, which was followed by an early Mesoproterozoic magmatic event.

Data from a 1996-97 dynamite-sourced deep seismic reflection survey in New South Wales (Gibson et al. 1998) have been reprocessed using current seismic processing techniques and the results combined with the Curnamona 2003-04 vibroseis-sourced deep seismic survey (Goleby et al. 2006) to produce a single 400 km long transect across the entire Curnamona Province from the Darling Basin in the east to the Flinders Ranges in the west. This transect across the Curnamona Province has provided the first seismic transect across an entire mineral province in Australia, and has provided insights into its crustal architecture and geological evolution (Korsch et al. 2006a).

The original interpretation of the seismic transect in New South Wales indicated that the dominant features seen in the seismic data were a series of reflections that had an apparent dip to the southeast (Gibson et al. 1998). These reflections were interpreted to represent shear zones, some of which were inferred to cut deep into the crust (e.g. Mundi Mundi Fault and King Gunna Shear Zone). A short high resolution seismic line immediately to the east of Broken Hill acquired in 2005 has provided a much improved image of the upper ~3 km of the crust, including the region between the Stephens Creek and Globe-Vauxhall shear
zones (Korsch et al. 2006b), which crosses the northeast extension of the Broken Hill line of lode. This confirmed the southeast dip and thrust geometry to the shear zones.

In South Australia, the seismic transect shows an upper crustal thrust belt, with east-dipping thrusts cutting the Willyama Super-group, which has been folded to form hanging wall anticlines. This thrust belt sits on a “decollement” defined by strong reflectivity at ~6-9 km depth. The high level thrust belt propagated westwards, with the amount of displacement dying out to the west, and the shortening being accommodated into broad wavelength folds in the near surface.

The seismic transect shows the presence of a linked westward-propagating thrust belt. The thrusts are thick skinned and cut deep into the crust in the core of the orogen in the vicinity of Broken Hill, whereas to the west, principally in South Australia, the thrust belt is thin skinned and consists of thrusts that link onto a shallow detachment at a depth of ~6-9 km.

Because the thrust belt includes individual folds and thrusts that are interpreted as D3, it is inferred to have formed late during the ~1600 Ma Olarian Orogeny. Nevertheless, the structures may have been reactivated during Neoproterozoic and/or Palaeozoic (Delamerian) deformational events. Shear zones exhibiting this timing are well documented at the surface in the southern Curnamona province, and Delamerian deformation is seen at the western end of the profile, where Neoproterozoic rocks are intensely deformed.

The Kalkaroo Cu-Au-Mo deposit, a large tonnage, relatively low grade polymetallic resource, located about 4 km to the north of the seismic line, appears to be associated with second order synthetic D3 faults associated with hanging wall anticlines above a bounding east-dipping fault at depth. The fault beneath the anticline could have been the conduit for fluids moving from the deep crust to upper crustal levels where they could have migrated into favourable depositional sites associated with the second order structures.

The western limit of the Curnamona Province is defined by a possible suture zone between two different types of lower crust, with the crust in the west below the Flinders Ranges being overthrust by sub-Curnamona crust in the east. The eastern limit of the province is also defined by a crustal scale east-dipping structure that thrusts the Neoproterozoic-Phanerozoic Koonenberry Belt over rocks of the Curnamona Province.

4 THOMSON OROGEN-LACHLAN OROGEN BOUNDARY (FRONTIER TERRAIN)

The Neoproterozoic to middle Palaeozoic Thomson Orogen occupies a vast area of western and central Queensland and northwestern New South Wales, but very little is known about it because it is covered by Cainozoic sediments and the Mesozoic Eromanga Basin. A ~290 line km deep seismic reflection survey was conducted in 2005 in New South Wales to examine the tectonic and metallogenic implications of a major east-west tectonic boundary with the Lachlan Orogen to the south flanked to the north by a major east-west gravity high, curvilinear aeromagnetic highs and mafic to intermediate igneous rocks reported from drill holes in the southern part of the Thomson Orogen (Glen et al. 2006).

In the seismic, the boundary between the Thomson and Lachlan orogens is imaged as a north-dipping fault zone that cuts through the crust and offsets the Moho. Latest movement was in the Carboniferous, during the Kanimblan Orogeny, because Late Devonian rocks are truncated and deformed at the suture.

North of this boundary, the similarity of the gravity responses north of this boundary with those of accreted gold- and copper-rich Ordovician Macquarie Arc sampled by seismic reflection profiling in 1997 and 1999 (Glen et al. 2002) suggests that the boundary may be a convergent margin, marked by the possible development of island arc and ocean crustal igneous rocks.

South of the boundary, there is now increased potential for mineral systems in Early Devonian rift basins (possibly of the style of the nearby Cobar Basin generated by movement on the Thomson-Lachlan boundary imaged by the seismic beneath Late Devonian strata in the Nelyambo Trough of the Darling Basin. The seismic also indicates the possibility of Mississippi Valley mineral systems along the margins of the Mt Jack High, that marks the thrusted southern edge of the Nelyambo Trough.

5 CONCLUSIONS

Deep seismic reflection profiles in mineral
provinces in Australia are identifying the main crustal-scale architecture which is the key to determining regional scale controls on mineralisation and possible fluid migration pathways. The results constrain the crustal architectures during the building of 3D geological maps of the regions, and are challenging our current understanding of the geology, ore deposit models and prospectivity of Australia.

ACKNOWLEDGEMENTS

We thank the many geoscientists, particularly those from state geological surveys, who have been involved in various stages of the seismic acquisition, processing or interpretation phases for their input, and Andy Barnicoat and Richard Blewett for their reviews. Published with permission of the CEOs of the *pmd* CRC and Geoscience Australia and the Deputy Director-General, New South Wales Department of Primary Industries – Mineral Resources.

REFERENCES


Korsch RJ, Fomin T, Stevens BPJ (2006b) Preliminary results of a high resolution seismic reflection sur-

vey at Broken Hill. *Geoscience Aust Record* 2006/21: 110-115


"Digging Deeper" C.J. Andrew et al (editors)
ABSTRACT: Results of the FIRE (Finnish Reflection Experiment) reflection seismic program in Finland provide insights into deep crustal architecture, which facilitate our understanding of structural controls on Archaean and Palaeoproterozoic mineral deposits. Over 2100 km of seismic imaging throughout Finland record the structure of the crust to depths of up to 80 km. Several metallogenic zones are transected by the profiles. Interpretations show the Palaeoproterozoic VMS deposits of the Vihanti-Pyhäsalmi Zn-Cu-Pb metallogenic zone, together with Ni-Cu intrusions within a tectonically complicated zone accreted to the Archaean craton margin, and the possibility of crustal scale imbrication controlling distribution of granitoids associated with orogenic Au. The structural geometry of the Outokumpu Cu-Zn-Ni-Co deposits is also well defined and imaged seismically. Palaeoproterozoic PGE mineralization of southern Lapland occupies a major zone of Palaeoproterozoic rifting at an Archaean/Proterozoic boundary. The typical orogenic tectonic setting of Palaeoproterozoic Au mineralization in Central Lapland is confirmed by FIRE data, but significant new structures are identified and the influence of these on Au-Cu deposit distribution requires review.

KEYWORDS: Finland, mineralization, structural architecture, Palaeoproterozoic, seismic reflection

1. THE FINNISH REFLECTION EXPERIMENT

Understanding the origin and distribution of mineral deposits is increasingly reliant on an appreciation of their regional geological context. Accordingly, deep crustal seismic reflection survey data are being widely used in defining crustal scale architecture, in relation to rifting and basin evolution, as well as structurally controlled orogenic mineral systems. In Finland, the recently completed FIRE (Finnish Reflection Experiment) program enabled acquisition of crustal-scale reflection seismic data along a number of profiles traversing key geological units and mineral provinces.

A total of 2104 km of 2-dimensional common mid point survey profiles were acquired using Vibroseis sources. Good data quality was achieved to depths down to 60-70 km. The FIRE results (see Kukkonen & Lahtinen 2006) have led to refinement of tectonic interpretations for much of Finland, and the purpose of this presentation is to illustrate the crustal structure interpreted for a selection of significant metallogenic zones transected by the FIRE profiles (Figure 2).

2. IMAGED GEOLOGY

FIRE profiles 1 and 3+3A both transect the boundary between the NeoArchaean Karelian cratonic domain and the Palaeoproterozoic (1.9-1.8 Ga) Svecofennian domain to the southwest. Although this boundary zone includes a 2.2-1.95 Ga rifted cratonic margin basin system, which includes the Talvivaara black-shale hosted Ni-Zn-Cu system and the volcanic-related graywacke-hosted Hammaslahti Cu-Zn-Au mineralization, intense orogenic reworking hinders reconstruction of original architecture in the seismic data. The FIRE 3+3A profile also provides constraints on the structural setting of the Outokumpu Cu-Co-
Zn+Ni deposits, while within the Svecofennian domain, profiles 1 and 3A both offer insights into the 1.91 Ga Vihanti-Pyhäsalmi VHMS Zn-Cu-Pb province and the 1.89 Ga Kotalahti intrusive-hosted Ni-Cu zone. Within the Karelian craton, Profiles FIRE 1 and 3 cross the Au-prospective Kuhmo and Hattu greenstone belts respectively, but neither zone appears to be associated with significant features or trends in the seismic images.

FIRE 2 and 2A image rocks that constitute the internal structure of the Svecofennian Orogen - the inferred magmatic arc complexes of western and southern Finland. These rocks host the Orijärvi Zn-Pb-Cu+Fe metallogenic zone (a continuation of the Bergslagen base metal province in Sweden), Palmottu U, Pori-Vammala-Kylmäkoski Ni-Cu and Haveri-Orivesi Au metallogenic zones.

FIRE profile 4 transects the northern Archaean/Proterozoic boundary. Significant PGE mineralization occurs at this boundary (e.g., Narkaus and Suhanko reefs). The continuation of FIRE profile 4, and profiles 4A and 4B cover the Palaeoproterozoic greenstone sequences of central Finnish Lapland (Kittilä Au-Cu metallogenic zone). This area is best known for orogenic type gold occurrences, but also contains mineralization with some similarities to Fe oxide-Cu-Au deposits, and Cu-U mineralization.

3. TECTONIC SETTING INTERPRETED FOR SELECTED METALLOGENIC ZONES USING FIRE DATA

3.1. Vihanti-Pyhäsalmi Zn-Cu-Pb metallogenic zone of central Finland

The massive sulphide ores within the Vihanti-Pyhäsalmi area (Zone 1 in Figure 2) define the most important Zn province in Finland (e.g., Pyhäslami Mine operational since 1962, 31 Mt proven+probable+measured resource @ 1-2.6% Zn, 0.8-1.1% Cu and minor Au; Inmet 2005). This zone is characterized by a bimodal metavolcanic association and metaturbiditic rocks accreted to the craton margin shortly after their formation at about 1.91 Ga (Koistinen and Saltykova 1999; Korja et al., 2006 and references within).

The Vihanti-Pyhäsalmi Zn province experienced high grade metamorphism and anatexis from 1.89 Ga, accompanying a transition to a transpressive geodynamic regime with strike-slip shear zones and tectonic transport subparallel to the former cratonic margin. These struc-
tures, and the spectacular listric imbricate thrust system are imaged in the FIRE 1 and FIRE profiles. This deformation facilitated melt migration and emplacement of 1.89-1.87 Ga granitoids as sheet-like bodies which appear to provide a favourable structural framework for vein-hosted orogenic Au mineralization (Sorjonen-Ward, 2006). Similarly, numerous gabbroic intrusions, with ultramafic cumulates, are prospective for intrusive-hosted Ni-Cu.

3.2. Outokumpu Cu-Co-Zn-Ni metallogenic zone of eastern Finland

The Outokumpu deposits (eg. Keretti deposit 28.54 Mt or ore grading 3.8% Cu, 0.24% Co, 0.12% Ni, 1.1 % Zn, 8.9 ppm Ag and 0.8 ppm Au and Vuonos deposit 5.82 Mt e. @ 0.2% Ni and 0.04% Cu; Puustinen et al. 1995) are hosted by hydrothermally altered serpentinites, derived from depleted mantle harzburgites, enclosed within an allochthonous package of Palaeoproterozoic black shales and turbidites, and Archaean basement gneisses (Kontinen et al., 2005). The structural evolution of the Outokumpu region is well-documented (Koistinen, 1981) and readily reconciled with reflective events in the seismic data (Sorjonen-Ward, 2006). Localization of the main deposit appears to be within a thrust duplex developed during tightening of a regional synform. This in turn is seen as a consequence of orogen-parallel crustal shortening accommodated by bivergent thrusting and strike-slip shear systems that evidently also facilitated the emplacement of sheet-like bodies of granitoids by strike-slip shearing and doubly-vergent thrusting accompanying granitoid emplacement.

3.3. 'Contact style' Ni-Cu-PGE mineralization of southern Lapland

In southern Finnish Lapland 2.44 Ga ultramafic layered intrusions contain Ni-Cu deposits within which PGMs are economically significant metals. In the contact-style deposits in the marginal series of the Suhanko Intrusion (resource 183.6 Mt @ 1.54 2PGE+Au g/t; Outokumpu OYJ and Gold Fields Ltd 2002), Ni-Cu-PGE mineralization occurs close to the basal contacts of the layered intrusions.

This and other mineralization in the Tornio-Näränkävaara belt of layered intrusions are interpreted using FIRE 4 data as occupying a major zone of Palaeoproterozoic rifting at an Archaean/Proterozoic boundary (Patison et al. 2006).

3.4. Kittilä Au-Cu metallogenic zone of central Lapland (northern Finland)

Gold occurrences are known throughout central Lapland (e.g., Suurikuusikko deposit, resource size 14.2 Mt @ 5.2 g/t Au, 4.3 Mt @ 1.6 g/t Au, and 4.4 Mt @ 6.7 g/t Au probable, indicated and inferred resources respectively; Agnico-Eagle 2007), associated with structures within the metavolcanics and metasediments of the 2.5-2.0 Ga Central Lapland Greenstone Belt. Many Au and Au-Cu mineralization are associated with complex deformation at the southern part of this belt.

Traditionally, deformation in this area is considered dominated by thrusting overprinted by strike-slip deformation (Sorjonen-Ward et al., 2003). Such a setting is consistent with data from FIRE profiles 4 and 4A. However, a number of significant new structures have been identified from these FIRE profiles, prompting rethinking of the structure of this area and the extent of gold-prospective areas (Patison et al. 2006).

CONCLUSIONS

The first-pass interpretations of the FIRE reflection seismic data have provided valuable insights in to crustal architecture in Finland, across major tectonic domains and metallogenic provinces. In several cases, there is good correlation between seismic patterning and structural features and geometry mapped at the surface. There also appears to be good agreement between crustal scale and higher resolution survey results.

However, some crustal units, such as narrow, relatively steep Archaean greenstone belts are not clearly imaged, and it is difficult to define rifting and extensional basin architecture due to strong orogenic overprinting. Partitioning of seismic reflectivity into distinct layers, with marked listric geometry in the middle and lower crust is reminiscent of crustal imbrication observed in other mineralized Archaean and Proterozoic terrains.

ACKNOWLEDGEMENTS

The examples used in the presentation are based on profile interpretations published in
Kukkonen & Lahtinen (2006). The FIRE working group includes the following organisations and individuals: Geological Survey of Finland (E. Ekdahl, I. Kukkonen, R. Lahtinen, M. Niironen, A. Kontinen, J. Paavola, H. Lukkarinen, A. Ruotsalainen, J. Lehtimäki, H. Forss, E. Lanne, H. Salmirinne, T. Pernu, P. Turunen, E. Ruokanen), Institute of Seismology, University of Helsinki (P. Heikkinen, A. Korja, T. Tiira, J. Keskinen), Department of Geosciences, University of Oulu (S.-E. Hjelt, J. Tiikkainen), Sodankylä Geophysical Observatory, University of Oulu (J. Yliniemi), Terramecs Ky (E. Jalakanen), and Spetsgeofizika S.E. (R. Berzin, A. Suleimanov, N. Zamoshnyaya, I. Moissa, A. Kostyuk, V. Litvinenko). Data collection was done by Russian seismic contractor Spetsgeofizika S.E. with Machinoexport S.E. Collection of the FIRE data was a component of a debt conversion agreement between the Russian Federation and Finland.

REFERENCES


Coupled chemical-fluid flow modelling of the Irish Carboniferous Basin.

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ABSTRACT: We explore 2D and 3D numerical models of the Irish Zn-Pb deposits. Specifically we examine the geometry of mixing of a saline fluid derived from sea water with a more dilute fluid driven by topographical flow. The models involve full coupling between deformation, fluid flow, thermal transport and chemical reactions although the chemistry has been simplified to involve only the influence of chloride concentration upon sphalerite solubility. We conclude that for a wide range of possible scenarios, north dipping faults in the Irish Basin are the most prospective for mineralization.

KEYWORDS: Irish Zn deposits, 3D modeling, coupled modeling, fluid flow.

1 DETAILS OF THE MODELS

The aim of this work is to explore and evaluate a particular scenario for the formation of Irish-type Zn-Pb deposits through geodynamic modelling, with a focus on Waulsortian-hosted Zn-Pb deposits of the Central Irish Midlands.

We explore two and three dimensional regional and local-scale, numerical models for the development of Irish Zn-Pb-Ag mineralization. Geological evidence indicates that mineralization resulted from mixing of two fluids of different salinities in the hanging walls of faults undergoing active inversion during mineralization. Hence, the numerical models involve coupling between volume changes arising from elastic-plastic deformation, single phase fluid flow and mixing of saline fluids together with thermal transport both by conduction and by advection. We evaluate critical parameters that optimize mixing of these two fluids with different salinities in three dimensions at the regional scale and in two dimensions at the local scale. The complete four fold coupled problem where deformation, fluid flow, thermal transport and chemical reactive-transport is modelled in three dimensions is computer intensive and as a forerunner to carrying out such modelling we adopt the following approach as a surrogate. The instantaneous rate of mineralization of Zn, \( Q_{Zn} \), in any system where the fluids are saturated with respect to the Zn species is given by:

\[
Q_{Zn} = -u \cdot \left( \frac{\partial c_{Zn}}{\partial T} \nabla T + \frac{\partial c_{Zn}}{\partial P} \nabla P + \sum_i \frac{\partial c_{Zn}}{\partial c_i} \nabla c_i \right)
\]

where \( c_{Zn} \) is the equilibrium concentration of Zn, \( T \) is the temperature, \( P \) is the fluid pressure, \( c_i \) are the equilibrium concentrations of the other chemical species in solution, \( u \) is the Darcy fluid velocity vector, \( \nabla \) is the (vector) gradient operator and the symbol \( \cdot \) represents the scalar product of the two vectors concerned. In particular, the results reported here involve only \( c_{NaCl} \) as the only \( c_i \) in the above equation.

Values of \( \frac{\partial c_{Zn}}{\partial T} \), \( \frac{\partial c_{Zn}}{\partial P} \), and \( \frac{\partial c_{Zn}}{\partial c_{NaCl}} \) may be read from Figures 1 and 2. We plot \( \int_0^\Gamma Q_{Zn} dt \) at each point in the two and three dimensional models where \( \Gamma \) is the time of the simulation, which in some instances may be several million years, and \( t \) is time.
The stratigraphic detail incorporated into the models presented here (Figure 3) is not sufficient to distinguish between shortening and inversion scenarios associated with orogeny. Moreover, both shortening and inversion produce similar fault dilatancy. Hence this modelling is not sensitive to either a shortening nor an inversion scenario. The critical points are that topographic relief exists at the time of mineralization and that deformation is critical in maintaining permeability over the mineralizing period.

The models indicate that a process competing with topographic flow arises, involving convection of high salinity fluids, originating as partially evaporated sea water, which mix with lower salinity fluids driven by topographic relief. At the regional scale, although there is substantial fluid flow through the Old Red Sandstone aquifer, considerable flow of basin-derived fluids also exists through the basement, consistent with isotopic data, with subsequent focusing upwards through extensional faults reactivated during mineralization. A critical feature of the models is that these basement fluids (Fluid 1) are focused upwards into both northward and southward dipping faults, but it is only within the vicinity of northward dipping faults that optimal temperatures, fluid velocities and mixing geometries develop.

The second fluid is driven down into the rock column by convection; it has exposure to both the Old Red Sandstone and the basement before mixing with Fluid 1. The positions of these fluid mixing sites involve a balance between topographically driven flow and convection in three dimensions at a regional scale. Changes in porosity and permeability induced by plastic deformation play a role in allowing fluid mixing geometries to arise at the local, ore-body scale and in enhancing local Darcy flow rates at mineralizing sites. Mixing at the local scale results from the interplay of fault dip direction, displacement, deformation induced

Figure 1. Calculated Zinc solubility (ppm) in a 1m NaCl solution equilibrated with sphalerite as a function of P & T together with solubility sensitivities with respect to T and P (\(\frac{\partial Zn}{\partial T}\) and \(\frac{\partial Zn}{\partial P}\) respectively). Note the change in sign of \(\frac{\partial Zn}{\partial P}\) at temperatures >300°C and pressures <2.5 kbars.

Figure 2. Solubility sensitivity to chemistry of Zn (sphalerite) at 1 kbar. Black line – Zn solubility, Grey line - *Zn/Cl* solubility.

Figure 3. Conceptual model. Length is 120km. Depth of aquifer plus basement is 10 km. Aquifer – grey; basement – black; aquifer-highlands – medium grey.
dilation, seal thickness and integrity.

2 DETAILS OF MIXING GEOMETRIES

Based on the range of permeability structures, hydraulic potential gradients and basal heat flows, four basic types of behaviour can develop. These comprise a spectrum from essentially (vertical) convective driven fluid flow to (horizontal) topographically driven flow, and there are presumably gradations between each. Some examples of mixing fronts are shown in Figures 4 and 5.

In both figures, flow of low salinity fluids (black) down from the mountains competes against flow of high salinity fluids (light grey) down from the basin.

Type 1: This is characteristic of models with zero or small gradients in hydraulic potential. Fluid flow is focused up the relatively permeable faults from the basinal and basement rocks and mixes with fluids drawn down from the sea floor in the hanging walls of both north and south dipping faults. Temperatures in the mixing locations are low (50-100°C) and flow rates are relatively small (ca. 3.5x10^-2 my^-1 near south dipping faults and ca. 2.1x10^-2 my^-1 near north dipping faults), so that the mineralization rate is also expected to be low. However, south dipping faults tend to have the highest fluid flow rates and so may be expected to be preferentially, but weakly, mineralized. This is perhaps the situation with respect to small deposits that occur on south dipping faults, such as Keel, Oldcastle, Garrycam and Carrickittle which are distal from the South Munster Basin (SMB) and hence would be associated with the weakest gradients in hydraulic potential.

Type 2: This is characteristic of models with high gradients in hydraulic potential but relatively low horizontal permeability.

Significant convection cells develop in both the hanging wall and footwall of north dipping faults producing an environment where seawater drawn down from the sea floor mixes with basinal fluids that have been driven through the basement by the hydraulic potential gradient. Temperatures in the mixing zone are relatively high at 150°C to 250°C but Darcy fluid flow rates are relatively low at ca. 2x10^-2 my^-1. Thus, although the geometry and temperature of mixing is ideal for mineralization, the flow rates suggest that the actual mineralization would be weak. This mixing geometry does not occur on south dipping faults since the high horizontal flow rates arising from high gradients in hydraulic potential tend to favor the development of surface convection cells further to the north.

Type 3: This is characteristic of moderate gradients in hydraulic potential and intermediate values of horizontal permeability (Figure 6). There is the opportunity for both horizontally driven topographical flows and convective flows to be of similar importance. This is the most common type encountered in the systems explored here. Flow is driven by the topographic relief and passes mainly from the basin and through the basement to mix with
seawater drawn down quite deeply by a convection cell on the hanging wall of only north dipping faults; this does not occur on south dipping faults. Temperatures are relatively high (150°C to 200°C), as are Darcy flow rates (ca. 0.25 m y⁻¹ to ca. 0.5 m y⁻¹), so that this makes an ideal situation for high grade mineralizing systems to develop. However, the maximum flow rates in systems that lack deformation are about half that modelled typically for MVT deposits.

Type 4: This is characteristic of high horizontal flow scenarios. This tends to sweep and distort any shallow convection cell well to the north. The mixing geometry, with a shallow convection cell that brings seawater down into the rock column, is conducive to fluid mixing and the Darcy flow rates are high (ca 1.5 m y⁻¹). However temperatures tend to be low at the mixing site (20-50°C), so that this model is not ideal for mineralization.

3 DISCUSSION

Our analysis highlights a curious relationship, that 70% of the classified deposits (the number analysed is 60) are associated with north dipping faults (Figure 7). Deposits with defined resources are dominantly of this category, and this includes all economically significant deposits, ranked by Total Metal Value (TMV). This relationship of economic deposits to fault dip direction has clear exploration implications. The modelling reported here explains why this relationship exists. Conceptual and numerical regional scale models of epigenetic Zn-Pb-Ba-Ag deposits in Ireland indicate fluid flow is driven by three coupled processes: (i) topographic relief, (ii) convection, and (iii) deformation induced volumetric changes. Optimum conditions for mineralization are when fluid flow driven by topographic relief is approximately of equal importance to flow arising from convection. This occurs for moderate topographic relief and moderate permeabilities. In particular, changes in porosity and permeability induced by dilation during plastic deformation play a major role in allowing critical fluid mixing geometries to arise and substantially enhance focussing of local Darcy flow rates at mineralizing sites. Fluids forced out of the SMB through both sedimentary aquifers and basement rocks focus into faults. In such conditions, shallow convection cells develop that bring seawater down into the rock column and mix with the focussed basinal fluids. Mixing occurs preferentially on north dipping faults and produce temperatures in the mixing site in the range 150-250°C, in agreement with observations on these deposits. Other combinations of topographic relief and horizontal permeability lead to low temperatures at the mixing site and/or low Darcy flow velocities.

At the local scale, two types of models, with and without thermal coupling, are explored where seawater is drawn down faults to mix with basinal brines driven northwards by topographic relief. In both types of models, mixing occurs at the base of the limestone and at higher levels, but preferentially in the hanging walls of north dipping faults. The efficiency of mixing at the ore body scale involves an interplay of fault displacement, seal integrity and chemical and deformation enhanced permeability.

The modelling results are compatible with empirical data from the Irish ore field suggesting that north dipping faults preferentially host economic deposits. This translates to an exploration strategy for major deposits that, in Ireland, targets the hanging walls of north dipping, seal-breaching faults.

ACKNOWLEDGEMENTS

We acknowledge the support of the Predictive Mineral Discovery Cooperative Research Centre.
Architecture of the Tanami goldfields revealed by deep crustal seismic surveys

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ABSTRACT: Deep crustal seismic surveys of the Tanami goldfields of northern Australia show fundamental, crustal-scale controls on gold mineralization and relationships between the Tanami and Aileron tectonic provinces. Crustal-scale shear zones provide the plumbing-system for lode Au mineralization. Deposition can be mapped to thrusts imaged in the upper crust. Precursors to these thrusts may be extensional structures related to formation of the basin in which the host units of the Tanami Group were deposited.

KEYWORDS: Tanami, gold mineralization, northern Australia, seismic

1 INTRODUCTION

The Tanami goldfields of northern Australia contain about 12 Moz Au, including the giant Callie deposit (~7 Moz Au). Gold was first discovered in the Tanami field in 1900, but production only became significant during the last twenty years. With the discovery of the Callie deposit in 1991, it became apparent that the Tanami field is potentially world-class. The gold-deposits of northern Australia and those of the Trans-Hudson Orogen in North America are the major contributors to the global Palaeoproterozoic endowment, the two amounting to about 70 Moz.

Outcrop in the Tanami is almost non-existent, with the bedrock of whole region being virtually covered by sand-plains. Interpretations of solid geology come from mapping of sparse outcrop, drill-core, and interpretation of potential-field data. Understanding of the crustal architecture and the role of shear zones in the Au mineral-system is difficult to refine unless geometric and structural constraints can be applied to interpretations of the above data-sets. To this end, in 2005, Geoscience Australia, in collaboration with the Northern Territory Geological Survey, the Geological Survey of Western Australia, Newmont Exploration Pty Ltd, and Tanami Gold NL, acquired 720 line-km of deep crustal seismic data from four intersecting traverses: a backbone traverse of 354 line-km and three high-angle traverses of 85 line-km to 180 line-km (Fig. 1). The data returned excellent results, imaging the crust from surface to the Moho, and provided valuable information on the three-dimensional structure of the Tanami region of the North Australian Craton.

The regional geology, tectonic history, and economic geology are summarized in Lyons and Huston (2006) and we refer the reader to this publication and the references therein.

2 PRINCIPAL RESULTS

The Tanami seismic survey revealed the crustal suture between the Tanami and Aileron.
Figure 2. Main features of the Tanami backbone traverse. Approximate base of Tanami Group shown by dotted line. Suture between Tanami and Aileron tectonic shown by heavy lines. Coomarie and Frankenia granites marked C and F, respectively. Moho shown by dashed line. Length 354 km. Depth ~66 km. Northwest end of traverse to left.

provinces (Fig. 2) and the association of Au deposits with major crust-penetrating shear zones. The crustal suture shows as a classic crocodile-structure (Meissner, 1989), suggesting collision between the Tanami crust and the Aileron crust, to the south, occurred before about 1840 Ma, when the overlying units of the Tanami Group and Lander Rock package were deposited.

Major accumulations of gold mineralization coincide with the surface projection of crustal-scale shear zones, some of which may connect to the Moho. In the upper crust, the shear zones are associated with hanging-wall anticlines showing the relationship between structures of the Tanami Orogeny (~1830 Ma) and mineralization (~1800 Ma). Some similarly structurally anomalous areas with no known mineralization should be considered worthy of exploration.

3 STRUCTURE OF THE TANAMI REGION

The host Tanami Group shows varying thickness. In the northwest, it attains a maximum thickness of about 10 kilometres (3.5 s TWT), thinning to about 3 km in the southeast (1 second TWT). Variations in the seismic character of the Tanami Group suggest the existence of early, discrete depocentres and the preservation of associated half-graben. An inference being that the thrusts formed by inversion of older extensional structures.

Two prominent granite bodies, hitherto mapped as the cores of domes (the Coomarie and Frankenia “domes”) are underlain by inward-dipping reflections, suggesting that the plutons were emplaced before generation of surrounding structure.

The suture-zone between the Tanami and Aileron provinces marks a thickening of the crust from about 40 km to over 60 km, coincident with the Willowra gravity ridge. The origin of the gravity ridge is still unclear, but it may be due to uplift of denser granulite-facies rocks from the mid-crust. The seismic survey did not extend sufficiently into the Aileron province to show if the thickened crust continues to the south.

The steeply dipping, west-northwest trending trans-Tanami structures, prominent in regional magnetic data, do not disrupt any reflectors below a depth of a kilometre, or so, and probably represent late-stage brittle adjustments of the crust.

4 BACKGROUND TO MINERALIZATION

At the scale of the seismic data, specific deposits cannot be imaged, but the association with thrusts and crust-penetrating structures is apparent. Because the seismic traverses intersect, the orientation of structures can be viewed in 3-D.

The scale of the mineral-system shows involvement of whole-of-crust and the whole of the basin containing the Tanami Group. Local factors influencing sites of deposition are probably due to chemistry of host rocks and changes in local stress-states. What the seismic data show is that the most favourable host rocks of the Tanami Group, the Dead Bullock Formation, are widely distributed through the region and, because of structural reorganization, are not confined to the lower parts of the basin. Although dominantly siliciclastic, the tightly folded Killi Killi Formation, shows seismic character, in places, suggesting that it, too, has mafic components which are also more favourable for sites of deposition. Thus, the evolution and architecture of the Tanami Group during the basin-phase maintained a fundamental influence on gold-mineralization in the Tanami region of northern Australia.
ACKNOWLEDGEMENTS

The seismic data were acquired by ANSIR, the National Research Facility for Earth Sounding. We thank ANSIR staff for their efforts and expertise, and personnel from Newmont Exploration Pty Ltd and Tanami Gold NL for assistance during the field operations and input during the interpretation of the data. Staff from Geoscience Australia processed the seismic data.

REFERENCES


Significance of extensional tectonics in orogenic gold systems: an example from the Eastern Goldfields Superterrane, Yilgarn Craton, Australia

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ABSTRACT: Historically, the emphasis on unraveling the structural geodynamic history of the Eastern Goldfields Superterrane of the Yilgarn Craton, Western Australian has been on compression. A systematic study of: structural overprinting relationships; links with the rock record and architecture, reveal extension has been the dominant tectonic mode of the geodynamic evolution of the Eastern Goldfields. Extension was associated with: deposition of the greenstone sequence; emplacement of voluminous granites; onset of gold mineralization; dextral transtension and subsequent orogenic collapse. While compression or transpression structures host the majority of gold mineralization these events are restricted to short protracted periods of time.

KEYWORDS: Yilgarn Craton, extension, geodynamics, gold mineralization

1 INTRODUCTION

In the Achaean Eastern Goldfields Superterrane (EGS) (Cassidy et al., 2006), Yilgarn Craton, the emphasis on unraveling the structural geodynamic history of the region has been on compressional tectonics and its relationship to gold mineralization (eg. Groves et al. 1998). This emphasis is complementary to the view that the EGS is a product of the WSW directed accretion of at least three separate terranes.

While this may be the case, the results of a three year AMIRA and Geoscience Australia research project done under the auspices of the pmd*CRC documenting structural overprinting relationships in greenstones and granites (Blewett et al., 2004) indicate that extension has had a significant role in the orogenic gold mineralization system.

Past workers such as Williams & Currie (1992), Williams & Whitaker (1993), Swager & Nelson (1997) and Davis & Maidens (2003) have identified the role of extension in the geodynamic evolution of the region. However, most of these workers failed to recognize the combined significance of extension in terms of its: timing, vector, relationship to the rock record, role in establishing the gross architecture and the onset of gold mineralization.

2 EXTENSION AND GEODYNAMICS

There are three distinct periods of extension and a period of transtension in the EGS. These events are related to: 1) early greenstone volcanism, 2) Late Basin formation and mantle-derived granite magmatism, 3) dextral transtension and 4) orogenic collapse.

The oldest rocks in the EGS are between 2810 and 2750 Ma, a likely record of an earlier orogenic cycle. A consistent rock record is not recorded until ~2720 Ma which is the focus of this study.

The first stage of extension is related to the formation of the greenstone sequence. From ~2720 Ma onwards (Figure 1) an intermediate volcanic arc was established on the eastern side of the EGS (Kurnalpi Terrane) and the western part (Kalgoorlie Terrane) was dominated by basalts and komatiites in an inferred back arc setting (Barley et al., 2002). To generate the necessary accommodation space for this arc and in particular the back arc the dominant tectonic mode must have been one of extension.

From ~2690 Ma to the remainder of the volcanic rock record at 2670 Ma, felsic volcanism
occurred across the central part of the EGS. The termination of volcanism (~2670 Ma) possibly resulted from the amalgamation (ENE compression) of the various terranes comprising the EGS. While map scale folds are attributed to this event it is difficult to precisely ascribe fabric elements to either compression or extension up to and including this amalgamation. This is due to the complexity and ambiguity of structural overprinting relationships developed in this dynamic volcanic arc environment where rocks were formed (together with space during extension), and subsequently rapidly deformed (in compression).

The second stage of extension is associated with the peak of granite plutonism and Late Basin deposition. The onset of felsic plutonism occurred at 2690 Ma and culminated with the emplacement of High-Ca granites at ~2673 and 2660 Ma (Figure 1). Mafic granite magmatism

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**Figure 1.** Geodynamic synthesis of the Eastern Goldfields Superterrane gold mineral systems.
culminated at 2665 Ma between these two peaks of High-Ca granites. The timing of mafic granite intrusion is temporally associated with the initiation of late Basin formation (Figure 1). These basins wrap around NNW and SSE edges of granite domes, contain granite detritus and overlay a pre-folded sequence. Shear zones, with extensional kinematics, occur in the footwall to these basins, and wrap around the edges of adjacent granite domes. There is a strong spatial and kinematic link between most late Basins and granite domes.

Extension related to the formation of these basins initiated orthogonal to the earlier ENE direction of compression, possibly as a result of orogenic escape and by 2660 Ma was unidirectional towards the ENE. This switch in extension direction is preserved within the rock record as younger, consistently N to NNW-striking late Basins inferred to have developed within extensional grabens. This hypothesis is supported by E-W seismic profiles (Figure 2). They show shear zones which envelope granite domes are of equal dip to those in the footwall to these basins and both sole into a common detachment at depth. The kinematics of the shear zones and their geometries are extensional and thereby indicate these basins are also related to the extensional doming event. 2D and 3D map patterns and seismic sections show that this second stage extensional event was responsible for establishing the gross architecture (granite cored domes and synclinal greenstones) of the region. It was this architecture that was inverted during two subsequent gold bearing deformation events.

The first of these deformation events involved regional E-W directed transpression that folded the Late Basins and developed NNW-striking sinistral strike-slip faults that are related to gold mineralization at mines such as the Golden Mile and St. Ives (Bateman & Bierlein, in press; Cox & Ruming, 2004). This event occurred during a switch in granite magmatism (Champion & Sheraton, 1997) from mantle related melts (High-Ca and Mafic) to high temperature crustal melts (Low-Ca). Palaeostress analysis of these structures shows a large variation in the local stress field across the region. It is suggested here that the local stress heterogeneity was a natural consequence of inverting a highly anisotropic dome and basin architecture (established during the previous extensional event). The deformation of this anisotropic architecture resulted in the establishment of highly variable fault geometries favorable for gold mineralization.

The second inversion of the architecture and third extension related event is a major gold bearing deformation. It coincides with the emplacement of Low-Ca granites (across the entire Yilgarn Craton) within a dextral transtensional tectonic mode. This deformation is characterised by N to NNE striking predominately brittle dextral transtensional faults. Structures related to this event host gold at mining camps such as, Wiluna and Mt. Charlotte (Hagemann et al., 1992; Bateman & Bierlein, in press). Palaeostress analysis of this event shows a consistent local and regional stress field of NE-SW compression.

There are two pulses of Low-Ca granites related to this event with the second peak showing a diachronism from oldest in the east to youngest in the west across the EGS. This suggests that the related dextral trans-tension event is also diachronous. The youngest peak of Low-Ca magmatism corresponds with the youngest gold ages in the EGS.

Following dextral transtension, the region was affected by a period of late orogenic collapse the fourth extensional event. The resultant structures include horizontal crenulations in highly foliated rocks and brittle normal faults in more competent units (Davis & Maidens, 2003).

### 3 EXTENSION AND MINERALIZATION

While gold mineralization in the EGS is predominantly hosted within compressional or trans-tensional structures the second-stage extensional event (~2660 Ma) marks the first onset of significant gold mineralization in the EGS. Deposits such as Sons of Gwalia and Lancefield lie in extensional shear zones related to this event (Figure 3). While this is the earliest onset of significant mineralization in the EGS it is nevertheless late in the orogenic cycle (2720-2630 Ma), a feature of many lode gold systems (Groves et al., 1998).

There is a relationship between the onset and termination of granite magmatism and the timing of gold mineralization (Figure 2) which suggests that granite magmatism is a critical factor in the formation of orogenic lode gold deposits. Each of the peaks in the various types of granite magmatism (Figure 1) correspond with periods of extension as this tectonic mode was necessary to accommodate the large volumes of granite emplaced into the crust.
4 CONCLUSION

Extension or trans-tension has been the dominant tectonic mode of the geodynamic history of the EGS. It was associated with the deposition of the greenstone sequence, the emplacement of granites, dextral trans-tension and subsequent orogenic collapse. All periods of compression are short protracted events in time.

The second stage of extension related to the formation of the last part of the supercrustal rock record and peak in voluminous granite magmatism also marks the onset of gold mineralization in the EGS. The subsequent period of compression and followed trans-tension are the two most significant structural events in terms of mineralization.

ACKNOWLEDGEMENTS

We thank the sponsors of the AMIRA P763 project for their support and Leonie Jones from Geoscience Australia for reprocessing parts of the NY1 seismic line for us. We publish this abstract with the permission of the CEOs of Geoscience Australia and pmd*CRC.

REFERENCES


Bateman R, Bierlein FP (in press) On Kalgoorlie (Australia), Timmins-Porcupine (Canada), and factors in intense gold mineralization. Ore geology reviews.

Blewett RS, Cassidy KF, Champion DC, Whitaker AJ (2004). The characterisation of deformation events in time across the Eastern Goldfields Province, Western Australia. Geoscience Australia Re-
cord, 2004/10 [CDROM].


Fooling Ourselves – Dealing with Model Uncertainty in a Mineral Systems Approach to Exploration

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ABSTRACT: Deposit models are belief systems that are based on a combination of inspiration, intuition and logic. They contain a large degree of uncertainty that is arguably hard, and in many instances impossible, to quantify. This uncertainty is mainly linked to our incomplete understanding and imperfect interpretation of geological systems, the inherent variability of geological objects and biases and uncertainties linked to the geoscience data upon we base our interpretations. While these biases and underlying uncertainties are well recognized within the mineral exploration community, we contend that there is little appreciation for the heuristics (mental shortcuts) and biases (errors) that stem from translating mineral systems to exploration systems. While the systematic application of a detailed mineral systems model can give the outward appearance of providing much more accurate and precise targeting outcomes, these outcomes can in fact seriously bias a prospectivity analysis to the point where it is less effective and decreases our probability of success in discovering a valuable mineral deposit. This paper investigates these issues and concludes that in translating the critical process parameters of a mineral systems model to mappable exploration criteria, it is critical to identify and manage potential heuristic errors, avoid bias due to the large uncertainties in our understanding of mineral systems, and generate criteria that map the key processes in the genesis of mineral deposits, broad P-T-X gradients and system architecture, on appropriate length and time scales.

KEYWORDS: mineral systems, uncertainty, deposit models, mineral exploration

1 INTRODUCTION

Deposit or exploration models are reflections of our understanding of the processes of ore genesis. Traditionally these models have been based on the geological elements that are seen to occur in known deposits, and searching for analogies of these deposits in other areas. In the past decade, much has been written of the mineral systems approach to mineral exploration (cf. Wyborn et al. 1994), which in turn takes a page from the petroleum sectors’ widespread use of this approach for the past three decades (Magoon & Dow 1994). This process-based approach to mineral systems (as opposed to simply geological elements) is heralded as bringing a less-biased approach to mineral exploration models, and the targeting criteria the industry searches for in various geoscience datasets. But are we kidding ourselves? Is the more detailed understanding of mineral system processes truly resulting in more effective exploration criteria? This paper sets out to examine this issue.

2 THE APPLICATION OF MODELS

The application of preexisting geological ideas is essential in mineral exploration. Models are useful for communication, reference and learning and form a vital part of the exploration targeting and decision-making process at any scale, but particularly when it comes to ground selection decisions (Hronsky 2004) where models are used to (1) identify mappable criteria at appropriate scales, (2) generate targets, (3) prioritize and rank targets, and (4) evaluate targets (Fig. 1). This process is formal or intuitive, conscious or subconscious and ranges from the most ‘boots on ground’ exploration attitudes to the most sophisticated approaches of systematic and statistical analysis in the computer envi-
environment.

This point is illustrated by comparing two philosophically different approaches: empirical models versus conceptual process-based models. Empirical models are based on the occurrence of features associated with known mineral deposits in time or space. An empirical model may be based on as little as a single criterion, such as a specific host rock, or spatial trend in known deposit occurrences. For example, many companies that explored for Archaean lode-gold deposits in the Eastern Goldfields Province (Yilgarn Craton, Western Australia) focused on differentiated zones of dolerite sills, and if a target was in a dolerite sill it would have been given a higher ranking. This was not an entirely unwise strategy, given the common spatial association in this province of major gold deposits and dolerite sills (e.g., Ho et al. 1990). In this example, the dolerite is well mineralized due to its chemical favourability (high Fe/Fe+Mg ratio promoted scavenging of sulphur and gold from the fluid via desulphidation reactions) and the fact that dolerite is much more brittle (quartz and plagioclase content) than the surrounding ultramafic rocks and basalt. Hence, the dolerite attracted more fracturing during deformation and therefore greater fluid flow. Therefore, the dolerite reflects specific chemical and physical processes that favour localized gold deposition. However, the companies did not hunt the process, but only one (albeit good) possible manifestation of this process. Hence, this exploration model could neither find the large Wallaby (~7 Moz Au), Sunrise Dam (~6 Moz Au) and Kanowna Belle (~5 Moz Au) gold deposits nor the myriad of other significant deposits in the Eastern Goldfields Province that are not hosted in dolerite.

On the other end of the spectrum, we have the discoveries that were made on the basis of conceptual process models; the Olympic Dam iron oxide-copper-gold-uranium deposit (Gawler Craton, South Australia) arguable being the most prominent amongst them. The model that drove the early work by WMC Ltd focused on reduced sedimentary rock packages adjacent to major fault zones that could have tapped copper-bearing fluids emanating from underlying oxidized and altered basalts (e.g., Haynes 2006). This process model helped WMC Ltd to direct exploration into the right area but the model was actually designed to predict the location of sedimentary-hosted copper rather than oxide-copper-gold deposits.

The differences may appear subtle, but are important. In the first case, the hunt for a specific geological element blinded companies to the potential in other host lithologies of the Yilgarn, and in the second, the focus on a process-based model allowed for the serendipitous discovery of another deposit type altogether. These differences will be expanded upon below.

3 RECOGNIZING UNCERTAINTY IN MODELS

In short, models are important but are detailed models important, and do the details make a difference? Exploration models, like all belief systems contain a large degree of uncertainty (Fig. 1) that is mainly linked to (1) our incomplete knowledge of geological systems, (2) our imperfect interpretation of these systems, (3) the inherent variability of geological
objects and processes, (4) the uncertainty associated with the geoscience datasets upon which we base our interpretations (e.g., Bardossy & Fodor 2001).

In our understanding of mineral systems, the uncertainty in the underlying data is substantial, as we are generally looking at data with very uneven sample support, quality and resolution. Similarly, the inherent variability in geological objects and processes is recognized, and can be very difficult, or even impossible, to quantify (e.g., Bardossy & Fodor 2001; Couleleli 303). It is our incomplete knowledge of geological systems and imperfect interpretation of these systems that we often do not recognize as impacting on our exploration strategies. It is in this arena of interpretation and limited understanding that the real danger lies and where we can seriously fool ourselves.

Model uncertainty is in part a product of the inherent limitations of human cognitive processes (“bounded reality”). This means that by the very architecture of our brains we cannot handle complex situations without simplifying them (Simon 1983). This is the basis of heuristics (e.g., Tversky & Kahneman 1974), rules of thumb or mental shortcuts, that reduce the time and effort of decision-making, enable us to undertake pattern recognition, and make interpretations from incomplete datasets but they can also seriously bias our interpretations, models and exploration strategies (e.g., Solomon 1992, Vann 2005, Welsh et al. 2005).

The four main heuristics to consider are: (1) Representativeness: we have a tendency to over-generalize from a few characteristics or observations. Therefore, the quality of our interpretations is extremely depended upon data density and quality. (2) Availability: we tend to ignore the total number of possibilities to focus on those options that come to mind more easily (i.e. are more available). Hence, we are heavily biased toward our personal experience base. (3) Anchoring: our initial interpretation provides an anchor that influences the final outcome. Any adjustments of the initial model are typically insufficient, narrow and biased towards the anchor (i.e. it is easier to patch up an existing model than to construct a new one). (4) Salience: we tend to more easily recognize features that we have focussed on recently, and we tend to have an emotional investment in our models, or in the words of Vann (2005) “the more we publicly defend (or promote) a particular model, the more difficult it is to radically challenge it.”

4 EXAMPLES

Take the model for Archaean lode-gold deposits. Even after decades of research there is plenty of controversy about the source of the gold and processes of ore genesis: e.g., (1) magmatic input versus no magmatic input, (2) two ore-forming fluids versus one fluid, or (3) late versus early timing with respect to multiple phases of deformation. Even though some people hold firm belief systems about specific aspects of the model (e.g., magmatic input to Archaean lode-gold systems) they often do not explore that way (i.e. they do not develop a targeting strategy that considers the inferred magmatic input). In the case of magmatic inputs to Archaean lode gold deposits, if the exploration criteria are heavily weighted to anomalous gold in soils, structure and favourable host lithologies, then the magmatic model is not relevant to the exploration strategy. Conversely, if from a magmatic model the presence of an intrusive body is taken as a critical targeting criterion, the prospectivity analysis and target ranking would be heavily impacted. While addition of this targeting criterion may give the appearance of a more restricted and precise targeting outcome the outcome is possibly biased, inaccurate, and therefore less effective, given that we do not know if (or what types of) intrusions actually played a critical role in the formation of Archaean lode-gold deposits. Moreover, including the targeting criteria “intrusive body” would not have found the Golden Mile (>90 Moz Au) at Kalgoorlie.

Impacts of specific targeting criteria on predicting prospective ground can and should be evaluated in GIS-based simulations of the translation of models to mappable criteria and the weighting of these criteria (e.g., Brown et al. 2004). In our opinion, detailed models are useful only where they impact on formulating targeting criteria and weighing schemes for target ranking.

5 THE WAY FORWARD

The more ‘clever’ we become about a particular model and specific details, the greater the chance that we are fooling ourselves. Given the examples above, how do we prevent our detailed models from biasing us to the point where we target less effectively? (1) Using a
mineral systems approach (e.g., Wyborn *et al*. 1994; Hronsky 2004) to help focus exploration on the geological factors that control the generation and preservation of mineral deposits and the processes that are involved in mobilizing ore components from a source, and transporting and accumulating them in more concentrated form. (2) Staying with the basics: crustal-scale P-T-X gradients for source and transport aspects, local-scale P-T-X processes for 'trap' aspects, and factors that control system architecture and the preservation of mineral deposits (e.g., Barnicoat 2006). The impact of uncertainty in a given model is a function of how well we translate the model to mappable criteria at appropriate scales. The key mappable criteria reflect the basic processes of heat and mass transfer through the crust. For example, some explorers map changes in mica composition that they believe are signals of magmatic input. In our approach, mapping changes in mica composition equals mapping regional chemical gradients for source and transport, and local chemical gradients for deposition. In our opinion, chemical gradients are good targeting criteria whether magmatic or not. (3) Being aware of and managing the biases and heuristics that affect every human being when making decisions under conditions of significant uncertainty.

REFERENCES


Ho SE, Groves DI, Bennett JM (eds) (1990) *Gold deposits of the Archaean Yilgarn Block, Western Australia: nature, genesis and exploration guides*. *Geology Department and University Extension, University of Western Australia Publication* 20, 407 p
ABSTRACT: A simple, large-scale, generic granite-related gold deposition scenario is modelled using a new finite element reactive transport code (pmdPyRT) coupling chemical reaction, mass-heat-fluid transport, and dynamic permeability evolution. Detailed analysis of the results of this model show complex evolution of many of the parameters in both time and space. Results from this work are used to illustrate that this type of modelling can be used as an effective tool in aiding predictive mineral discovery and complex system analysis.

KEYWORDS: numerical modelling, mineral system, gold, granite

1 INTRODUCTION

Reactive transport modelling has been applied to problems in the earth sciences where we are interested in the coupling and feedback between different physical/chemical processes. In particular the coupling and feedback between heat and mass advection, chemical reaction and porosity-permeability is especially important at sites of active mineral deposition. While reactive transport modelling is commonly applied to environmental and contaminant/waste problems (i.e. nuclear repository, contaminant plume etc), it has only limited application in hydrothermal studies (with notable exceptions i.e. MVT Pb-Zn, rollfront U etc).

This work describes the reactive transport code being developed within CSIRO as part of the Predictive Mineral Discovery Cooperative Research Centre. Using a simple case study this work demonstrates the potential application of this type of modelling and the implications for predictive exploration.

2 THE RT CODE

PmdPyRT (see Cleverley et al., 2006) forms part of a collection of software codes (python/C+/++) used for solving the equations relating to the transport of fluid, mass and heat, and chemical reaction. The partial differential equations are solved using FastFlo4 (Gross, 2002) via the Python scripting language (Python 2.3). This means that code written in multiple languages can be used together in a seamless interface to solve multi-process problems.

The code solves the equilibrium chemistry using the WinGibbs solver (v.4.0, Shvarov, pers. Comm.) which is an update to the gibbs energy minimisation solver used in the geochemical modelling code HCh (Shvarov and Bastrakov, 1999).

Model geometry is built and meshed using a finite element structured or unstructured meshes, and this approach enables much smoother geometries and the ability to mesh geometric models from GIS software such as GoCad.

3 MODEL DESCRIPTION AND DETAILS

The model presented in this paper has been used to explore the relationships between granite derived fluids, a generic greenstone architecture, and gold deposition. The model represents a metamorphosed mafic sequence and underlying felsic sequence cut by a listric fault with a granite situated at the base of the model (see Fig. 1). The whole model is 30km wide and 15km deep and contains ~15000 mesh elements.

3.1 Pressure-Temperature Conditions

The top of the model is fixed at 5 MPa and 40°C (~500m depth) and the initial P-T condi-
tions are based on hydrostatic pressures and 30°C/km gradient. The base of the model is constrained with a fixed heat flux (85 mW/m²).

The granite is initialised at 600°C (T₀) and is allowed to cool via Heat advection and conduction. Heat flux at the base of the granite is elevated (100 mW/m²) for the first 0.15 Ma model time, after which the value is the same as the rest of the base of the model.

The initial porosity-permeability structure of the model is initialized at 0.15/10⁻¹⁵ mafic units, 0.05/10⁻¹⁷ basement, and 0.4/10⁻¹⁵ granite. The porosity is dynamic and is calculated at each time step as a function of the liquid volume of the nodes and changes are a consequence of the precipitation or dissolution and transport of material. Permeability is calculated as a function of porosity using the Carman-Kozeny relationship,

\[ \kappa = \kappa_0 \left( \frac{\phi}{\phi_0} \right)^3. \]

3.2 Chemistry

Initial Solid and aqueous chemistries were defined for each of the model units and the mineralogy broadly consist of: mafic unit: albite – quartz – calcite – tremolite - chlorite – pyrrhotite – graphite; felsic volcanics: quartz-albite-muscovite-k-feldspar-pyrite; and granite: quartz-albite/anorthite-k-feldspar-biotite-magnetite with H₂S in the fluid.

The fluid phase is populated initially with a mixed brine (Na,K,Ca,Fe) at ratios close to equilibrium for that rock, H₂S±SO₄, Au⁻ (1e⁻⁹ and 1e⁻⁵ molal for background & granite respectively), and CO₂. The ΣC_(aq) is minor in the mafic rocks (CH₄), dominant in the felsic volcanics (CO₂) and absent in the granite. The initial chemical step (with no transport) will define the fluid composition in full equilibrium with the rock at the fluid/rock defined by the specified porosity of that unit. As each bulk chemical composition is defined across a temperature-pressure range the equilibrium phase assemblage will also vary across the model unit.

4 RESULTS

Figure 1 shows the spatial distribution of total precipitated gold (g/t, > 1 ppb) at the end of the model (1.15 Ma), along with the darcy fluid flux vectors and the underlying model architecture. There are two areas of gold deposition, a) the roof zone of the granite and, b) the area of mafic rocks overlying the fault and granite.

4.1 Granite-hosted gold

The gold precipitated in the granite may be considered as a function of the inability to transport much of the gold away from the granite because of the low permeability cap rocks (10⁻¹⁶ m²), but more importantly the large gradient in the temperature driving the solubility down during cooling (600 to 450°C). This gold zone will not be considered further here.

4.2 Mafic-hosted gold

The upper gold zone displays a two prong shape concentrated at, and above, the fault-mafic interface. There is also a broad column of low grade Au above this zone (> 1 ppb, Fig. 1). Calculated maximum concentrations in this zone are ~1.2 g/t rock. This may not appear at face value to be of great significance economically but it is worth considering that this is a 2D model where the source region is limited volumetrically and also temporally in this model (i.e. hot granite only occurs once and is limited in extent).

5 ANALYSIS OF RESULTS

5.1 Spatial-Temporal Patterns

In complex system modelling it is important to fully analyse the results such that we gain an understanding of the processes that operated leading to ore formation (which are the key processes and which are secondary). This type of coupled modelling also helps us to extract process understanding that can be applied to similar mineral systems even if the geometries are not the same.
When analysing the results of a coupled model the assemblage distribution is a product of changing processes and interactions over time, and this is especially true in non-steady state systems (i.e. cooling granites). Therefore in order to analyse the results we have to consider the temporal and spatial evolution of the system.

Using the FEMstats utility the temporal history of a single coordinate can be extracted. Figure 2 shows the evolution of the mineral assemblages (and gold) over time for a point in the high-grade section of the upper gold zone ($x_{14586}, y_{7314}$). Active gold precipitation occurs between about 0.16 and 0.52 Ma (of the granite has cooled to the background geotherm by ~0.10 Ma). The gold event is marked by a decrease in albite and epidote and increase in calcite, muscovite->paragonite, and Fe-sulphide phases (pyrite-pyrrhotite). The post-gold event is marked by increasing epidote - graphite, and decreasing calcite - muscovite as these minerals are overprinted.

Figure 3a and b shows some of the key physical parameters for the same location with time. The $X_{CO2}$ ($CO_2/\Sigma C_{fluid}$), tracking redox, shows a distinctive pulse-like evolution which is partly related to the passage of granite-derived fluid (monitored by the inert tracer), which presence is observed through-out the gold event. Detailed analysis of key times depicted as A, B, C and D reveals:

1) $CO_2$ pulse A is related to broad up flow of the ambient fluid from the felsic rocks as a consequence of displacement by the granite fluid and the thermal pulse that this invoked.

2) Pulse B and C represent the focussed ascent path of hot, granite derived fluid. However this column moves around and is not fixed in space. Pulse B and C are times when the column was located at the monitoring point, at the time in-between the up-flow zone is distal but still influencing the monitoring point at its margins.

2) Time D represents a return to circulation of the ambient mafic fluids because thermal collapse of the system has moved the up flow zone to the left.

The greatest gold precipitation gradient ($\delta_{Au}/\delta_t$) occurs in response to the first granite-derived fluid pulse and this is also associated with an increase in the total S in the fluid and the temperature (~300°C compared to the background 270°C, Fig. 3b). The second pulse as observed in the tracer-$X_{CO2}$ (Fig. 3a) is not associated with increased S and/or temperature, in fact there is a general temperature decrease towards time D (Fig. 3a) that represents the down welling and mixing of fluids from the upper portions of the mafic unit.

Using this information it can be seen that it is vitally important that you analyse the correct spatial relationships relative to the temporal evolution in order to understand the key processes.
5.2 Gold deposition process

By studying in detail the spatial chemistry at 0.189 Ma (maximum $\delta_{Au}/\delta_t$), the deposition mechanism for gold under these conditions appears to be, at least in part, sulphidation of epidote Fe into pyrrhotite and the concomitant destabilisation of Au(HS)$_2^-$ (95%) and AuHS (5%) from the granite derived fluid. The transported CO$_2$ reacts with Ca in the mafic rock (epidote) to form calcite.

5.3 Alteration patterns

The dominant proximal (100-1000 meters scale) alteration assemblage is calcite-quartz-pyrrhotite-muscovite-paragonite and chlorite. At the larger scale, within the column of alteration above the gold zone (5-8 km) there is a strong transition from Mg-chlorite to Fe-chlorite and tremolite with increasing distance (Fig. 4), and graphite forming at the margins of the column.

Figure 4: Chlorite composition (XMg) and tremolite distribution (contours, lines) at 1.14 Ma. Note the change in these parameters with depth towards the gold zone (see Fig. 1).

Using the predicted spatial relationships of mineral assemblages further developments are being made to incorporate predicted physical parameters (i.e. density, magnetic susceptibility) and their geophysical derivates (gravity, magnetic profiles).

6 CONCLUSIONS

This work highlights the importance of detailed analysis of the numerical modelling results and some of the key predictive outcomes that can be produced as a product of this (i.e. spatial assemblage maps, scales of alteration). Large- (crustal, terrane) and small-scale (mine) reactive transport modelling can now be accomplished to aid in better testing and prediction of the evolution of hydrothermal mineral systems.

ACKNOWLEDGEMENTS

This work is published with the consent of the CEO of the Predictive Mineral Deposit Cooperative Research Centre. My thanks go to Peter Hornby, Thomas Poulet and Lutz Gross who were instrumental in making this all work.

REFERENCES


Influence of strike length in area selection for fault-related hydrothermal ore deposits

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ABSTRACT: At a regional, terrane scale, it is often found that the long strike length faults and related potential field gradients correlate with elevated metal distributions. This is linked to the concept that large dimension structures are intrinsically weaker, wider damage zones that act as pathways for fluids at different crustal levels. A GIS-based technique is described here that uses the strike length of fault-related structures as an area selection filter. This methodology is especially relevant when exploring in under-cover regions using potential field (gravity, aeromagnetic) data which has been processed using edge detection routines. If applied at an early stage in the exploration process, this can lead to a significant reduction in the search area, and appears to increase the chance of discovery.

KEYWORDS: hydrothermal deposits, faults, potential field, multiscale wavelets, GIS analysis

1 INTRODUCTION

Area selection is central to exploration success. This goes beyond “anomaly picking” and requires one to filter across scales to outline more prospective areas, while rejecting areas of less potential. A key question is what elements of regional scale data can best predict the location of ore systems? For fault-controlled hydrothermal deposits, this becomes a question of which fault (or fault intersection) is most important, and how to rank such elements within what is a hierarchy of fault size. Often it appears, at a deposit scale, that small faults localise ore. Yet, in a broader view of the mineral system, proximity to regional scale faults seems to control the spatial distribution of deposits, such as those that occur in linear trends.

The explorer has a priori knowledge of varying reliability on which to base area selection decisions. There is a need to better constrain and quantify the selection process in the analysis of faults and potential field (gravity and aeromagnetic) data. Gradients in the potential field reflect density and/or magnetic susceptibility contrasts, such as due to abrupt changes in rock type. The positions and nature of such gradients are a key element in developing a geological interpretation as a basis for area selection. This can be approached using GIS-based tools for evaluating regional scale data, and a methodology has been developed by the pmd*CRC which is illustrated here with examples from the Irish Zn province, the Palaeozoic Tasmanide province of SE Australia and the Archaean Yilgarn Au province in Western Australia.

2 REGIONAL SCALE PARAMETERS

Prospectivity analysis of regions works best where there is a comprehensive spread of data (e.g. faults) whose attributes can be evaluated against other spatial data (e.g. deposits) to determine their relationships, empirically and predictably. However, it is commonly the case that there are few numerical parameters that one can use effectively and reliably to narrow the exploration search area. In the first instance, geological information is not uniformly distributed, being sparse or particular to an outcropping area. In such regions, fault strike and length are of particular interest and are more readily determined than fault dip and depth extent. Potential field data is often superior in that it provides a regionally uniform coverage of gradients, many of which are fault-related. However, there is inherent ambiguity in poten-
tial field interpretation (see below). Notwithstanding this, such gradients (or edges) have strike and length parameters, as well as apparent dip and depth extent. As such, it should be possible to combine different data sets (gravity, aeromagnetics) to evaluate regional scale distributions. In this presentation, the focus is on fault and gradient length and their relationship to metal distribution.

Fault growth models demonstrate a scaling relationship of increasing displacement relative to increasing fault length and width (Watterson, 1986; Walsh & Watterson, 1989). In general, longer strike length faults accumulate greater overall displacement, have wider damage zones and are inherently weaker than small dimension faults. Geometric considerations almost always demand that long faults will generally have greater depth extent than similarly oriented short faults. A corollary of this is that fault length may be a loose proxy for depth extent. This is relevant to hydrothermal deposits as depth extensive faults are potential pathways for accessing fluids from different crustal reservoirs that may then migrate to mix with other fluids, or to cool and un-mix, leading to mineral deposition. The inference is that fluids migrate away from large dimension structures to localise deposits along small faults that are peripheral to these “parental” structures. We seek to evaluate and quantify this through spatial queries on a GIS platform.

3 POTENTIAL FIELD GRADIENTS AND MULTISCALE WAVELET ANALYSIS

The geological interpretation of potential field data (gravity, aeromagnetics) is a highly subjective aspect of regional analysis that impacts on area selection decisions. CSIRO, in collaboration with Fractal Graphics in Perth, developed an automated edge detection routine to help reduce this ambiguity, using multiscale wavelet-based algorithms to detect the positions of maximum gradients (loosely termed “worms”; Archibald et al. 1999; Hornby et al. 1999; Holden et al. 2000). The advantage of this approach is that it provides a 3D map of the population of upward continued gradient fields that permits rapid, repeatable interpretations of the data to be made. “Worms” are now routinely used, particularly in Australia but increasingly elsewhere, to help constrain terrane- and district-scale architectures. From a mineral exploration perspective, the gradient data facilitates a quantitative analysis of the spatial relationship to known mineralization, from which inferences of prospectivity can be drawn.

The worming technique is applied to gravity and aeromagnetic data across multiple levels (heights) of upward continuation to yield points of maximum gradient. Where there is a density or susceptibility contrast in the data, this generates a worm across different heights, depending on the nature of the geological source (e.g. faults, intrusive and stratigraphic boundaries). At low levels of upward continuation, “fine scale” worms relate to high frequency, shallow level edges while, at high levels of upward continuation, “coarse scale” worms derive from low frequency gradients that typically (though not always) relate to deep level sources (Archibald et al. 1999). Gravity and aeromagnetics naturally provide contrasting, but also comparable, gradient fields. The pmw*CRC’s research techniques (and software) provides thematic maps of these gradients as points, vector lines and images which are attributed with a range of parameters (e.g. trend, length, straightness, height). Strike length is an easily determined, unifying character of the gravity and aeromagnetic data sets. In the interpretation of the data, there is subjectivity in determining where faults end, are offset or are terminated. Ockham’s Razor (“entities should not be multiplied unnecessarily”) is employed in the interpretation routine, seeking to emphasis continuity rather than segmentation (as per the original data). Images of strike length can be readily extracted from the vector line interpretation.

4 TERRANE SCALE EXAMPLES

The Upper Palaeozoic Irish Zn carbonate-hosted mineral system shows clear evidence of fault control on the location of deposits (Johnston 1999). Key faults are those that penetrate the basement, such as the Navan-Silvermines Fault. Typically, the ore deposits occur in the first carbonate unit (the Navan Beds and/or basal Waulsortian) above the basement and are located in the hanging walls of normal faults, especially northward dipping faults. Hitzman (1999) sees the latter association as a preservation phenomenon, however numerical modeling of the processes that drive the genesis of Irish-type deposits (fluid flow, deformation, thermal transport and fluid mixing) provides a strong rationale for fault dip direction having a
key control on the localization of mineralization (Murphy et al. in review; Ord et al., 2007). Worming of the Irish gravity and aeromagnetic fields to 30 km height of upward continuation reveals a number of these regional scale features. Such data can provide a basis for area selection in this terrane, focusing on laterally continuous and persistent gradients over multiple levels of upward continuation. Figure 1 shows the gradient points coalescing as a series of worm sheets, with the NE trending gradients representing penetrative faults and these are cut by less continuous NW trending gradients representing cross faults. The Tynagh ore bodies are spatially related to the NE trending worm through the central part of the image.

The Lower Palaeozoic Tasmanides region of SE Australia is a multi-commodity province, with world-class gold and base-metal mineral deposits where fault-controls have been recognized for some time (e.g. Walshe et al. 1995). For the VHMS deposits of Western Tasmania, there is a close spatial relationship of deposits with regional scale faults, such as the Rosebery, Henty and Great Lyell Faults. Worming of gravity and aeromagnetic data in this region reveals a spatial association of major deposits with large dimension features. This is emphasized though imaging strike length parameters of the data (Fig. 2). In this, the brighter grey areas represent regions of longer structural elements and seem to have higher potential to host major deposits (Murphy et al. 2004).

The Archaean Yilgarn region of Western Australia is a world-renowned gold producing region where both regional and small scale faults play a controlling role in metal distribution. This is emphasized in a quantitative analysis of faults and related gravity gradients by Bierlein et al. (2006) who showed that gold is preferentially distributed in small faults that are relatively proximal to larger, regional scale faults and related gravity worms. The traces of such gradients can guide area selection decisions in the province and its under-cover extents.

CONCLUSIONS

Area selection is ultimately a subjective decision made by applying a number of variably reliable filters to available data sets. Strike length distributions of faults and fault-related
potential field gradients provide some insights to the possible first order controls in the localization of fault-related deposits where regional or crustal scale elements are seen. Large dimension structures being weaker, wider damage zones can act as pathways for fluids at different crustal levels. Such structures are also commonly associated with significant potential field gradients. The application of a length filter at an early stage in the exploration process can lead to a significant reduction in the initial search area while increasing the chance of discovery.

ACKNOWLEDGEMENTS

Published with permission of the CEO of the pmd*CRC. Pasminco (Australia) Ltd, Fractal Graphics (Geoinformatics) and Fractore P.L. are acknowledged for provision of worm data in the Irish mineral province.

REFERENCES


Murphy et al 2006 3D modeling AJES

Practical application of numerical modelling to predictive targeting

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ABSTRACT: While numerical modelling is a well established component of geoscience research, it is not a common tool in mineral exploration. This reflects various perceptions held by mineral explorers including: (1) unfamiliarity with numerical modelling techniques, (2) absence of a widely understood workflow for applying them to targeting, (3) practical difficulties in using the software, (4) disbelief that the complexities of geology can be dealt with in a useful way by such methods. This paper outlines an approach and workflow, illustrated by one case history, which shows that practical benefits can be obtained using these methods in several types of ore deposits in useful time frames. The key requirement for predictive success is successful completion of the initial model validation step on a known ore system in which a process of simplification and extensive parameter testing is followed.

KEYWORDS: numerical modelling, deformation, fluid flow, gold mineralization, targeting

1 INTRODUCTION

Numerical modelling of geological processes is well established in the geological sciences. It is recognised as a tool for analysing geological processes where conceptual approaches are unable to unravel complex geological behaviours arising from the interplay of multiple geological parameters (e.g. rheology, geometry, strain rate, chemical interaction etc). Application of numerical modelling to targeting in mineral exploration remains uncommon. Reasons for this include: (1) unfamiliarity with these techniques among geoscientists in the mineral industry, (2) absence of a widely understood workflow to convert numerical modelling outcomes into useful targeting decisions, (3) practical difficulties in using the software (e.g. user-unfriendly interfaces, code instability, long run times etc), (4) disbelief among exploration geoscientists that the complexities of geological geometries and processes can be dealt with in a useful way by such methods.

The Computational Geoscience research group at CSIRO and its predecessors have been working on these problems for the past 20 years. Since 2001, the group has been supported by the Predictive Mineral Discover Cooperative Research Centre (pmd*CRC). Through this support, significant advances have been made both in the development of the technology and its application to mineral industry targeting problems.

The research focus within the pmd*CRC has been to develop and apply a system for numerical modelling of the coupled processes involved in the formation of non-magmatic hydrothermal ore deposits i.e. deformation, fluid flow, thermal evolution and chemical reaction.

2 WORKFLOW AND APPROACH

The approach developed in the pmd*CRC was designed in light of the following considerations: (1) Evaluation of the entire mineral system is necessary during the information-gathering process which precedes numerical modelling. Ore localisation is affected by processes which occur on a vast range of time and length scales. Therefore the process of framing the questions for numerical modelling experiments needs to take into account existing knowledge at all scales in the mineral system. (2) This application of numerical modelling is aimed at increased targeting efficiency and hence reducing discovery cost rather than obtaining a perfect success rate. For this reason,
there is no absolute requirement to develop predictive models of ore formation that are correct in every detail. The key requirement is to generate targeting strategies that are more efficient than traditional empirical approaches. Therefore, generating predictions of possible ore location based on a number of equally likely working hypotheses is an acceptable methodology. (3) Many of the most powerful insights are obtained from geometrically and/or conceptually simple models. Thus, the process of acquiring predictive understanding is usually derived from analysing different geological phenomena via a series of simple experiments and, from that, building an understanding of the complex interplays in real geological systems. (4) The workflow has been developed for those ore systems in which the geological processes can be simulated with reasonable confidence using the computational tools that are currently available. This has meant a focus on orogenic gold deposits (Goldfarb et al., 2001; Schaub et al., 2006), sediment-hosted massive sulphides (Ord et al., 2006) and uranium deposits (Ord et al., 2004) formed above the brittle-ductile transition in the middle crust. (5) Typically, an evaluation of many different scenarios involving variations in various model parameters (e.g. rheological properties, stress field orientation etc) is required. Thus, software and hardware solutions are required that enable rapid problem set-up, simultaneous simulation of many scenarios, rapid visualisation and interpretation and fast individual model runs (ideally 12 hours or less).

The workflow that emerges from these considerations consists of the following elements: (1) mineral system analysis using a “5 Questions” approach (Price & Stoker, 2002), (2) development of a set of questions which are testable by numerical modelling and can generate answers which relate directly to ore localisation in space and time, (3) preparation of numerical meshes embodying the geological geometries under consideration, (4) running the models, (5) visualisation and interpretation, and (6) incorporation of the results into targeting strategies.

This workflow is generally employed in a two stage process: (1) A model validation step applied to a known ore system in which the appropriate critical parameters (e.g. rheological properties, stress history, fluid chemistry etc) are identified through a large number of experiments in which a probable set of conditions for ore localisation are established and (2) A “predictive” step in which less well known (prospect) areas with different geological geometries and/or rock types are evaluated using the same set of parameters that produced the optimal results in the model validation step. More than one set of model parameters may have generated the observed geological relationships in the model validation step. If so, the predictive step would employ each set of parameters in keeping with the multiple working hypotheses approach outlined earlier.

The model validation step is similar to the process of geophysical inversion and some techniques have been developed to explore the
model parameter space more efficiently than simple exhaustive stepwise testing of different parameters (Boschetti & Moresi, 2001).

3 CASE HISTORY – STAWELL, WESTERN VICTORIA, AUSTRALIA

The area’s location and regional geology is shown in Figure 1. The case history is fully described in Schaubs et al (2006). Gold mineralization at Stawell is located in quartz-veins and shear zones located on the south-western side of the Magdala basalt dome (Fig. 2).

The mineral system analysis which preceded the numerical modelling study was carried out by a team based at Melbourne University (Miller & Wilson, 2002). Of particular value was a detailed analysis of the relationship between the deposit’s complex structural history and the gold mineralizing events (Miller & Wilson, 2004). In addition, work with MPI Mining (subsequently Leviathan Resources) mine staff provided rheological property measurements and guidance on the modelling questions relevant to mineral exploration.

The model validation step aimed to obtain a robust understanding of the localization of the mineralization on the western basalt-sediment contact.

The Stawell numerical models were carried out using the computer program FLAC3D (Cundall & Board, 1988), a code which can be used to simulate coupled rock deformation and fluid flow behaviours. Modelling identified a pattern of fluid flow vectors which was broadly coincident with the ore outline (Fig. 3).

The localization of fluid flow vectors results from the interplay between various parameters, including host rock geometries and rheological properties, stress field and pore fluid pressure gradient present at the time of mineralization.

The coincidence between the mineralization outline and the fluid flow vectors is inferred to show that the key control on ore localization was the orientation and magnitude of the pore fluid pressure gradient with respect to the local fluid flow vector. Some host rock control on gold precipitation is also possible, specifically the presence of the Stawell Facies sediments (Fig. 2). However the latter cover a large part of the basalt dome so, from an exploration point of view, their presence does not provide sufficient focus for drill targeting. Here, we can see that the principle of simplifying the conceptual problem, in this case by focusing only on deformation and fluid flow, can yield a useful result.

The “predictive” phase of modelling was then carried out on various prospects located north of Stawell, including the Kewell prospect.
Here, using a similar set of model parameters, an area of focused fluid flow was identified at the southern end of another basalt dome (Fig. 4) concealed beneath approximately 100m of post-mineral cover. Two earlier diamond drill holes testing geochemical anomalies in the central part of the western flank had failed to obtain ore grade and width gold mineralization. The target resulting from the model results was drilled subsequently and the first hole intersected 4.1m at 12.6 g/t Au (MPI quarterly report, December 2003). The time taken from commencement of the modelling effort to delivery of the first fluid flow models at Kewell was approximately 3 months.

**ACKNOWLEDGEMENTS**

We acknowledge Jon Dugdale and his colleagues from Leviathan Resources and Tim Rawling from Melbourne University for their involvement, inspiration and guidance in the Stawell modelling program. We thank the CEO of the pmd*CRC for permission to publish.

**REFERENCES**


**4 CONCLUSIONS**

Under some circumstances and for some hydrothermal ore deposit types, it is now possible to generate improved drill targets for the mineral explorer through numerical modelling. The initial model validation step described above can obtain a robust understanding of ore localisation through a process of simplification and extensive parameter testing on known ore systems. A “predictive” step employing that understanding can then be applied to less well explored areas. This work flow is capable of delivering drill targets within a few months.
The architecture of shear systems and controls on orogenic gold endowment: examples from the Eastern Goldfields Province, Western Australia

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ABSTRACT: The linked Bardoc Tectonic Zone (BTZ, ~100t Au) and Boulder-Lefroy Shear Zone (BLSZ, >1,500t Au) system provide an ideal setting to study the regional controls of gold endowment within Archaean granite-greenstone terranes. This study demonstrates that these shear systems were subject to the same regional shortening regime but, due to their different bounding rock units, have developed as vastly different shear systems. These differences help account for their variable gold endowments. For the BTZ, the bounding competent granite domes help explain why it developed as a broad (5-12km) and uniformly striking shear system, which arguably dispersed upwelling fluids during orogenesis. Due to the absence of bounding granite domes along the BLSZ, this shear system developed as a more tortuous and narrow (<2km) structure, which is argued here to favour fluid focusing and the formation of large gold deposits.

KEYWORDS: Gold endowment, shear systems, Archaean

1 INTRODUCTION

The Bardoc Tectonic Zone (BTZ) and the Boulder-Lefroy Shear Zone (BLSZ) are situated within the Eastern Goldfields Province (EGP) of the Archaean Yilgarn Craton (inset, Fig. 1). This craton is made up of mainly >3.0Ga granite or granite-gneiss units within its western parts and <2.72Ga granite-greenstone units in its eastern parts. The greenstone units dominantly comprise ultramafic and mafic volcanogenic rocks and associated sedimentary rock sequences.

During the late Archaean, the EGP underwent a significant phase of tectonic activity and granite intrusion, which resulted in the development of regional NNW-trending shear systems that are mainly developed within the greenstone sequences (Fig. 1; e.g. Myers 1995). The latter stages of this orogenic period, broadly constrained between 2.66 to 2.62Ga (e.g. Groves et al. 2000; Vielreicher et al. 2003; Salier et al. 2005), is associated with significant episodes of auriferous fluid infiltration and the formation of globally significant orogenic gold deposits (e.g. Groves et al. 2000).

Auriferous fluids are transported within regional shear systems, and orogenic gold deposits are spatially and temporally associated with these shear systems through a crustal continuum (Groves 1993). However, due to their variable structural histories, architectures and resultant capacity to focus fluids, some shear systems host many world-class (>100t Au) gold deposits or camps (e.g. BLSZ), whereas other shear systems host sub-world-class deposits (e.g. BTZ), or are even barren (e.g. Moriaty Shear Zone; Fig. 1; e.g. Groves et al. 1987). Through field studies, analysis of regional potential field data and theoretical constraints, this study systematically documents the geometrical characteristics of the BTZ and BLSZ to further understand the variable gold endowments between these connected shear systems. In doing so, this study potentially defines critical factors associated with the formation of world-class gold deposits.

2 DIFFERENCES BETWEEN THE BTZ AND BLSZ

Field studies of the BTZ, in conjunction with interpretations from regional map patterns and
potential field data are used to characterise the regional architecture and deformation history of the BTZ. These results are then compared to the well studied BLSZ (Table 1). The BTZ is characterised by: a) a uniform geometry along strike, b) a broad zone of deformation (5-12km across strike), c) highly attenuated lithological units that dominantly underwent dip-slip shearing, d) is closely bounded by competent, pre- to syn-deformation granite domes (Fig. 1), and e) multi-scale gravity gradient data to upwards continued heights of 60km suggest the architecture as defined by surface mapping is also applicable to a depth of at least 20km.

In contrast to the BTZ, the BLSZ is characterised by: a) a narrow and more tortuous geometry (0.2-2km across strike), b) it is dispersed throughout a more heterogeneously strained terrane with abundant structurally thickened supracrustal units, c) it is linked to numerous subordinate faults, d) it has undergone a more variable deformation history consisting of dip- and strike-slip shearing (Table 1), and e) it is not bounded by large-scale competent granite domes.

<table>
<thead>
<tr>
<th>Produced gold</th>
<th>Boulder-Lefroy</th>
<th>Bardoc</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;1500 t Au</td>
<td>Golden Mile,</td>
<td>Paddington,</td>
</tr>
<tr>
<td></td>
<td>St. Ives,</td>
<td>Talbot South,</td>
</tr>
<tr>
<td></td>
<td>Jubilee - New</td>
<td>Yunndaga</td>
</tr>
<tr>
<td></td>
<td>Celebration</td>
<td></td>
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<table>
<thead>
<tr>
<th>Length</th>
<th>&gt;100km</th>
<th>~80km</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width</td>
<td>100’s of m to</td>
<td>&lt;12km</td>
</tr>
<tr>
<td></td>
<td>2km</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Strike variation</th>
<th>N310-345</th>
<th>N325-350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regional fold structures</td>
<td>Boomerang, New Celebration and Kambalda Anticlines</td>
<td>Only attenuated lithologies were identified</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Deformation styles/events</th>
<th>Isolated thrust stacking, major upright folding and reverse shearing and later ductile and brittle-ductile strike-slip faulting</th>
<th>Pervasive reverse-dominated ductile shearing and later, low offset (&lt;100m) brittle-ductile strike-slip shearing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineralization events</td>
<td>During reverse shearing, ductile strike slip and brittle-ductile strike-slip events</td>
<td>- Syn-reverse shearing. - Brittle-ductile faults dominantly post-date mineralization</td>
</tr>
<tr>
<td>Number of gold deposits and prospects</td>
<td>10-20</td>
<td>~80</td>
</tr>
<tr>
<td>Metamorphic facies</td>
<td>Mainly green-schist to lower-amphibolite</td>
<td>Mainly green-schist to lower-amphibolite</td>
</tr>
<tr>
<td>Bounding rock units</td>
<td>Variable sequences of supracrustal rocks</td>
<td>Regional granitic domes</td>
</tr>
</tbody>
</table>

Table 1. The major differences between the BLSZ and BTZ. Comparisons based on Witt (1993); Bateman & Hagemann (2004); Hodkiewicz et al. (2005); Weinberg et al. (2005)
as discussed within this section, ultimately controlled fluid focussing and their variable gold endowments.

To an interpreted depth of at least 20 km, the BTZ is bounded by large-scale, pre- to syn-deformation granite domes (Witt and Swager 1989), with an architecture characterised by many steeply-dipping, NWW-trending and uniformly-striking structures interspersed throughout attenuated supracrustal units. As schematically shown in Figure 2, this architecture is likely to disperse any upwelling auriferous fluids during orogenesis. Furthermore, competent mafic rocks, which are a favourable host for vein-gold formation (e.g. Witt 1993), are highly attenuated and limited in their spatial extent. A system that disperses auriferous fluids over many pathways would produce many small gold deposits, as substantiated by the numerous (>80) sub world-class gold deposits known to occur within this shear system (Witt 1992).

During deformation within the BTZ, the constraints imposed by the competent bounding granite domes require that the supracrustal units rapidly rotated orthogonal to the shortening direction so that all units were highly attenuated and rotated orthogonal to the regional shortening direction. This created a uniformly-oriented shear system, lacking in major jogs or geometrical complexities (cf. Hodkiewicz et al. 2005). As substantiated by surface mapping, a uniform geometry would limit strike-slip shearing along NWW-trending planes during regional ENE–WSW shortening. The lack of geometrical complexities and variable deformation events restricts host rock dilation; reducing the potential for the formation of large (>100 t Au) gold deposits.

The terrane hosting the BLSZ is not bounded by regional granite domes, which allowed for heterogeneous strain partitioning through the development of narrow, high-strain shear zones interspersed throughout lower-strain, structurally thickened domains. This favoured the formation of a more variably striking and narrow (<2 km wide) shear system linked to higher-order splay faults in the vicinity of geomechanically complex host units. In contrast to the BTZ, the narrow shear systems favoured the formation of high permeability fluid conduits and the structurally complex and thickened host lithologies, which are linked through secondary splay structures (e.g. Eisenlohr et al. 1993), provided a more favourable setting for the formation of world-class orogenic gold deposits.

ACKNOWLEDGEMENTS

This manuscript forms part of A. Morey’s Ph.D. research under the predictive mineral discovery Cooperative Research Centre (pmd*CRC) and has been released with permission of the CEO, pmd*CRC. The authors thank Fractal Graphics and Geoinformatics for permission to use Fracwormer™ software. Also thanked are Russell Korsch (review comments), Bruce Goleby, Adrian Hitchman, Peter Milligan (Geoscience Australia) and Laurent Ailleres (Monash University). Placer Dome Asia Pacific (now Barrick Gold Corporation) are also thanked for field support and logistical assistance.

REFERENCES


Proceedings of the Ninth Biennial SGA Meeting, Dublin 2007
nematic timing of orogenic gold deposits and significance for computer-based exploration techniques with emphasis on the Yilgarn Block, Western Australia. *Ore Geology Reviews* 17:1-38


Salier BP, Groves DI, McNaughton NJ, Fletcher IR (2005) Geochronological and stable isotope evidence for widespread orogenic gold mineralization from a deep-seated fluid source at ca. 2.65 Ga in the Laverton Gold Province, Western Australia. *Economic Geology* 100:1363-1388


Witt WK, Swager CP (1989) Structural setting and geochemistry of Archaean I-type granites in the Bardoc-Coolgardie area of the Norseman-Wiluna Belt, Western Australia. *Precambrian Research* 44:323-351
Numerical simulation of deformation and controls on mineralization at the Sunrise Dam Gold Mine, Western Australia.

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ABSTRACT: Economic mineralization at the Sunrise Dam Au mine has occurred as a result of two main deformation events. The first event, $D_3$ (NW-SE compression) involved predominantly reverse shearing and reactivation on shallow dipping structures and strike slip deformation on steep dipping structures, and formed important NE-SW shear hosted structures in the form of tension and breccia vein styles that host gold mineralization. The second mineralising deformation was $D_4$ (NE-SW compression) which again reactivated existing structures, resulting in both steep and flat dipping sets of veins and brecciation, and which hosts the majority of the known high grade gold mineralization. One of the main shear zones, the Sunrise shear zone, may have acted as a seal, allowing fluid pressure to increase towards lithostatic levels, which in combination with deformation has resulted in tensile failure and precipitation of ore below the Sunrise shear zone. Three dimensional numerical models predict areas of high shear strain, dilation and areas most likely to fail as a result of increased fluid pressure. Some of these areas coincide with existing mineralization, and these results have great potential to be used in a predictive capacity for future exploration strategy.

KEYWORDS: numerical modelling, deformation, Au mineralization, Sunrise Dam

1 INTRODUCTION

The world-class Sunrise Dam Gold Mine (SDGM) is located within the Laverton Tectonic Zone, of the Western Australian Yilgarn Craton. The mine is situated 850km ENE of Perth and 45km SE of Laverton, WA. The SDGM deposit has produced 4.8 Moz of gold at an average grade of 4.2 g/t Au. As of the 1st January, 2007, remaining resources stood at approximately 36.7 Mt @ 3.1 g/t (3.6 Moz), and reserves of 16.7 Mt @ 3.5 g/t Au (1.9 Moz: Erickson et al, 2006; unpublished data). The structural evolution and deformation responsible for the main mineralization periods of the SDGM can be categorised into two major events, which are locally known as $D_3$ and $D_4$. During $D_3$ (NW-SE compression) reactivation of pre-existing structures such as the Sunrise shear zone (SSZ) resulted in NE-SW shear-hosted structures in the form of tension veins and brecciation which are host to moderate Au grades with a notable lack of coarse Au associated with shear failure. During $D_4$ (NE-SW compression) reactivation of pre-existing structures was also important with precipitation of coarse Au (with sulphides and tellurides) in both steep and flat dipping sets of veins and brecciation (e.g. the Dolly lodes).

Numerical modelling has been proven as a useful tool in simulating coupled deformation and fluid flow processes (e.g. McLellan et al, 2004), and in targeting mineralization (e.g. Schaubs et al, 2006). The main aims of this study were to firstly ascertain the distinct structural events and primary stress vectors that led to mineralization by conducting a 3D-stress analysis for inputs into numerical models, and secondly to simulate numerically both major deformation events with a view to identifying areas requiring minimum fluid pressures needed for shear or tensile failure, and areas of increased shear strain and/or dilation.

2 CONCEPTUAL AND MATHEMATICAL MODELS

The conceptual models were developed (Fig.1) using the 3D geological modelling package GOCAD version 2.08 (Earth Decision
Sciences) which offers a high degree of flexibility in dealing with complex geological geometries (e.g. Galera, et al., 2003). The conceptual models were based on the current understanding of the main structures evident within the mine surroundings from geological mapping and underground drilling programs. S-Grids were then generated for transfer to the numerical software FLAC3D (Itasca Consulting Group, Inc. 2005) where coupled process modelling was undertaken.

The numerical modelling was based on the D3 and D4 deformation events. Sensitivity analysis and several variations of stress states, kinematics and fluid pressures were tested using stress analysis results. The models were tested as a) stress state analysis without kinematics, and b) dynamic models with kinematics. For both deformation events inversion of fault slip data was carried out to give the principal stress orientations and phi \((\phi)\) values \((\phi = (\sigma_2 - \sigma_3) / (\sigma_1 - \sigma_3))\). Stress values were calculated from \(\phi = 0.45\) for D3 and 0.7 for D4. The magnitude of the differential stress was constrained by Mohr-Coulomb failure criteria with a tensile cut-off, with the general stress magnitude formulation;

\[
\sigma_1 = \frac{\sigma_2(1 + \sin \theta)}{1 - \sin \theta} + \frac{2(\text{coh} \times \cos \theta)}{1 - \sin \theta}
\]  

where \(\theta\) = friction angle and \(\text{coh}\) = cohesion value.

The value of lithostatic stress was estimated from work by Brown et al. (2003): this value was assigned to \(\sigma_2\) which was vertical in both deformations. The kinematic boundary conditions were obtained from moment tensor summation of the P and T axes of the fault slip data.

Rock packages present in the mine consist mainly of volcanic and sedimentary rocks. Volcanic packages were assigned to the bulk of the model which were separated by a banded iron formation (sensu stricto), the major shear zones (Western shear zone - WSZ, Cleo shear zone, Sunrise shear zone - SSZ and the Carey shear zone) and the Dolly porphyry body, forming an accurate geological representation of the SDGM and surrounds (see Fig.1). One of the main hypotheses tested was whether the SSZ may have acted as a seal during D4 to generate mineralization in its footwall.

3 RESULTS

The stress boundary condition numerical models tested stress states at hydrostatic, 0.5 x lithostatic and lithostatic pore pressure conditions, and examined shear strain and pore fluid pressure required for failure in shear or tension. The results indicated that less fluid pressure was required for failure in the main shear zones, and that the models were particularly prone to shear failure during both deformational events. The kinematic models allowed us to test several variations of pore pressure conditions and examine the influence of active deformation on shear strain, deformation induced dilatancy and plasticity states. During D3 (\(\sigma_1\) at 135°) maximum values of shear strain are focused on the shear zones, and when pore pressures are increased towards lithostatic values,
dilation is focused in two particular locations above the SSZ (Fig. 2), which may be a result of the inflections of the shear zones.

Initial model results for \( D_4 \) deformation (\( \sigma_1 \) at 038°) indicate little dilation at medium pore pressures, and shear zones are contractional during deformation (Fig. 3).

When the permeability of the SSZ is reduced, to simulate a system seal, we see a different behaviour during \( D_4 \) deformation. Pore pressure gradients across the SSZ are increased and tensile failure is predominant below and around the Dolly region (Fig. 4).

The distribution of dilational areas below the Dolly region towards and below the Carey shear zone indicates potential targets for similar mineralization styles as a result of \( D_4 \) deformation (Fig. 6).

4 CONCLUSIONS

Within the Sunrise Dam system, numerical simulation of the two main deformation/mineralising events display distinctly different patterns of failure and dilation as a result of variations in pore pressure distribution and orientation of maximum principal stress to structural complexities within the mine. During \( D_3 \) shear strain is accommodated within the SSZ and WSZ and dilation is evident both above and below the SSZ. At low pore pressure gradients during \( D_4 \) deformation, dilation is limited and shear failure is evident within the major shear zones which are predominantly
contractional. When the pore pressure is increased towards lithostatic values and the permeability of the SSZ is lowered there is a distinct change in pore pressure gradients across the SSZ, and failure patterns are altered from previous models. The focus of tensile failure within the models at depth can be seen to be in and around the Dolly region, which is the result of both increased pore pressures and deformation in this area. The distribution of both tensile failure and dilation below the Carey shear zone and Dolly region may be a strong indication that the processes that formed the Dolly lodes may have also operated below the Carey shear zone. The numerical results from this study have a strong potential to be used in a predictive capacity, if similar processes are believed to have taken place at depth.

ACKNOWLEDGEMENTS

We would like to thank Anglogold Ashanti and the team at Sunrise Dam Gold Mine for supporting this work. James Cleverley, Tim Baker and the Computational Geoscience Team at CSIRO, Perth, are thanked for their input. Work here was conducted as part of a 1:1 project within the predictive mineral discovery Cooperative Research Centre and published with permission of Anglogold Ashanti and the CEO pmd*CRC.

REFERENCES


Terrane-scale to ore-shoot scale controls on the Victory-Defiance gold deposit, Yilgarn Craton, Western Australia – a mineral systems analysis

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ABSTRACT: Interaction of at least two different fluids of different redox state resulted in gold deposition at the Victory-Defiance gold deposit, Yilgarn Craton, Western Australia. The different fluids are associated with different structures. The oxidized fluid was most likely related to felsic or intermediate porphyry intrusions and possibly consisted of CO₂-SO₂ gas. The reduced fluid was controlled by subvertical WNW-trending structures and locally shallow-dipping thrusts. Fluid interaction was inhibited because of the separation of the fluids along the pathways. Fluid mixing occurred at the depositional site.

KEYWORDS: Kambalda, gold, hydrothermal fluids, mineral system

1 INTRODUCTION

Future mineral discoveries require the understanding of the whole mineral system to be able to predict deposits at all scales. Whilst there are numerous studies which focused on the understanding of a mineral system at a particular scale (e.g., terrane scale, deposit scale), attempts to describe a particular mineral system across scales are less common. The predictive mineral discovery Cooperative Research Centre (pmd*CRC) follows an approach to document mineral systems across scale and fundamentally understand the making and controls of the system.

In order to develop a systematic approach to research the mineral system it was framed into five questions originally by the Australian Geodynamics CRC and subsequently used by the pmddCRC. These questions are (Walshe et al., 2005):

1. What is the geodynamic setting and PT history of the system?
2. What is the architecture of the system?
3. What are the fluids, their source and/or reservoirs?
4. What are the fluid flow drivers and pathways?
5. What are the metal and sulphur transport and deposition processes?

Underlying this approach is the desire to document the mineral system at all scales from a terrane scale down to ore shoot and micro-scale. The purpose of this abstract is to describe the processes of gold transport and deposition of gold in the Victory-Defiance gold deposit (St Ives gold camp, eastern Yilgarn Craton, Western Australia) within the framework of the five question mineral system analysis and ultimately predict gold deposits at all scales within the camp.

What is the geodynamic setting of the system? The terrane scale

At the terrane scale key parameters which drive a mineral system are zones of greatest heat and fluid flux and geological elements which might temporarily prevent it. Key elements are (Walshe et al., 2006):

1. A crustal penetrating architecture with some evidence of structure within the mantle; both parallel to the volcanic arc and cross-arc allowing sufficient fluid flux.
2. Presence of late clastic basins which act as temporary seals.
3. Some evidence of a switch in chemistry of granite magmatism about the time of cessation of basin formation with increased mantle component.
The St. Ives gold camp is located proximal to, and in the hangingwall of, the transcrustal Boulder-Lefroy fault zone. Based on geophysical evidence and extensive drill core data Conners et al. (2003) identified major, broadly E-W trending structure which probably formed during the formation of the volcanic basin. The greenstone sequence is overlain by the Black Flag Formation and the Merougil sedimentary basin. Seismic profiles indicate that Victory-Defiance is situated above a domal shaped zone which is interpreted to contain significant felsic to intermediate intrusions (Blewett & Hitchman, 2004; Connors et al., 2003; Henson et al., 2005). In the deposit, abundant porphyry intrusions form the top of the intrusion at depth.

Given this gross architecture, the St. Ives gold camp and the Victory-Defiance deposit likely formed the focus of regional fluid flow through both a transcrustal structure as well as cross-volcanic arc structures. The latter are likely to have been reactivated or were passive zones of fluid flow during gold mineralization. Both the Black Flag volcaniclastic sediments as well as the Merougil sediments have been interpreted as possible seals in the system.

2 WHAT IS THE ARCHITECTURE OF THE SYSTEM? THE CAMP SCALE

Gold mineralization is controlled by second-order structures such as the Playa-Repulse reverse fault and a third-and higher-order thrust network (Nguyen et al., 1998). Importantly, the spatial distribution of hydrothermal alteration at a camp scale provides vital insights in the architecture of the mineral system. In the Central Corridor of the St. Ives camp, which contains dominantly oxidized alteration assemblages associated with gold, two main domains with respect to the redox conditions of the hydrothermal alteration are distinguished during the intermediate fluid cycle (Neumayr et al., 2003; Neumayr et al., 2005): (1) oxidized (pyrite-magnetite, pyrite-haematite assemblages) centred around gravity lows in the Victory-Defiance and Revenge areas, and (2) reduced (pyrrhotite-pyrite, pyrrhotite-arsenopyrite, pyrrhotite assemblages) broadly flanking the oxidized domains. A similar pattern emerges also for epidote-bearing assemblages with epidote-pyrite-chalcopyrite-magnetite (relatively more oxidized?) assemblages flanking the Central Corridor.

Gold mineralization is preferentially located at the domain boundary between oxidized and reduced fluid flow domains. Important examples include the Revenge and Victory-Defiance gold deposits. The location of gold mineralization at the redox domain boundary points towards a redox control on the deposition of gold mineralization.

3 WHAT ARE THE FLUID FLOW DRIVERS AND PATHWAYS? THE DEPOSIT SCALE

At the deposit scale, zonation of hydrothermal alteration and new stable isotope data allow deciphering of the chemical and structural architecture of the system. The mineral system is cored by felsic and intermediate porphyry intrusions both underneath and above the Repulse thrust fault. Major epidote-magnetite alteration is particularly abundant in mafic rocks beneath the Repulse thrust but also adjacent to porphyry intrusions above the Repulse thrust. This mineral assemblage is interpreted to represent oxidized fluid conditions. This interpretation is further supported by sulphur isotope data with the most negative values in pyrites (δ34S -7.9 to -8.7 ‰) beneath the Repulse thrust. Along shallowly-dipping shear zones, predominantly in interflow metasedimentary units beneath the Repulse thrust biotite-actinolite alteration assemblages occur. Actinolite-biotite assem-
blages are also focused in steeply-dipping to subvertical WNW-trending structures. These assemblages are interpreted to represent reduced fluid flow along these shallowly dipping shear zones and the subvertical structures. The interpretation is supported by the most negative C isotope numbers in the camp. The Repulse thrust shows evidence of mostly oxidized fluid flow but locally also reduced fluid flow.

4 WHAT ARE THE METAL AND SULPHUR TRANSPORT AND DEPOSITION PROCESSES? THE ORE SHOOT SCALE

The depositional processes were studied at two ore shoots in the Victory-Defiance deposit in detail. The ore shoots form steeply plunging pipes of about 50m diameter and are about 60m tall. The pipes are located proximal to the intersection of a magnetite bearing (moderately oxidized to oxidized fluid flow) NNW-trending structure and a WNW-trending sub-vertical structure containing biotite-actinolite alteration. The pipes typically contain oxidized hydrothermal alteration assemblages around mineralization such as magnetite-pyrite, haematite and anhydrite. In contrast, drill core through the WNW-trending structure contains mainly biotite and actinolite as the dominant alteration assemblage. New sulphur isotope data are negative (between -6.5 and -7.7 ‰) in the pipe and positive or slightly negative proximal to the WNW trending structure and outside the ore pipe. Carbon isotopes are extremely negative ($\delta^{13}C = -8$ to -12 ‰) within the actinolite-biotite alteration assemblage in the WNW-trending structure. It is interpreted, that oxidized fluid flow occurred along the steeply-dipping ore pipes during gold mineralization. In contrast, reduced fluid along the WNW trending structures was broadly contemporaneous with the oxidized fluid flow.

5 DISCUSSION

The Victory-Defiance gold deposit is controlled by a transcrustal fault zone and its subsidiary structures. The transcrustal fault zone and across volcanic arc structures allowed fluid flow from the deep crust or the mantle into the depositional site. The proximity to the Mereougile sedimentary basin indicates a potential seal beneath which fluids could pond. Victory-Defiance is sited above a major domal shaped felsic to intermediate intrusion at about 1000 – 2000m below current surface. Camp-scale hydrothermal alteration mineral distribution indicates that gold deposition occurred preferentially at the domain boundary between oxidized and reduced alteration mineral assemblages. Furthermore, the alteration assemblages can be linked to specific structures and the proximity to the felsic to intermediate intrusion at depth. It is proposed that the felsic and intermediate intrusions mainly drove the oxidized fluid flow of CO$_2$-SO$_2$ gas which ponded beneath the Repulse thrust. Reduced fluid flow was mainly facilitated by steep WNW trending structures and contained CO$_2$-CH$_4$-N$_2$ (Petersen et al., this volume). Interaction of these fluids was only possible at specific sites, i.e. intersection of structures. Deposition of gold mineralization is controlled by the mixing of the two different fluid types. It is clear that other gold depositional processes were also contributing to the overall gold budget such as phase immiscibility and fluid-wallrock reactions, but evidence points towards a minor contribution of these processes.

ACKNOWLEDGEMENTS

The study is financially supported by the Predictive Mineral Discovery Cooperative Research Centre (pmd*CRC) Y3 project, MERIWA and St. Ives Gold Mining Company (Pty) Ltd. (SIGMC) The authors acknowledge the permission to publish from the CEO of the pmd*CRC. Geologists at SIGMC are thanked.
for their support. Greg Hall and Scott Halley are thanked for their contributions to the research.

REFERENCES


Petersen, K. J., Hagemann, S. G., Neumayr, P., and Walshe, J. (this volume) Multiple hydrothermal fluid pulses through time at the Kambalda gold deposits, Yilgarn Craton, Western Australia.


Resolving the structural setting of the Mt Gordon copper deposits, using numerical modelling, North Queensland, Australia.

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ABSTRACT: The Mt Gordon copper mine (Mammoth and Esperanza deposits) has been the focus of several structural studies. Although these studies agree that the timing of mineralization is syn to post D3, they fail to agree on the orientation of the maximum principal stress at the time of mineralisation. Using distinct element modelling techniques, the orientation of the mineralizing stress field has been resolved. Numerical modelling suggests that a maximum principal stress orientation of 112º-292º results in the most suitable conditions for mineralisation at both the Mammoth and Esperanza deposits. Numerical modelling results have been tested and validated by specific underground mapping of veins and mineralization. The study has implications for the migration and deposition of copper in fault zones and has potential application to regional exploration programs.

KEYWORDS: numerical modelling, UDEC, Mt Gordon, stress mapping

INTRODUCTION

The Mt Gordon copper mine (MCM) is located in the Western Succession of the Mount Isa Inlier (Figure 1); a richly mineralized base metal province, containing world class Cu-Co, U-REE and Ag-Pb-Zn deposits. Two orebodies comprise the GCM; the Mammoth and Esperanza deposits. The Mammoth deposit is hosted by the Palaeoproterozoic Whitworth Quartzite, of the Myally Subgroup (Crossing, 2004) and the orebody lies at the intersection of the ENE striking Mammoth Fault and the NS striking Portal Fault.

Approximately 1km to the west of the Mammoth deposit is the Esperanza deposit, which is confined to the Esperanza Formation, a well bedded, black carbonaceous dolomitic siltstone and shale unit. The Esperanza Formation is part of the McNamara Group and has a depositional age of approximately 1650 Ma (Betts & Lister, 2002), some 120 Ma after the Whitworth Quartzite depositional age. As with the Mammoth deposit, the Esperanza orebody is structurally controlled, found in the intersection of the Esperanza Fault, the Mammoth Extended Fault and the Mammoth Fault (Figure 2).

Figure 1 The Mt Isa Inlier can be divided into 3 main terranes-- the Western Succession, the Kalkadoon-Leichhardt Belt and the Eastern Succession (Blake, 1987).
1.1. Previous work at Mt Gordon Mine

The Mammoth and Esperanza copper deposits have been the focus of several structural studies. Although a substantial body of work has been completed on the structural regime of the Mt Gordon deposits, discrepancies remain over the orientation of the maximum principal stress at the time of mineralization.

Documented thoughts on the stress regime include:

- Askew (1992) – overall kinematics of the mine area during D3 are transpressional with maximum principal compressive stress orientated ENE-WSW
- ERA Maptec (1994) – copper mineralisation occurred during a steeply inclined EW compression event resulting in NS extension.
- Connors (1997) – copper mineralization occurred during NE-SW transpression

The orientation of the shortening field should, theoretically, be easily resolved by mapping slip vectors on the major faults; however an earthy haematite overprint on faults within the mine surrounds masks most deformation features and makes this a difficult task. Although these authors fail to agree on the orientation of the maximum principal stress, they all agree that mineralization is syn- to post-regional Isan D3 (E-W shortening) - late in the deformation history of the Mt Isa Inlier. Askew (1992) and Connors (1997) agree that mineralisation is related to predominantly strike-slip movement on the Mammoth and Mammoth Extended Faults. This is supported by very shallow dipping, syn-mineralization slickenlines found on Mammoth Fault parallels within the mine sequence.

1.2 Numerical Modelling – UDEC Overview

UDEC is a distinct element modelling code (Itasca Consulting Group Inc., 2005). It is best applied to epigenetic hydrothermal mineral deposits, where fluid flow is enhanced in faults, rather than through the bulk rock mass (Mair et al., 2000). Most of this type of “stress mapping” is carried out in two dimensions in plan view using geological maps. It is suitable for terranes with steeply dipping lithostratigraphy and faults, and an inferred strike-slip movement on those contacts. The effectiveness of this numerical modelling is maximised if
mineralisation was late in the evolutionary history of the host terrane, and hence the structural geometry of the terrane and contained deposits were essentially that expressed today (Mair et al., 2000). Mt Gordon, with its steeply dipping faults and late-stage deformation related mineralization, is an ideal candidate for UDEC modelling.

### 1.3 Conceptual Model

A 2.3km x 2.3km model geometry was created, based on the present day fault and lithological architecture (Crossing, 2004), in effect testing the hypothesis that mineralization was related late-stage deformation. The three orientations of $\sigma_1$ proposed by the previous authors were tested. Two further orientations, both ESE-WNW, were tested. These were proposed following field mapping, to initiate dextral movement on the Mammoth Fault (see Table 1).

<table>
<thead>
<tr>
<th>Author</th>
<th>$\sigma_1$ Orientation</th>
<th>$\sigma_1$ Bearing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Connors</td>
<td>NE-SW</td>
<td>045-225</td>
</tr>
<tr>
<td>Askew</td>
<td>ENE-WSW</td>
<td>067-247</td>
</tr>
<tr>
<td>ERA Maptec</td>
<td>E-W</td>
<td>090-270</td>
</tr>
<tr>
<td>Keys</td>
<td>ESE-WNW</td>
<td>101-281</td>
</tr>
<tr>
<td>Keys</td>
<td>ESE-WNW</td>
<td>112-292</td>
</tr>
</tbody>
</table>

Table 1 Orientations of $\sigma_1$ proposed for the mineralising event at the Mt Gordon copper mines.

### RESULTS OF MODELLING

Of the three orientations of $\sigma_1$ proposed by the previous authors, only the E-W shortening model proposed by ERA Maptec (1994) indicated dilatancy in the known mineralized and brecciated areas. The Connors (1997) and Askew (1992) models tested, resulted in contraction and not dilation in the known mine areas. These models also resulted in left lateral movement on the Mammoth and Mammoth Extended Faults. This is inconsistent with field data collected from the Mammoth deposit, where striations on the Mammoth Fault indicated a right lateral sense of movement at the time of mineralisation. Though the ERA Maptec model indicated dilatancy, the dilation was not mine locality specific. Modelling results were most consistent with field mapped breccias when $\sigma_1$ was oriented 112º-292º (WNW-ESE). Dilation generally coincided...
spatially with known breccia bodies and deposit locations (Figs. 3A, 3B & 4).

The modelling also predicted Mammoth as being confined to the western side of the Portal Fault, as it is known to be (Figs. 3B & 4). The model was interrogated for fluid pressure increases required for failure. Mohr-Coulomb theory suggests failure, both shear and tensile, is more likely in areas requiring small increases in fluid pressure. The Mammoth and Esperanza deposits were identified as areas requiring small increases in fluid pressure for failure (Figure 4).

![Figure 4](image)

**Figure 4** Plot of fluid pressure increase required for failure. Lighter shades indicate zones requiring high fluid pressure for failure and darker areas requiring lower fluid pressures for failure.

CONCLUSIONS

With numerical modelling and field validation, the maximum principal stress orientation ($\sigma_1$) for mineralisation at the Mt Gordon Mines has been resolved. A $\sigma_1$ orientation of 112º-292º (ESE-WNW) has initiated dominantly strike-slip dextral movement on the Mammoth and Mammoth Extended Faults and dilation corresponding to the known deposit locations. Subsequent numerical modelling and field work completed within the pmd*CRC, both regionally and on other Mt Isa Western Succession deposits (Mt Isa, Mt Kelly and Investigator) (McLellan, Keys & Miller, 2006, *unpubl. data*), has also shown a WNW-ESE oriented $\sigma_1$ to be best suited for mineralization.

ACKNOWLEDGEMENTS

Many thanks go to Craig Irvine, Barry Brown, and all other mine geologists from Aditya Birla Minerals, Mt Gordon Mine that have contributed to this study. The study is funded by the Predictive Mineral Discovery CRC. Thanks also to Aditya Birla and the CEO pmd*CRC for permission to publish this material.

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
Can the petroleum industry’s probabilistic approach to targeting and resources definition be applied in predicting mineral discoveries?

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ABSTRACT: Use of rank statistics, power laws and graphic probabilistic methodologies, such as probability-log plots, has been sporadic in mineral exploration in spite of their successful use in oil exploration. This paper attempts to apply these methodologies to characterise the nickel exploration potential of the Archaean greenstone belts of the Yilgarn Province of Western Australia by analysing the ranking and size distribution of 63 Ni sulphides deposits discovered to date. Their sizes appear to abide to a power law and plot well as discrete points along a Zipf curve, providing a way of estimating the “residual” endowment, i.e. the number and size of as yet undiscovered deposits and of the probability that a possible discovery may exceed a given size. Significant recent research in the application of rank statistics to Internet access, income and urban development distributions etc. is generating new insights and a deeper understanding of these controversial statistical systems and justifies further investigation of their application in the area of exploration targeting. Greater acceptance will depend on “reality checks” such as whether and where the footprint of postulated targets could be hidden in the current geological datasets and interpretations, given sampling density and quality and the depth and effectiveness of geophysical and drilling penetration.

KEYWORDS: Nickel sulphides, deposit size distribution and prediction, rank statistics, targeting.

1 INTRODUCTION

Estimates of the size distribution of oil or gas recoverable reserves are usually calculated by multiplying the area of the closure, the net pay (a determinant of the volume holding the hydrocarbons) and a hydrocarbon recovery yield (a measure of porosity, hydrocarbon saturation, recovery factor and the formation volume factor) (Rose, 2001). According to the central limit theorem, as each of these individual parameters is a stochastic variable, their multiplicative result abides to a lognormal distribution featuring few large deposits and many small ones. Lognormal probability properties are routinely and successfully used in petroleum exploration and development to predict the size of a deposit given a discovery at different levels of confidence (e.g. P10, P50, P90 respectively).

While the possible transfer of petroleum system methodologies to mineral systems has inspired much recent research (Wyborn et al., 1994), the use of rank statistics and probability-log graphical methods to predict the size of mineral deposits has at best been sporadic.

The pre-development inventory of mineral deposits is a sample of the size distribution of the original “natural” endowment of the relevant geological terrane.

Log normally, discovered deposit sizes often abide to a power law and can be represented by discrete points along a Zipf curve, implying that the largest deposit should be approximately twice the size of the second largest, three times that of the third and so on. A comparison between the number and size of deposits that should theoretically exist in a terrane and those discovered to date provides an indication of the “residual”, yet undiscovered, endowment, and of the degree of exploration maturity of the area (Folinsbee, 1977; Fagan, 2006).

Once the size of the largest undiscovered deposit is estimated, then the probability that a possible future discovery will exceed a specific target size can be predicted. Irrespective of its inherent uncertainty and surrounding controversy, this type of information represents a critical input to exploration targeting.
2. WA NICKEL SULPHIDES “NATURAL” ENDOWMENT

The Archaean greenstones belts of the Yilgarn Craton in Western Australia (WA) have been a fertile exploration area for komatiite-hosted nickel sulphides mineralisation and currently feature some 63 deposits with Ni metal contents greater than 500t. The mineralizing episodes that created these deposits are largely coeval at about 2.7 G.a. (Hoatson et al., 2006). This type of deposits and subordinately nickel laterites account for WA currently producing 180,000t of Ni p.a., representing 15% of world total. Deposit sizes have been extracted from the MINEDEX database, (Department of Industry and Resources of WA), with pre-development tonnages computed at the lowest reported Ni cut-off grade. As a consequence many of the deposits are not currently supporting commercial operations, nor can the tonnages used in this paper be reconciled with mining reserves published by relevant holding companies. The distribution of Ni deposit sizes in terms of contained metal is highly skewed with a few large deposits and many more small ones. The largest deposit, Mt.Keith, has reported geological resources of around 2,800,000t of Ni metal. However, given the open-cut focus, the current depth of drilling is limited. Consequently this figure is rather conservative, possibly by as much as 50% or more. The smallest deposit in this database is Trough Well at 540t Ni.

3 DEPOSIT SIZES DISTRIBUTION

Deposit sizes in ranking order plot along a straight line on probability-log graphs (Fig.1) and are best fitted by a log-normal distribution (low Anderson-Darling test value of 0.38) with mean = 173,810t, standard deviation = 982,630t, median = 30,270t and mode = 920t of Ni metal. This distribution also indicates that the deposit sizes may abide by a power law and that they may be represented as discrete occurrences on a Zipf curve, providing an insight as to the size distribution of all deposits in the “natural” endowment. The Zipf law (Adamic, 2007) follows the relationship \( y = C_1 \times r^{-b} \), where \( C_1 \) is a scaling constant, in our case the hypothetical size of the largest (Mt. Keith) deposit, and \( b \) an exponent, which in “steady state” systems approaches 1. In effect the larger deposit is twice the second largest, three times the third and so on. A comparison between the number and size of deposits that should theoretically exist in this terrane and those discovered to date provides an indication of its “residual”, yet undiscovered, endowment and of the degree of exploration maturity of the area. The process entails matching existing deposit sizes to same order of magnitude points on the Zipf curve, leaving the unmatched points to represent the size distribution of the “residual” endowment of the terrane (Fig. 2) on which future mineral discoveries depend. The largest as yet undiscovered deposit is at rank 5 at just under one million tonnes nickel followed by many in the half to one million tonnes category and a plethora of smaller but still significant ones. Predictably the four largest deposits have already been discovered (Hronsly, 2004), but the Zipf analysis suggests that the Yilgarn green-
stones are far from being a mature exploration area.

Conversely, if several large deposits are discovered, their size distribution can be used to predict whether the largest deposit remains undiscovered or whether it is incompletely delineated as in the case of Mt. Keith. One approach, as illustrated in Fig. 3, is to place the largest undiscovered deposit (951,538t) at P1 (the value at which there is a 1 per cent probability of getting an accumulation of that size or bigger) on the probability-log plot and draw a straight line joining it with the smallest possible deposit at P99 (300t) as obtained by linear regression in Fig. 1. The regression line joining these two points represents the size distribution of the “residual” endowment from which inferences about future discoveries can be made. For instance the median of the distribution has fallen from just over 30,000t to around 17,000t. This is a clear indication that many of the large deposits have already been discovered. The graph also shows that, given a discovery, there is about 10% probability that its size will exceed around 150,000t of contained Ni metal and about 2.4% chance that it will exceed 500,000t. This type of information clearly represents a critical input to exploration companies’ strategic planning to ensure that their targets are consistent with their corporate financial objectives and level of venture capital.

4. A DOSE OF HEALTHY SKEPTICISM

Application of the Zipf law to mineral exploration became fashionable in the 1970s (Folinsbee, 1977) but soon sunk under the weight of significant criticism about its realism. This ranged from flat refusal that natural phenomena may be subject to power laws to mathematical ambiguity particularly about the validity of setting the Zipf exponent $b$ to $\sim 1$. Resurgence of interest and research in rank statistics as applied to evolving socio-economic systems abiding to power laws, (e.g. Internet access, income distribution and urban development), is creating new insights and understanding of these statistical systems, which have been successfully applied to geological processes controlling faults and earthquakes distributions. Such evolutionary processes may be reflected in changing values for the $b$ exponent, which may tend to unity for “steady states” systems of which the Ni sulphides mineralization of the Yilgarn is an example. Given the good linearity of deposit sizes on a cumulative frequency versus size log-log plot, an attempt was made to estimate the $b$ exponent of the sample by fitting to it a Pareto distribution of which the Zipf law is a discrete expression. While the Pareto distribution was among the top four best fitting, assessing goodness of fit proved difficult for lack of tables of critical test scores relevant to it. A source of poor fit may have to do with the accuracy and comparability of the available resources estimates. Invariably with the establishment of mining operations the size of individual deposits tends to grow over time making them “climb” the Zipf curve claiming some of the vacant spots (Fig.2). How confident can one be that the current rank 1 deposit is actually the largest in the population? Many of these questions are more critical to the realism of the technique than relatively small differences in the $b$ exponent. The $b$ exponent estimated using the Pareto distribution is 0.8036 generating a larger number of slightly larger undiscovered deposits. Clearly there is promise but a long way to go in understanding how the evolution of mineral systems relates to their size distributions.

5. THE NEED FOR A REALITY CHECK

In the petroleum industry, statistical “reality checks” have been developed for size distributions at various phases in a project cycle, from frontier wildcat exploration, through exploration on oil trends to the development stage. For example, for an oil trend prospect Rose & Associates (2006) indicate that the ratio of
P10/P90 should fall between 10 and 120 at the same time the Swanson mean size (i.e. 0.3 * 
P10 + 0.4 * P50 + 0.3 * P90) (Megill, 1996) 
should fall between the P17 and P33 percentiles. If these conditions are not met then the 
distribution is unrealistic and must be revised by reducing the P1 value to a point where it 
passes the reality check. This may entail re-
viewing the realism of the individual compo-
ents (i.e. area, net payoff, yield etc.) on which 
the maximum size estimate was based.

Assuming that exploring for nickel in ko-
matiites belts already hosting nickel sulphides 
deposits is equivalent to exploring for hydro-
carbons on an oil trend, it may be more than 
serendipity that the “residual” nickel endow-
ment, with a Swanson mean below P33 and a 
P10/P90 ratio of around 85, also abides to this 
“reality check”. Sadly mineral exploration is 
still a long way from being able to rely on 
quantified individual components of the min-
eral system, e.g. metal source, transporting flu-
ids, structural conduits, depositional loci etc.

It would be legitimate to ask what is the Zipf 
curve actually measuring? In the Yilgarn, past 
nickel exploration has only directly tested a 
small percentage of the total volume of permis-
sibly mineralized ultramafic rock. Most of the 
ultramafic rocks continue at depth not yet tested 
by relatively shallow drilling and presumably 
many deposits have been eroded. There is also 
doubt whether the largest deposit has actually 
been discovered and, if so, adequately deline-
ated. Deposit complexity, aspect ratios, ‘foot-
prints’ and past exploration history must be 
considered in deciding the realism of resulting 
P1 value. The question arises whether the foot-
print of the largest deposit may have gone un-
detected given the current geoscience datasets 
and interpretations, geochemical and geophysi-
cal knowledge and the density and depth of 
drilling? Could there be in the Yilgarn an even 
larger nickel deposit in the remaining volume 
of greenstones, which has been blind to and un-
reachable by current technology? Is there poten-
tial to develop technology that expands its 
footprint in a way that makes it detectable? In 
summary the realism of the postulated maxi-
mum size deposit is a function of (historical 
exploration detection effectiveness, target foot-
print and erosion).

The size limit of the largest remaining hy-
drocarbon accumulation can more easily be as-
sessed in petroleum exploration targets because 
of lower structural complexity and vertical as-
pect ratios, pools displaying their largest di-
ensions in the horizontal plane, and excellent 
seismic imagery. However, in many metal sys-
tems, the largest aspect ratio of the deposit can 
be sub-vertical (e.g. shear zone hosted Au), giv-
ing them a small surface ‘footprint’ relative to 
their size, making the process a much more dif-

cult task. The structural complexity and verti-
cal continuity in many metal systems also ren-
ders complete delineation of deposits difficult 
or impractical. For example the Archaean 
Golden Mile Au deposit, Australia and Palaeo-
proterozoic Ashanti Au deposit, Ghana are still 
being delineated more than 100 years after dis-
covery. Conversely, the Century Pb-Zn deposit 
in Australia, with its horizontal continuity and 
relatively simpler geometry, was essentially de-
lineated in a single drilling campaign.

6. CONCLUSIONS

Irrespective of inherent uncertainty and of 
the controversy surrounding the use of Zipf 
curves, there appears to be significant potential 
benefits to be derived from greater use of rank 
statistics in predicting the size of undiscovered 
mineral deposits in setting more geologically 
and financially justifiable investment targets.

REFERENCES

Adamic, L.A. – 2007 – Zipf, power-laws and Pareto – A 
ranking tutorial - www.hpl.hp.com


Hoatson D.M. Jr, Jaireth S., Jaques A.L. - Nickel sulfide 

deposits in Australia: Characteristics, resources, 
and potential - Ore Geology Reviews 29, Elsevier, 

Fagan, R.K., 2006 - Modelling how much gold is left to 
be found in the Eastern Goldfields of W.A. - AIG 
Kalgoorlie 2006 Conference

Megill, R.E. – 1996 – The business side of Geology – 
AAPG Explorer, February 1996.

Needham T., Yielding G. & Fox R., 1996. Fault popula-
tion description and prediction using examples 
from the offshore U.K. Journal of Structural Ge-
ology, 18, 155 to 167.

Penney, S.R., Allen, R. M., Harrison, S., Lees, T.C., 
Murphy, F. C., Harrisson, S., Lees, T.C., 
Norman A. R. and Roberts P. A., 
2004 - A global-scale exploration risk analysis 
technique to determine the best mineral belts for 
Min. Metall. B) September 2004 Vol. 113

Rose P., 2001, Risk Analysis and Management of Petro-
leum Exploration Ventures, AAPG Methods in 
Exploration Series, No 12, AAPG, Tulsa, Okla-
homa, U.S.A
Numerical Modeling in Exploration

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ABSTRACT: The application of numerical modeling codes to mineral exploration for gold and copper deposits undertaken by Placer Dome Inc in the 1980’s and 1990’s is described. This work involved the use of various codes and numerical solutions including UDEC, MAP3D, Thermodata, Connolly Diagrams and Isodilate Analysis. These studies demonstrated that the exploration process can be enhanced in a number of ways including the prediction of the location of undiscovered mineralization and patterns of alteration.

KEYWORDS: modelling, gold, copper, stress, thermodynamic.

1 INTRODUCTION

Numerical modeling codes were introduced to Placer Dome Inc in 1989. The codes are used to predict and/or confirm interpretations of geological data during exploration.

2 2D STRESS MAPPING

UDEC is a 2D distinct element code that is used to model stress distributions implicit in geological maps at 1:100,00 and to thus predict the location of gold deposits. Geological maps are synthesised into simplified configurations. The blocks defined by the map interpretation are given internal strength properties depending on lithology and the boundaries of the blocks are given slip properties depending on the nature of the contact. The original ‘test of concept’ was applied to published geological maps in 1989. These maps show the regional geology of 9 significant gold deposits.

Kambalda – Victory Defiance, Revenge
Kalgoorlie – Golden Mile, Mt Charlotte
Agnew – Emu, Redeemer, Deliverance

The analytical solution produced 9 areas of low mean stress, 5 of these are coincident with known gold deposits.

Subsequent tests of other areas (not known to host any gold deposits) produced maps with very few low mean stress areas.

Varying the cohesion of a major controlling fault produced two different solutions in one map sheet. Both solutions were coincident with separate known mineral occurrences separated by 5km. The occurrence coincident with a slippery main fault is a foliation controlled “ductile” mineralization within that fault. The occurrence coincident with a sticky fault boundary is quartz vein tension gash “brittle” mineralization, located in granite, 5km from the fault.

Varying the angle of principal compression showed most solutions to be robust up to ±20-30° of variance of principal stress.

Varying rock strength properties has significantly less impact on solutions, with low mean stress solutions often remaining constant when rock compositions were all varied to the most rigid unit (granite).

The models are sensitive to initial conditions i.e. interpretations of the geological data producing the map to be modeled. Complexity in these maps often created “poor” coincidence with known mineralization.

The models were sensitive to loading factors. Models were not loaded to fail, rather to produce a map of rock stress distribution immediately prior to failure. This condition is consistent with the interpretation that faults fail to allow fluid flow (i.e. act as valves, not pumps) and that fluids flow into areas of low...
mean stress, then precipitate the failure by lowering the friction angle on the fault.

Extensional environments were simulated by compression oriented orthogonal to the extension direction.

Stress modeling of the Laverton region created low mean stress targets that comprised one element of a targeting strategy that predicted the location of the Keringal deposit (0.7m oz gold resource), discovered in 1992 and Wallaby deposit (5moz gold resource) in 1997.

Despite the obvious weakness of 2D modeling, the solutions were surprisingly accurate for most post-tectonic ore deposit styles.

A total of 12 maps were modeled in the period 1989 – 1990 (Hall, 1990).

3 3D STRESS MAPPING

MAP 3D is used in 3D stress analysis to simulate rock mass response under imposed external stress.

This approach was used at two mine sites where the 3D geometry has been well defined by drilling. The application was designed to understand the controls on mineralization and thus allow prediction of other mineral positions (Ojala & Holyland, 1994)

3.1 Granny Smith –

The 3D geometry of the granite sediment contact is a primary control on mineralization. 2D modeling shows the tangential impingement of the granite (rigid body) on the early thrust (slippery fault) is the primary control in plan view. In section, areas of flattening in the contact are sites of preferential dilation.

3D modeling showed the contact had a variable response to compression. Flat zones, up to 70m wide and possessing some roughness (hills and hollows) are optimal. These zones form an arched roof of sediment that propagates off the roughness. Such “hills” showed peak low mean stress that correlate with highest grade. The predicted rotation of the principle stress vector matched the in field principle stress orientation (measured from the bisectrix of mineralized conjugate fracture zones).

Flat zones in excess of +100m width are not well mineralized due to the inability of the rock strength to sustain openings that large. Instead low mean stress occurs as isolated outliers on concave inflection points. These isolated outliers occur wherever the contact steepened and are independent of dip angle.

3.2 Kidston

3D stress modeling (Ojala 1996) was used to understand the controls on the unusual bowl shaped geometry of mineralized veins in Kidston breccia pipe. The modeling was used to predict the low mean stress location in an annular array of veins located 400m from the pipe margin.

The simulation of low mean stress in Kidston breccia pipe showed the ring fault at the top of the piston had to be fixed for a bubble of high pressure to form in the roof of the pipe. The boundary of high/low pressure defined the bowl shaped geometry of vein arrays formed when the seal was breached. The annular ends of the ring veins showed maximum low mean stress in the tension position, that is the north and south ends of the pipe for E-W maximum compression direction.

The model predicted an envelope of veins, located outside the pipe, would dip at 45° and propagate from any constriction point in the pipe at depth. These outer vein swarms show maximum low mean stress in an orthogonal position (east and west) compared to veins within the pipe (north and south).

Drilling of an IP anomaly beneath a waste dump intersected a vein swarm dipping at 40° located several 100’s m outside the pipe margin. Drilling within the pipe showed a second vein set at 800m to 1000m BSL.

A vein swarm lies within the pipe at Mack’s Knob – North Knob (north end of pipe). Veins are short cutting an angular corner of the pipe as well as following the contact, creating a large “mega-block” of brecciated breccia. Sheeted veins are continuous beneath this mega block.

The modeling showed that magma withdrawal is not a necessary pre-condition of vein formation.

4 THERMODYNAMIC MODELLING

Thermodata is a thermodynamic code. The code was used to predict the alteration zoning around the Osborne Mine shortly after the discovery of an ore grade intercept in 1989.
Drilling undercover was the only means of sampling the deposit. The deposit was believed to be of Starra type and was modeled using fluid inclusion data derived from this deposit (Davidson 1991). The protoliths observed at Osborne were interacted with a Starra fluid under Starra fluid temperature and pressure conditions. A three-fold zonation is predicted.

Table 1.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Mineralogy</th>
<th>Ratio</th>
<th>Actual</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner</td>
<td>Magnetite</td>
<td>1</td>
<td>80m</td>
<td></td>
</tr>
<tr>
<td>Middle</td>
<td>Sericite</td>
<td>2</td>
<td>160m</td>
<td>Calc-silicate</td>
</tr>
<tr>
<td>Outer</td>
<td>Haematised Albite</td>
<td>2</td>
<td>160m</td>
<td></td>
</tr>
</tbody>
</table>

Disseminated magnetite is predicted to extend to the edge of the outermost zone. Measurement of magnetic susceptibility confirmed this prediction and geophysical modeling of the observed magnetic data required inclusion of this 400m thick zone of disseminated magnetite.

The middle zone is a calc-silicate assemblage because the Osborne system is hotter and deeper than Starra.

5 GEOMETRIC MODELLING

Connolly Diagrams and Isodilate Analysis are numerical solutions to space creation by differential movement on a primary control surface.

The programs were used at Granny Smith and Big Bell gold deposits to model the total displacement and direction of that displacement that occurred during development of the ore zone. The inferred sense of displacement can be compared to kinematic indicators that developed synchronous with mineralization. The sense and direction of displacement is determined by modeling the 5 different senses of possible relative movement on the modeled plane.

The contours of the inferred space created by each of the five possible movements are then compared with grade thickness contours of the deposit. The inferred sense of displacement is the movement sense that gives the best fit to the grade thickness contours.

5.1 Granny Smith

The flat granite-sediment contact is the dominant controlling surface. The predicted sense of displacement is reverse and minor dextral. Total displacement is 30m.

The mineralized shelf is a lip developed by the early diorite intrusion being breached by a later granodiorite phase.

5.2 Big Bell

The principal control is an early thrust fault (now a graphite shear). A foliation developed during amphibolite grade metamorphism is imprinted on sinistral retort-shaped granite porphyry in the structural hangingwall of the thrust. The foliation is dilated during later dextral shearing, synchronous with ore formation.

The predicted sense of displacement is dextral dip slip and total displacement is less than 100m.

REFERENCES


ABSTRACT: We present a new method for translating ore deposit models into a flexible, probabilistic decision-making structure that is based on the critical processes of ore formation: (1) extraction of ore components from crustal or mantle sources, (2) fluid- or melt-assisted transport of ore components from source regions to trap zones, (3) formation of ‘trap’ zones that can focus melt or fluid migration and accommodate large amounts of metal, and (4) operation of the physicochemical processes that promote and sustain the deposition of metal from fluids or melts passing through a particular trap site. Our modeling approach integrates these critical processes with concepts of probability theory and decision analysis, with the principal objective of making ore deposit models more quantitative, amenable for management of risk and uncertainty and suitable for communication of geological concepts to managers or financial stakeholders who do not have a geoscience background. We constructed probabilistic models for lode-gold, porphyry copper, stratiform lead-zinc and magmatic nickel-sulfide systems. These models are based on our assessment of the current state of knowledge and our personal views, prejudices and experience. However, users can easily modify the model templates to suit their own beliefs, knowledge or specific local circumstances. We do not imply that our modeling approach is superior to others, but simply that the resulting ore systems models are flexible, probabilistic and internally consistent, and structured according to previously published petroleum and mineral systems approaches.

KEYWORDS: ore deposit model, mineral exploration, probability of success, risk, decision-making

1 INTRODUCTION

Recent financial modeling of the business of mineral exploration has demonstrated that there are three principal levers that control the return on exploration investment at the portfolio and program levels (Etheridge et al. 2006): (1) the number of projects effectively tested and turned over, (2) the average expenditure per project, especially on those that failed, and (3) the average probability of success across the portfolio. By and large, the minerals industry attempts to manage the probability of success by applying superior geoscience and allocating investment dollars to the best projects. In order to identify the top projects and prioritize capital expenditure, mineral explorers use a range of project ranking schemes.

At the core of most ranking schemes, and indeed much of our exploration judgment, are ore deposit models that describe those characteristics that are considered by the model author(s) to represent the key aspects of the type of mineral deposit that is sought within a particular area. Whilst generally referred to as either conceptual or empirical, most of the widely used models include a variably complete array of process factors of ore-formation, products of the mineralization process, characteristics of the regional and local geology and structure, inferences about the tectonic setting, and grade and tonnage data (e.g., Henley & Berger 1993; Hronsky 2004).

Our starting point for the research described in this paper was that most of the widely used ore deposit models, while being useful for communication, reference and learning, are not designed to support quantitative decision systems.

This paper describes a method of translating...
ore deposit models into flexible, probabilistic decision-making structures with the principal objective of demonstrating that probabilistic structures are superior to the widely used ore deposit models in terms of flexibility, quantitative management of risk and uncertainty, and communication of geological concepts to managers and financial stakeholders. Formulation of the probabilistic ore systems models closely followed the principles of the petroleum (Magoon & Dow 1994) and mineral (Wyborn et al. 1994) systems approaches, and the probabilistic approach to measuring exploration success by Lord et al. (2001).

2 WHAT IS THE MODEL DESIGNED TO DO?

The probabilistic ore systems model is a flexible, ExcelTM-based template that is intended to calculate the probability of success (Ps) and Expected Value (EV) of an investment decision. Pay-off values, computed by Precision-Tree™ (Palisade Corporation) for each decision path, are given as EVs.

The EV concept (e.g., Newendorp & Schuyler 2000) is intended to calculate the average pay-off per project or investment decision that would be realized if the same strategy were to be applied and alternative returns were accepted over a series of repeated trials. The EV equation is defined as:

$$EV = \sum_{i=1}^{N} V_i \times P(V_i)$$

where \( EV \) = expected value of the sum of the investment decisions, \( V \) = value of an investment decision (Net Present Value at decision-to-mine, or any other agreed measure of monetary value), \( P(V) \) = probability of achieving \( V \), \( N \) = number of investment decisions, and \( i \) = investment decision 1, 2, 3, …, \( k \).

A project with positive EV is an investment; one with a negative EV is a gamble. The merit of the EV concept lies in the explicit incorporation of risk and uncertainty into a future value estimate. As such, the EV concept is a decision-making tool that facilitates project ranking according to company-specific risk and value standards.

3 HOW IS THE MODEL STRUCTURED?

The Excel™-based modeling template consists of three worksheets.

Worksheet 1 contains a decision tree (Fig. 1) that was constructed in PrecisionTree™, an Excel™-compatible decision tree tool. The tree structure, which is intended to calculate the EV of an exploration project, offers three main decision paths: (1) drill, (2) additional targeting technique, and (3) terminate. Decision path 1 is based on the scenario where the target has a prior \( Ps \) that is at or above a level required to justify immediate drill testing. Decision path 2 is tailored to the situation where the prior \( Ps \) of a target is below the level required to justify drilling, but where the application of an additional geochemical or geophysical targeting method is expected to result in a posterior \( Ps \) that would warrant immediate drill testing. Decision path 3 reflects the scenario where, in spite of skillful exploration, no drillable targets were defined, and where the application of further targeting techniques is perceived as futile.

Worksheet 2 is intended to calculate the prior \( Ps \) that feeds into the various decisions paths offered in Worksheet 1. The computation of \( Ps \) is based on the available evidence for the critical processes of ore formation having occurred within a the area of interest: (1) extraction of ore components (i.e. fluids, metals and ligands) from crustal or mantle sources, (2) fluid- or melt-assisted transport of ore components from source regions to trap zones, (3) formation of trap zones (i.e. very effective melt or fluid channels) that can accommodate large amounts of metal but as narrow as necessary for efficiently focusing melt or fluid migration; and (4) operation of the physicochemical processes that promote and sustain the deposition of metal from fluids or melts passing through a particular trap site (e.g., Wyborn et al. 1994; Lord et al. 2001).

Worksheet 3 contains probability distribution functions that were created in @RISK™ (Palisade Corporation), an Excel™-compatible risk analysis and Monte Carlo simulation tool, and feed into the decision tree in worksheet 1: (1) Pert distributions of the costs of geochemical and geophysical surveying, drill testing and resource delineation that can be modified by the user, and (2) log-normal distributions of the values of discoveries that were fitted to the gold and base metals acquisitions (\( n = 343 \); Metals Economics Group), Australian gold discoveries (\( n = 59 \); Schodde 2004), and (3) global copper projects (\( n = 65 \); Leveille & Doggett 2006) databases. Worksheet 3 also requires a user estimate of the true positive rate of the additional targeting tool in decision path 2 (worksheet 1).
This value feeds into Bayes’ rule of conditional probability, from which the posterior $P_S$ is calculated.

4 HOW SHOULD THE MODEL BE USED?

Step 1: compile from the literature, or other sources, the critical processes of deposition of economic levels and localization of the target commodity. Step 2: focus on collecting evidence for the critical processes of ore formation having occurred within the target area. Step 3: based on the available geological evidence, assign probability values (on a scale between 0.0 and 1.0) to each of the critical processes. Step 4: use historic data to define the minimum, most likely and maximum costs of exploration. Step 5: use historic exploration data to define the true positive rates of your targeting tools. Step 6: run the model for your projects / drill targets. Step 7: rank the projects / targets according to $P_S$ and / or EV and use the modeling results as guideline for making your investment decision.

5 SUMMARY AND CONCLUSIONS

The probabilistic ore systems modeling approach is based on the critical processes of ore formation. The methodology integrates these critical processes with concepts of probability theory, decision analysis and financial modeling. As such, the model provides a useful tool for assessing the probability of success and EV of exploration projects, project ranking and project evaluation. The model is designed to assist geoscientists with recognizing possible outcomes and selecting the best course of action under conditions of uncertainty, whilst highlighting what additional types of geological information would have to be collected for achieving the best possible outcome.

We do not imply that our model definition is superior to others, but simply that the probabilistic ore systems tool is a flexible, internally consistent template that is structured according to previously published, proven petroleum and mineral systems approaches. Users can easily modify the model template to suit their own beliefs, knowledge or specific local circum-
stances, but must honor the model structure and basic rules set out in this paper.

ACKNOWLEDGEMENTS

This study formed part of an industry-collaborative research project at Macquarie University, Sydney. We gratefully acknowledge financial support by Macquarie University and industry sponsors BHP Billiton Ltd, Codelco, Geoinformatics Exploration Australia Pty Ltd, Gold Fields Australasia Ltd, Jackaroo Drill Fund Pty Ltd, Newmont Mining Corporation, Placer Dome Asia Pacific Ltd, Teck Cominco Ltd, and WMC Resources Ltd.

REFERENCES


"Digging Deeper" C.J. Andrew et al (editors)
Structure of the Isan Orogeny under cover to the east of the Mount Isa Inlier revealed by multiscale edge analysis and forward and inverse modelling of aeromagnetic data

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ABSTRACT: Aeromagnetic data reveals the presence of three north-south orientated, tens of kilometre scale, elliptical structures under cover to the east of the Mount Isa Inlier in Queensland, Australia. The Holy Joe Creek, Boot Creek and Nora Creek structures are typically defined by three narrow, continuous magnetic ridges. Highly magnetically susceptible amphibolite bodies, similar to those exposed in the Inlier, are probably the source of most of these magnetic anomalies. Multiscale edge analysis, 2D forward modelling and 3D inverse modelling methods have been used to resolve the geometry and near surface dip of the structures. These techniques indicate that the structures dip moderately to steeply around their edges. The Holy Joe Creek Structure exhibits sub-vertical to steeply west-dipping sides and a moderate plunge around the northern closure. The Boot Creek and Nora Creek structures are more complex magnetically, but their eastern edges also have sub-vertical to steep westerly dips. Diapirism and domes in an egg-box style (type 1) fold interference pattern are considered as possible origins for the elliptical structures. However, disparity between the shape of the structures and possible diapirc bodies and the lack of complementary basin structures to the domes, makes these two explanations unlikely. A more plausible alternative is that the structures are the result of deformation in a single phase, producing folds with a variable hinge-line plunge. These results indicate that east-west shortening during the D2 event of the Isan Orogeny was the major deformation in the buried rocks of the study area, suggesting a shared structural history with the Mount Isa Inlier to the west.

KEYWORDS: Mount Isa Inlier; Crustal structure; Magnetics; Multiscale edge analysis; Forward modelling; Inverse modelling; Isan Orogeny

1 INTRODUCTION

The Mt Isa Inlier in Queensland, Australia (Fig. 1), preserves a well-exposed record of major mid-Proterozoic deformation, metamorphism and plutonism – the ca 1.6 – 1.5 Ga Isan Orogeny (e.g. papers in Betts & Goleby, 2006). However, present and past relationships of the inlier to other Proterozoic rocks are not well understood because the inlier is surrounded by extensive areas of cover. A proper evaluation of the significance of the Isan Orogeny depends on being able to place it in its correct context. One step towards this goal would be a better knowledge of the effects of the orogeny on the areas adjacent to the exposed inlier. This study focuses on such an area to the east of the inlier, where a thin veneer of Cretaceous–recent cover overlies basement rocks that have been directly linked to the inlier (Queensland Department of Mines and Energy et al., 2000). Interpreting the geology of this area would assist in understanding the complex structure of the exposed area, and could also cast some light on the relationship of the Mt Isa Inlier to the similar Precambrian rocks of the Georgetown Inlier about 250km to the northeast (cf. Withnall, 1996). Furthermore, it is likely that any major new mineral deposit discovery will occur in an area such as this, where deposits are accessible through the shallow cover, as at the Ernest Henry and Eloise copper-gold mines.

2 GEOLOGY AND GEOPHYSICS OF THE STUDY AREA

Although the study area is entirely under cover, the Proterozoic geology (Fig. 1) has been previously interpreted in the Northwest Queensland Mineral Province Report (NWQMPR)
Queensland Department of Mines and Energy et al., 2000). Other sources of information about the geology beneath cover come from mine-scale data at the Eloise Au-Cu deposit, generally shallow drill holes, magnetic data and gravity data. Fig. 2 shows the first vertical derivative (1VD), reduced to pole (RTP) magnetic data of the study area. The area is typified by many prominent, narrow magnetic anomalies within relatively non-magnetic surroundings. The narrow anomalies define three elliptical structures that measure 58 x 22km, 32 x 8km and 21 x 8 km, referred to from west to east as the Holy Joe Creek, Boot Creek and Nora Creek structures.

Each structure is defined by one to several sub-parallel anomalies of which three can generally be clearly identified. Holy Joe Creek Structure (HJCS) is most clearly defined in the north, but the three anomalies can nevertheless be traced, somewhat discontinuously, around the southern closure of the structure. The Boot Creek Structure (BCS) and Nora Creek Structure (NCS) are defined on their eastern edge by...
one high-amplitude and several low-amplitude magnetic ridges. The western edges and southern closures of these structures are less distinct and their centres have a complex magnetic signature, unlike the northern half of the HJCS.

2 METHODS OF ANALYSIS

Multiscale edge analysis ("worms"), 2D forward modelling and 3D inverse modelling techniques have been applied to the magnetic data to study the upper crustal features of the Holy Joe Creek, Boot Creek and Nora Creek structures. The multiscale edge data for the study area was provided by Fractal Graphics. The 2D modelling was conducted on a series of eight sections perpendicular to the strike of the magnetic anomalies using ModelVision Pro. The 3D modelling follows the method presented by Li & Oldenburg (1996 and 1998a) for inverting potential field data to recover physical property distributions. This method has been tested on synthetic examples (Li & Oldenburg, 1996) and has proved to give useful results that are representative of true structures when applied to 'real' geophysical data (Williams et al., 2004).

3 RESULTS

The three methods applied provide consistent results for the upper crustal structure of the three elliptical features. The magnetic profiles that were forward modelled can be very closely matched by a series of tabular, steeply dipping bodies of relatively high magnetic susceptibility surrounded by a non-magnetic 'host' rock. The HJCS appears to have three main, parallel magnetic bodies that dip steeply to the west on the western and eastern sides. Around the northern closure the dip shallows, reaching a minimum value of around 60° to the north. Profiles over the eastern sides of the Boot Creek and Nora Creek structures suggest bodies that dip steeply to the west at angles similar to the eastern and western sides of the HJCS.

Based on 3D visualisation of the worms from the study area, in relation to synthetic examples, the general form implies source geometries typified by vertical to moderately dipping dyke-like features. Similarly, the 3D inverse model produces a single dipping body that represents the eastern sub-bodies identified in the 1VD magnetic data (Fig. 2). The inferred structure from the 3D model is the same as that of the multiscale edge analysis and the forward modelling. Certain features are more readily identifiable in the 3D model such as the abrupt change in dip direction that occurs around the sharp bend in the northeast corner of the HJCS.

4 DISCUSSION

Several lines of evidence concur that the narrow, linear magnetic anomalies that outline elliptical shapes are due to both metamorphosed gabbroic-tonalitic (amphibolite) sills and alteration associated with shear zones. The closed map shapes of the three elliptical structures suggest at least three possible origins. Firstly, they may be related to doming around solid state or magmatic diapirs. Secondly, the ellipses may be dome and basin or egg-box fold interference structures, produced by superimposing north-south and east-west shortening (type 1, cf. Ramsay 1967). Their elliptical shape would suggest that the east-west shortening was greatest. However, disparity between the shape of the structures and possible diapirc bodies and the lack of complementary basin structures to the domes, makes these two ex-
A third alternative is that the elliptical structures were produced in a single deformation event by folding with a variable hinge line plunge. Such folds can form by rotation of a fold hinge due to stretching during folding. The vertical stretching required for this to occur fits in with the moderate-steep south plunging L2 observed around the Eloise deposit (Baker & Laing, 1998).

5 CONCLUSION

Three buried crustal-scale elliptical structures are defined by aeromagnetic data to the east of the Mt Isa Inlier. Their geometries have been investigated by using available geological and geophysical information. They consist of typically three tabular bodies, interpreted as steeply dipping metamorphosed mafic rocks. The most likely explanation for the formation of these structures is folding during E-W shortening with hinge line rotation due to vertical stretching. A strong association between mafic bodies and both iron-oxide-copper-gold and Broken Hill type mineralization in the Eastern part of the Mt Isa Inlier makes these structures particularly interesting from an exploration point of view.

ACKNOWLEDGEMENTS

We acknowledge the Predictive Mineral Discovery CRC for their support of this project and the following for supplying data: Xstrata Plc. (formerly M.I.M. Holdings Ltd.), The State of Queensland, Department of Natural Resources and Mines and Fractal Graphics Pty. Ltd. (now Geoinformatics Exploration Inc.). The University of British Columbia, Geophysical Inversion Facility is acknowledged for access to the 3D inversion software (MAG3D). We are grateful to Richard Lane for his assistance with the inversion methodology, to Jim Austin for his help collecting data and Damien Foster, Tim Rawling and Pär Weihed for their constructive reviews.

REFERENCES


ABSTRACT: “Coltan” (columbite-tantalite) ore is the major source of tantalum, and is produced in many less developed countries by small-scale mining operations. In the framework of a trade transparency initiative, forensic tools are used to fingerprint the origin of coltan from pegmatite provinces in Africa. Our preliminary account indicates that a combination of mineralogical and geochemical methods will probably allow discrimination of coltan-bearing provinces.

KEYWORDS: coltan, columbite, tantalite, pegmatite, U-Pb dating, trace elements, microanalysis

1 INTRODUCTION

“Blood diamonds“ are well-known to the public and relate to conflict diamonds which sustained civil war in a number of African countries. “Blood coltan” was coined in the Congolese civil war as the sale of this mineral powered the fighting especially in the eastern provinces of the DRC.

“Coltan”, chiefly composed of minerals of the columbite - tantalite group [(Fe,Mn)(Nb,Ta)2O6], is the most important source of tantalum, a valuable metal (Dec 2006: 77 US$/kg tantalite, 30% Ta2O5) which is used in many components in the electronic industry.

Coltan is mined from highly specialized granitic rare metal pegmatites, which commonly show complex zoning. Although the major producers in Australia, Brazil and Canada account for more than 80 percent of the world production, small-scale artisanal mining is an important economic factor in many African countries. In the past, mining of columbite-tantalite in Central Africa has caused political problems, and money generated from mining was used to finance civil wars. Following the United Nations initiative to fingerprint the origin of conflict materials, the German Federal Ministry for Economic Cooperation and Development (BMZ) has decided to fund this pilot study on coltan ores.

2 SAMPLE LOCATIONS

Samples were obtained from the world’s major coltan producing areas. Special attention is, however, directed to samples and concentrates from Ta-Nb-Sn provinces in Africa. So far, 140 samples have been collected, with more than 50% from central and southern Africa. Most samples are from rare metal pegmatites, and their eluvial and alluvial placers, especially from tin granites and rare metal granites of Archean to Panafrcian age.

3 ANALYTICAL METHODS

Coltan concentrates are studied and analyzed in a step-by-step mode. One goal is to characterize the complete mineralogical and chemical variation of concentrates. Major and trace element concentrations are obtained by X-ray fluorescence analysis on bulk samples. Polished sections are prepared and investigated by reflected light microscopy, followed by fully quantitative mineralogical analysis using the Mineral Liberation Analysis software on a Quanta 600 F scanning electron microscope equipped with an EDAX system.

Columbite-tantalite and other Ta-Nb-bearing phases are further analyzed for major and trace elements by electron microprobe (CAMECA SX100) with detection limits of 30 to 50 ppm.
for trace elements, and for low levels of trace elements by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-IPC-MS; Merchantek 266 nm LUV, Nd:YAG; Agilent 7500i ICP-MS; University of Würzburg).

U-Pb dating is carried out both on crystal fragments using conventional thermal ion mass spectrometry (TIMS) (BGR; University of Toronto), and in-situ using LA-IPC-MS at the University of Frankfurt using a Thermo-Finnigan Element II sector field ICP-MS coupled to a New Wave UP213 ultraviolet laser system. Spot size varied from 30 to 60 µm. Raw data were corrected for background signal, common Pb, laser induced elemental fractionation, instrumental mass discrimination, and time-dependent elemental fractionation. Analytical reproducibility (GJ-1 reference standard) of the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ was usually better than 0.7%. No matrix dependent U/Pb fraction has been observed. The chemical procedures to separate U and Pb for TIMS analysis were adapted from Romer & Wright (1992) and Romer & Smeds (1994). U and Pb were measured in multi-collector mode on a MM354 TIMS (University of Toronto) and a ThermoFinnigan Triton (BGR). Isoplot (Ludwig 2003) was used for graphical presentation of U-Pb isotope data and age calculation.

4 RESULTS

4.1 Mineralogical composition

Concentrates of coltan ores carry abundant accessory phases, parts of which are intergrown with columbite-tantalite. These include pyrochlore-group minerals, tapiolite, wodginite, ixiolite, stibiotantalite, bismutotantalite, cassiterite, as well as silicate, phosphate and further oxide phases. Some of these minerals are characteristic of certain mining districts. A fully quantitative set of data for each concentrate is a fingerprint to the location sampled. This includes mineral associations, assemblages and their relative concentrations, grain sizes, and their intergrowth relationships.

4.2 Major and trace elements

The chemical composition of columbite-tantalite grains is controlled by crystallochemical parameters (Černý 1989). In addition, mineral chemistry reflects intrinsic parameters of ore-forming processes, source, and host rock relationships. Fractionation and contamination in the pegmatite melt are recorded in chemical zoning (Fig. 1) and trace element patterns within grains. The degree of zoning may vary considerably over the scale of a deposit or pegmatite province. The goal of this part of the study is to gain as much information as possible to decipher the overall variability in single crystals and concentrates. The classical approach using microprobe analyses of the major elements permits a rough classification of the pegmatite type (Černý 1989, 1992) but is insufficient for further discrimination of locations. As an example, variations in Mn-Fe (XMn) and Ta-Nb (XTa) ratios in two concentrates are shown in Figure 2. In the sample from Rwanda, zoning in single crystals affects either XMn, or

![Figure 1. Back-scatter electron image of a columbite-tantalite concentrate (Rwanda) displaying heterogeneous chemical composition shown by different grey values](image1)

![Figure 2. Variation in Mn-Fe and Ta-Nb ratios in single grains from concentrates (crosses: Brazil, other symbols: Rwanda). Full circles represent individual grains, whereas other symbols in the Rwanda sample reflect different zones in individual grains.](image2)
rarely XTa. The overall compositional range is very large, whereas the concentrate from Brazil covers a comparatively small area at high Mn-Fe ratios in the diagram.

However, certain trace elements do not follow crystallo-chemical laws in a strict manner. Normalization of trace element concentrations measured in situ to an arbitrarily selected columbite standard from Uganda (XMn = 65.7, XTa = 6.2) reveals distinct differences with respect to Li, Sc, Ti, As, Sb, Bi, Rb, Sr, the REE, Y, Hf, Zr, Sn, W, U and Th. Whereas some locations are characterized by low concentrations of the REE, others are highly enriched, especially in the MREE (Fig. 3), displaying high MREE/HREE ratios.

4.3 U-Pb dating

Relatively high concentrations of U, and low to very low amounts of common Pb in columbite-tantalite facilitate the application of the U-Pb system to date columbite-tantalite (Romer & Wright 1992, Romer & Smeds 1994). The results of TIMS and LA-ICP-MS analyses in three different laboratories are consistent and prove that columbite-tantalite from Africa mostly yields concordant and reliable ages. A few grains, however, also reveal slightly discordant ages (Fig. 4). In the concentrates analyzed so far from Africa, four age populations are evident (Figs. 4, 5): Archaean (>2.6 Ga), Palaeoproterozoic (1.9-2.1 Ga), early Neoproterozoic (Kibaran; 0.98-0.93 Ga); late Palaeozoic (ca. 0.5 Ga). Multiple LA-ICP-MS measurements and TIMS analysis of different fragments of submilligram size, both applied to single crystals, reveal isotopic homogeneity on the microscale. Age inheritance is not evident.

Therefore, different age populations in mixed concentrates can be distinguished. The $^{206}\text{Pb}/^{207}\text{Pb}$ ages obtained for columbite-tantalite from Rwanda (Fig. 4), Burundi and the DRC closely match U-Pb emplacement ages at 962 and 968 Ma obtained for slightly discordant columbite from the Kivuvu and Ruhembe pegmatites in Burundi (Romer & Lehmann 1995), and are in general accordance with alternative dates on late Kibaran so-called “G4” tin granites.

5 DISCUSSION

The chemical composition, including the chemistry and mineralogy of Nb-Ta oxides, of rare metal pegmatites has been used to distinguish distinct rare-element classes (Černý 1992). It is evident, that certain pegmatite types are clearly different from others. However, to date no successful attempt to discriminate different pegmatite provinces has been undertaken. Using modern, state of the art analytical tools, we are confident that mineralogical and chemical parameters obtained from columbite-tantalite ores will allow to distinguish between different ore provinces, probably even down to the deposit scale. This will provide an analytical tool to “fingerprint” coltan concentrates back to the mine, and assist in the establishment
of a control instrument in the envisaged certification of the production and trade chain of coltan and other ores.

ACKNOWLEDGEMENTS

Samples were kindly provided by a number of museums and individuals, namely the Royal Museum for Central Africa (Tervuren, Belgium), B. Lehmann (Clausthal), M. Wagner (BGR), J. Herselman (HAMC). Thanks are due to many people in the BGR for laboratory assistance.

REFERENCES


Figure 5. Concordia diagrams for columbite-tantalite from LA-ICP-MS measurements, University of Frankfurt
Cassiterite and columbite mineralization in pegmatites of the northern part of the Kibara orogen (Central Africa): the Gatumba area (Rwanda)

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ABSTRACT: The Central African Kibara orogen forms a metallogenic province that hosts a variety of granite-related mineralizations rich in cassiterite, columbite (also called “coltan”), wolframite/scheelite, gold, monazite, amblygonite and beryl. At ~ 986 Ma, the so-called “tin granites” intruded. After consolidation of this granite generation, pegmatites intruded at about ~ 970 Ma, of which some are associated with columbite mineralization. The pegmatites underwent intense alteration by hydrothermal processes: tourmalinization, silicification, greisenization and muscovitization. The cassiterite mineralization in the pegmatitic bodies is associated with the two last alteration stages. Greisenization and cassiterite precipitation occurred from a H2O-CO2-(X)-NaCl-KCl fluid (ThTot between 240° and 366°C; TmIce between -19.2 and -8.2°C).

KEYWORDS: Kibara orogen, Cassiterite, Columbite, Pegmatite, Greisen, Rwanda

1 INTRODUCTION

The Central African Kibara orogen extends from Katanga (DRC) in the south to southern Uganda in the north. It forms a large metallogenic province, which contains numerous granite-related ore deposits that are rich of minerals like cassiterite, columbite (also called “coltan”), wolframite/scheelite, beryl, spodumene, amblygonite, monazite, gold. The ore minerals occur as primary mineralization in quartz veins and pegmatites, but also in alluvial or eluvial deposits.

In this contribution, we focus on the primary cassiterite and columbite mineralization in the pegmatite area of Gatumba in the western part of Rwanda (Figure 1), which can be considered representative for this type of mineralization in the northern part of the Kibara orogen (Rwanda, Burundi and Kivu and Maniema in the DRC). Based on available geological and historical mining data, recent field work and geochemical and petrographic analysis, a preliminary metallogenic model is proposed.

2. GEOLOGICAL SETTING

The Kibara orogen formed and evolved between two pre-Mesoproterozoic domains: the Archaean-Palaeoproterozoic Congo craton to the west and the north, and the Archaean- and Palaeoproterozoic Tanzania craton and Bangweulu Block to the east and the south. The Kibara belt consists of two distinct segments, separated in the DRC by the northwest extension of the Palaeoproterozoic Ubende belt (SW Tanzania) across Lake Tanganyika. The "Northern" (Burundi, Rwanda, DRC, Uganda
and Tanzania) and "Southern" (Katanga (DRC)) segments should be viewed as two separate – albeit coeval – orogenic belts (Tack et al. 2006). The northern part of the Kibara orogen consists dominantly of Palaeo- and Mesoproterozoic rocks that have been intruded by different generations of granites (e.g. Cahen et al. 1984). The Sn-Nb-Ta-W mineralization is dominantly present in pegmatitic bodies and quartz veins.

The Gatumba area is situated between two granitic bodies and consists of an alternation of Mesoproterozoic phyllites and quartzites, characterized by a varying metamorphic degree (Gérards 1965). The difference in metamorphic degree has been explained by contact metamorphism due to the intrusion of the granites (Gérards 1965). The sedimentary rocks are intruded by different generations of mafic intrusions and pegmatites. The mafic rocks are dominantly dolerites and are interpreted as pre-tectonic (by reference to a compressional stage at ~1000 Ma). The pegmatites occur in 4 parallel zones between the granites (unpublished data SOMIRWA) and are interpreted to be syn-to post-tectonic. Only few mineralized quartz veins can be identified in the Gatumba area. Interpretation of aerial photographs indicates that the cassiterite mineralization in pegmatites seems to be located at the intersection of lineaments and pegmatites.

3. PETROGRAPHY

The coltan and cassiterite mineralization is present in pegmatitic bodies in the Gatumba area. The paragenetic sequence of the mineralization in the pegmatites in the Mesoproterozoic rocks belt has been studied on samples from different isolated pegmatitic bodies, e.g. Bijojo, Buranga, Gatumba North and South, Kirengo, Lohanga, Nyamissa Rongi, Shori, Sitwe. Unaltered pegmatite rocks in the Gatumba area dominantly consist of microcline, K-feldspar, quartz and muscovite. The host-rocks of the pegmatites show an intense alteration. In sedimentary rocks, the alteration dominantly consists of tourmalination, muscovitization and silification. If the pegmatites intruded mafic rocks, biotitization, tourmalination, silification-

![Figure 2. Paragenetic sequence of columbite and cassiterite mineralization in the Gatumba area](image-url)
tion and muscovitization occurred.

The original pegmatite composition has been completely altered by hydrothermal processes (Figure 2). The original K-feldspars have been altered to albite. Coltan minerals are crosscut by albite veins and are, therefore, interpreted to have precipitated prior to the albitization. Typical pegmatite-related minerals, e.g. amblygonite, beryl and spodumene, formed prior to the albitization. After albitization, large tourmaline crystals formed. The pegmatitic rocks subsequently underwent an intense greisenization during which the feldspars were completely altered into small sericite crystals. These sericite crystals are recrystallized to larger muscovite sheets. The cassiterite mineralization is associated with the greisenization and muscovitization stages. The cassiterite crystals are crosscut by minor haematite and goethite veins that formed during recent alteration.

Fluid inclusions studied in the quartz from the unmineralized greisen are > 10 µm and two-phase (L+V). The inclusions are firstly cooled until a temperature of -120° causing the inclusion to be frozen. \( T_{m, CO_2} \) occurred between -61 and -57.7°C, indicative for an additional gas component (e.g. CH₄, N₂, etc.) next to CO₂. The first melting of the aqueous phase, representative for the composition of the fluid, was only visible in a few inclusions and is around -21.5°C, indicative for a H₂O-NaCl-KCl composition. The temperature of the final melting of ice (\( T_{m, ice} \)) varies between -19.2 and -10.1°C. \( T_{m, clathrate} \) values are between -2.1 and 3.0°C. The total homogenisation temperature (\( T_{h, tot} \)) varies between 274 and 366°C. So, the fluid inclusions in the quartz veins have a H₂O-CO₂-(X)-NaCl-KCl composition.

Fluid inclusions in the cassiterite are <10µm and two-phase (L+V), with a gas volume >30%. First melting of the inclusions is around -21.5°C, indicative for a H₂O-NaCl-KCl composition. \( T_{m, ice} \) varies between -18.7 and 8.9°C. \( T_{m, clathrate} \) is between 5.6 and 12.1°C, indicating the presence of CO₂. \( T_{h, tot} \) is between 240 and 315°C. So, the primary fluid inclusions in the cassiterite have a H₂O-CO₂-NaCl-KCl composition.

5. STABLE ISOTOPES

Five quartz and one cassiterite were selected for stable isotope analyses to determine the origin of the mineralizing fluids (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Location</th>
<th>( \delta^{18}O ) (SMOW)</th>
<th>( \deltaD ) (SMOW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD1</td>
<td>quartz</td>
<td>Granite</td>
<td>Buramba</td>
<td>12.4</td>
</tr>
<tr>
<td>SD2</td>
<td>quartz</td>
<td>Granite</td>
<td>Kavika</td>
<td>11.2 -76.91</td>
</tr>
<tr>
<td>SD3</td>
<td>quartz</td>
<td>Pegmatite</td>
<td>Gatumba</td>
<td>10.0</td>
</tr>
<tr>
<td>SD4</td>
<td>quartz</td>
<td>Greisen</td>
<td>Rongi</td>
<td>11.0 -57.86</td>
</tr>
<tr>
<td>SD5</td>
<td>cassiterite</td>
<td>Greisen</td>
<td>Rongi</td>
<td>7.2</td>
</tr>
<tr>
<td>SD6</td>
<td>quartz</td>
<td>Greisen</td>
<td>Rongi</td>
<td>10.8 -65.02</td>
</tr>
</tbody>
</table>

Table 1. Stable isotope data of quartz and cassiterite from greisen, pegmatite and granite of the Gatumba area.

The \( \delta^{18}O \) value of the ambient fluids, responsible for the precipitation of the quartz in the pegmatites and granite is calculated based on the estimated formation temperatures of the pegmatites (550°C; Fransolet, unpublished PhD thesis 1975) and granites (750°C; Fernandez et al. 1986). The calculated oxygen isotopic compositions of the ambient fluid are between +9.9 and +11.1 V-SMOW for the granites and be-
between + 7.8 and + 8.8 V-SMOW for the pegmatites. In a δ¹⁸O and δD plot, the values plot in the field typical for primary magmatic fluids.

6. DISCUSSION AND CONCLUSION

In the Kibara orogen, the main granite generations G1-3 intruded the Palaeo- and Mesoproterozoic rocks at 1380 +/- 10 Ma (U-Pb SHRIMP zircon). The crystallisation of these granites did not result in an economic significant concentration of rare metals. At 986 +/- 10 Ma, the so-called Kibara “tin granites” were emplaced (U-Pb SHRIMP zircon). Geochemical investigation has illustrated that these granite should not really be called “tin granite” due to the low tin content (average value of 8 ppm). Using the recent classification, the Kibara G4 granites should be classified as “parental” granites for hydrothermal mineralization or for rare-metal pegmatites (Cerny 2005). After consolidation of the “tin granites”, pegmatites were emplaced at 968 +/- 8 Ma (Brinckmann et al. 2001). Some of these pegmatites are associated with columbite mineralization. The columbite mineralization has been dated in Burundi at 955 +/- 5 Ma (Romer & Lehmann 1995), which overlaps with the timing of pegmatite emplacement. This dating is confirmed by petrographical observation that indicates that the columbite minerals are present in altered and non-altered parts of the pegmatite bodies and the columbite is crosscut by later alteration phases. The limitation of coltan to the pegmatites and not in the hydrothermal alteration zones can be explained by the low solubility of Nb and Ta in aqueous solutions. The pegmatites have been subjected to an intense hydrothermal alteration. The original feldspar minerals have been submitted to intense albitionization, tourmalinization, greisenization and muscovitization. Cassiterite mineralization is associated with greisenization and muscovitization. Greisenization and cassiterite precipitation occurred from fluids with a H₂O-CO₂-NaCl-KCl composition. The altered and Sn mineralized parts of the pegmatites occur at the intersection of lineaments and pegmatites, which could have acted as pathways for the mineralizing fluids.

ACKNOWLEDGEMENTS

We would like to thank Jean-Claude Defleur and Gilbert Chartry for stimulating discussions on various aspects of the Sn-Nb-Ta ore deposits in Rwanda and the DRC. Herman Nijs and Rene Boyen kindly prepared the numerous thin and polished sections and the doubly-polished wafers.

REFERENCES


Whole-rock geochemical characteristics of a lithium pegmatite dike: a case example from Vintturi (Kaustinen), W-Finland

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ABSTRACT: Whole rock geochemical data on lithium pegmatite is presented from the Vintturi prospect, western Finland. Albite, quartz, spodumene, muscovite and K-feldspar are the main minerals in the weakly zoned pegmatite dike. The dike is peraluminous and the average Li2O content calculated from two cross-section is 0.87 wt%. Geochemical and mineralogical data are in favour of classification of the Vintturi pegmatite as albite-spodumene type of rare-element pegmatites.

KEYWORDS: spodumene, lithium, pegmatite, Finland, geochemistry

1 INTRODUCTION

Palaeoproterozoic ca. 1.80 Ga REL (rare element) pegmatites crosscut the Svecofennian ca 1.95-1.88 Ga supracrustal rocks in western Finland (Alviola 1989). Their distribution roughly follows the metasedimentary dominated Pohjanmaa belt and their emplacement appears to follow the peak of the regional metamorphism by at least 80 Ma (Mäkitie et al. 2001). Alviola et al. (2001) have shown that the different pegmatite types, classified according to Černý (1998), are located in different parts of the Pohjanmaa belt. Specific types of spodumene-bearing lithium pegmatites are known in the Kruunupyy–Ullava area of the Pohjanmaa belt (Fig. 1). Because of limited data, Alviola et al. (2001) proposed tentatively that these pegmatites may belong to the albite–spodumene subtype of the LCT (Li,Cs,Ta) family (see Černý & Ercit 2005). The aim of this paper is to give a brief overview and provide new whole-rock geochemical analyses of the lithium pegmatite prospect at Vintturi, from Kaustinen parish that belongs to lithium pegmatites of the Kruunupyy–Ullava pegmatite area (Fig. 1).

2 LOCAL GEOLOGY OF VINTTURI AND DESCRIPTION OF THE DIKES

The Vintturi prospect is presently under industrial mineral exploration by the Geological Survey of Finland with an aim to investigate its lithium potential. The bedrock is covered by quaternary glacial sediments. A boulder fan led to localizing the Vintturi spodumene pegmatite in the 1960’s (Säynäjärvi 1973).

At least three separate spodumene pegmatite dikes have been encountered in the Vintturi prospect on drilling. Other narrow albite-quartz- and K-feldspar-containing pegmatite dikes, which often lack spodumene, are associated with these dikes. The dimensions of the main (largest) spodumene-containing pegmatite dike are not well constrained, but based on available drilling data, it appears to reach at least 200m in length, and its thickness varies from few meters to nearly 20 meters. The main dike is nearly N-S trending and dips ca. 50–60° W. The host rocks are mica schists, interlayered by graphite- and sulphide-bearing schists. In the surrounding area, the mica schist occasionally contains andalusite porphyroblasts.

3 MINERALOGY AND GEOCHEMISTRY

The main minerals in the Vintturi lithium pegmatite are albite, quartz, spodumene, potassium feldspar and muscovite. Typically, spodumene is greenish in colour and it often shows preferred orientation. In some cases, spodumene has been replaced by yellowish muscovite. Common accessory minerals are apatite, graphite and columbite–tantalite.

This study is concentrated on the two widest cross-sections of the Vintturi pegmatites.
Average whole rock geochemical data on these two drill-core sections are presented in Table 1. Sections are 14.55m and 19.00m in length (DH7 and DH9 respectively) (Fig. 2). Averages consist of analyses made on typically 2m long drill core samples. Based on two cross-sections the average content of Li$_2$O is 0.87 wt%, which is apparently nearly totally caused by the spodumene. This corresponds to ca. 10% spodumene, which is in accordance with the visual estimate on drill cores. Vintturi pegmatite is peraluminous (A/CNK is ca. 1.5) and Na$_2$O > K$_2$O throughout the sections (Fig. 2).

Cross-sections reveal that the pegmatite dikes are weakly zoned. In both sections LiO$_2$ contents are highest in the central part of the dike, thus indicating highest spodumene content. Similarly, Na$_2$O content decreases in the central part of the dike, indicating decreasing albite content relative to spodumene. In the section DH 9 the K$_2$O content is highest near the footwall contact. The high Na$_2$O content in the same sample corresponds to the lowest Li$_2$O content of the section. Especially section DH9 shows that Ta and Nb contents are highest in the outer domains of the dike that also contain more albite. This feature is not observed in the section DH7, where the dike is narrower. Portions of Nb and Ta vary in different vein portions. The average contents show that section R7 contains more Nb than Ta, whereas section R9 contains more Ta than Nb. The average Nb/Ta ratio varies between ca. 1-2.

The Vintturi pegmatite exhibits low Rb contents like the Austrian Weinebene albite-spodumene pegmatites described by Göd (1989) (Table 1). High K/Rb reflects low levels of fractionation of these pegmatites compared with low K/Rb in spodumene subtype pegmatites of complex pegmatites.

4 DISCUSSION

According to Černý & Ercit (2005) spodumene is a typical mineral in the spodumene-subtype of the complex pegmatite type, as well
as in albite–spodumene type pegmatites. Spodumene subtype pegmatites tend to be characterized by an extreme level of fractionation and notably evolved internal structure (Černý & Ercit 2005). Pegmatites of albite-spodumene type show rather simple zoning and strong preferred orientation of spodumene K-feldspar laths. According to Černý & Ercit (op. cit) the subnormal to oblique orientation is a primary growth-induced fabric, which in some cases has been enhanced by later deformation or recrystallization. Spodumenes in the Vintturi pegmatite often show prominent orientation, relatively weak zonation and fractionation. It also contains more albite than K-feldspar. In addition, overall geochemical characteristics resemble fairly well with Weinebene pegmatites, which are considered as one of the type examples of albite-spodumene pegmatites (Černý & Ercit 2005). Thus, the Vintturi pegmatite has more similarities to the albite-spodumene type than to complex type pegmatites.

5 CONCLUSIONS

The average Li₂O content calculated for two cross-sections of Vintturi lithium pegmatite is 0.87 wt%. The dominance of albite, rather homogeneous internal structure, and preferred orientation of spodumene, together with a low level of fractionation are in favour of classification of the Vintturi dike as albite-spodumene type of rare element pegmatites.

REFERENCES


Mineralogical and geochemical characteristics of the pegmatite bodies of Awo-Ede area, southwestern Nigeria

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**ABSTRACT:** The study involves the detailed investigation of the pegmatites in the Awo-Ede area, southwestern Nigeria. The aim of the study is to assess the mineralogical and geochemical characteristics of the pegmatite bodies and establish their degree of mineralization in semi-precious stones and columbite/tantalite. The pegmatite dykes and sills intrude into biotite gneiss in the Awo area and amphibolites in the Ede area. Petrographic studies revealed a dominant feldspar-quartz-mica mineralogy with associated beryl, columbite/tantalite, tourmaline and garnet. The Na/K ratio is low to moderate, ranging from 0.05-3.41 reflecting albitization. The degree of fractionation as defined by K/Rb vs Rb and K/Rb vs Cs plots, and various elemental associations revealed that most of the pegmatites have ore potential and were emplaced during magmatic differentiation.

**KEYWORDS:** pegmatite, columbite/tantalite, albitization, Nigeria

1 INTRODUCTION

Geological information on the pegmatites of the Osun district of southwestern Nigeria is at present rather scanty and of reconnaissance nature. Such information is part of the general discussion on the pegmatite bodies of Nigeria, which are widely distributed in several areas of the country. Previous studies have shown that they characterize the Pan-African reactivation zones covering Ijero and the Wamba-Jamba areas (Jacobson & Webb 1946; Wright 1970; Matheis & Caen Vachette 1983; Kuester 1990; Garba 2003; Okunlola 2006). Two main types of pegmatite have been distinguished within the basement complex of Nigeria based on the associated metals and precious stones: barren and mineralized pegmatite. However, earlier workers have also used a relationship between pegmatite and granitic contacts to classify them into internal, marginal and external types. It was observed that mineralized pegmatites are of internal type, characterized by intense albitization and often contain economic minerals such as cassiterite, columbite, tantalite, beryl and gold.

The study area is located within latitude 07°35′26″-07°50′21″ and longitude 004°15′20″-004°35′16″ (Fig. 1). The major areas where pegmatite bodies were encountered include Awo, Ede, Sekona and along the river channels of River Osun. The present study involves detailed field mapping, petrological and geochemical assessment of the pegmatite bodies around the Osun district, southwestern Nigeria.

2 GEOLOGY AND FIELD OBSERVATION

The study area lies within the Nigerian basement complex affected extensively by the widespread Pan-African thermo-tectonic events. However, available isotopic data have
shown that the basement complex has been involved in several tectonic events, which include from the oldest the Liberian, Eburnean, Kibaran and Pan-African. Structural trends in the crystalline rocks are dominantly ENE/WSW with significant numerous associated NE/SW and N/S trends. These trends also serve as possible zones of emplacement of rare-metal pegmatite, as observed around the pegmatite bodies of the study area.

The pegmatite bodies consist of microcline, albitized feldspar, quartz and mica (muscovite, biotite and lepidolite) with associated accessory minerals such as tourmaline, tantalite, columbite and beryl (gem and non-gem varieties). The tourmaline is black, massive and with specks of sky blue lazurite. Beryl occurs as a euhedral light green crystal while garnet is reddish in colour. Structural orientation of the pegmatite is between 340-350° azimuths. Dip direction is conformable with the host rocks. However, most of the bodies are found intruding as dykes and sills into biotite gneiss in Awo and amphibolite in Ede.

Three shafts sunk on the intensely weathered bodies at Awo revealed that between 12 to 20 metres depth about 60kg of columbite-tantalite were excavated within the kaolinized zone of about 20 tonnes of ore body, and ore grade of about 300ppm was revealed. Further preliminary estimation showed an inferred resource of about 442 metric tonnes of contained columbite/tantalite.

3 PETROGRAPHY AND GEOCHEMISTRY

Petrographic examinations show a dominant feldspar-quartz-mica mineralogy, with the early formed microcline exhibiting assimilation texture. The intergrowth of microcline and quartz shows graphic texture while albite exhibits myrmekitic texture with quartz. Muscovite is colourless, lath shaped with bright yellowish to bluish interference colour.

Major elements analysis revealed that the SiO₂ content for the pegmatite ranges from 65-79 wt%. Al₂O₃ content is slightly enhanced in the pegmatite with values decreasing with increase in SiO₂ content (Fig. 2). Na/K ratio is low to moderate, ranging from 0.05-3.41 confirming appreciable albitization. The albitization trend is also consistent with the silica-alumina content. This observation is more pronounced where euhedral crystals of beryl and columbite/tantalite were discovered. A well developed assimilation texture is also characteristics of these zones. The content of TiO₂, MgO, CaO and FeOtotal are mostly below 1 wt%.

Pegmatite bodies of the study area are significantly enriched in Rb, Cs, Nb, Ta, Sn, Ba and Ga. The degree of fractionation defined by...
the plots of Rb vs K/Rb (Fig. 3) and K/Rb vs Cs plots revealed that most of the pegmatite bodies could be classified as mineralized although marginally endowed (Beus 1966). Na/K values revealed a positive correlation with the rare metal contents, with the albitization level increasing with the Ta and Rb concentration. The Sr/Rb plot indicates that the pegmatite bodies were emplaced during magmatic differentiation (Fig. 4). Rb/Sr crustal-thickness plot after Condie, 1976 indicated that the basement around Awo attained thickness between 20-30km during the emplacement of these pegmatites (Fig. 5).

A detailed channel sampling of the exploration pits dug at Awo and the subsequent chemical analysis of these samples revealed that the petrogenetic indicator elements (Rb, Cs and Be) increase with depth, correlating positively with increase in Ta, Nb, Na\textsubscript{2}O and K\textsubscript{2}O concentration.

4 CONCLUSIONS

We conclude that the pegmatite bodies around Awo are marginally mineralized with columbite/tantalite and precious stones and that the bodies were emplaced during magmatic differentiation. However, a detailed REE analysis of the whole rock and determination of the elemental composition of feldspars and muscovite is been proposed.

ACKNOWLEDGEMENTS

The project benefited from funding provided by the Nigerian Geological Survey Agency under the Economic Geology project of 2005.

REFERENCES


Condie KD (1976) Trace element geochemistry of Achean granite rocks from the Baberton region South Africa. Earth Planet. Sci. lett. 15:300-400.


Multistage metasomatism and mineralization at hydrothermal Fe oxide-REE-apatite deposits and “apatitites” of the Bafq District, Central-East Iran

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ABSTRACT: Initial results from the study of three Fe oxide-apatite-REE deposits and the coeval apatite-rich magmatic-metasomatic rocks (apatitites) of Chogart, Lakkeh Siah, and Gasestan in the Bafq district reveal a complex history of multistage metasomatic alteration and mineralization. Distal/regional alteration consists of K-feldspatization, albitization, selective replacement of the host rhyolites by the ore-related metasomatic mineral assemblage, sericitization, late talc and calcite metasomatism. The metasomatic mineral assemblage consists of monazite, F-Cl-REE apatite, magnetite (±haematite), allanite, Ca-thorite, zircon, titanite, rutile, xenotime, and synchysite, and Sr-barite. The ore-related metasomatism locally succeeded the broad-scale, multistage actinolitization and includes the following stages: (1) F-Cl-REE-apatite-monazite-magnetite(±fluorite±anhydrite), pyroxene or actinolite ± garnet; (2) actinolite, apatite, monazite, xenotime, allanite, Sr-barite; (3) precipitation of considerable amounts of carbonates and quartz; (4) local talc alteration, and minor pyrite ± chalcopyrite. Broad-scale alteration associated with Fe oxide-apatite-REE mineralization within rhyolitic rocks along the Bafq structural zone and the association with a bimodal volcanism indicate an early Cambrian tectonomagmatic control on the mineralization that was probably related to intraplate rifting.

KEYWORDS: Fe oxide-REE-apatite, “apatitite”, metasomatic alteration, Bafq, Iran

1 INTRODUCTION – TECTONOMAGMATIC SETTING

The Kiruna-type Fe oxide–REE-apatite ores of the Bafq district, Central East Iran, are coeval with a wide variety of unusual REE-bearing apatite-rich magmatic-hydrothermal rocks that we call here “apatitite”. The three studied deposits occur within the southern sector of the Bafq metallogenic province and contain apatite-rich rocks. This work represents initial results of a study that is aimed at contributing to the resolution of the genesis of this type of ore deposits.

The Bafq metallogenic province is a 100km long, N–S trending, narrow section of the Central-East Iran structural zone bordered by two deep crustal faults. It hosts major, high-grade Fe oxide–apatite-REE deposits (2000Mt, Fe 65–45%, NISCO 1980) and magmatic REE-phosphate deposits.

The Fe oxide–apatite ores and apatitites are spatially and temporally associated with a short-lived early Cambrian magmatic event and are hosted dominantly by rhyolites. Minor Fe oxide ore occurs within spilitic basalts such as at Mishdovan (Daliran 1990). These unmetamorphosed rhyolites largely occur as subaerial welded ash-flow tuffs or as subaqueous intercalations within a locally evaporitic volcanosedimentary unit (CVSU). Based on the geochemistry of the rhyolites, Ramezani & Tucker (2003) attribute the early Cambrian CVSU to felsic to intermediate magmatism (528 Ma) that was followed by emplacement of late granitoids (trondhjemite) at 524 Ma. They propose an orogenic arc setting along the Proto-Tethyan margin of Gondwana for this magmatic episode, but mention the existence of rift zones at Bafq. Association with spilitic basalts, regional alkali metasomatism, and development of an evaporite facies within the CVSU, however,
suggest the establishment of an extensional regime in this region that has been suggested to have been in genetic relationship with the mineralization (Haghipour 1974; Daliran 1990, 2002; Samani 1998). The timing of the rifting event and the spatial relationship with the orogenetic rocks are still unknown. The Early Cambrian magmatism was terminated by the emplacement of albitite and diabase dikes (Fig. 1).

The apatite–Fe-oxide ores (Fig. 2) and theapatitites form end-members of a continuum and display a similar style of alteration and mineralization. The magnetite ore is commonly Ti-V-bearing (<2 and <1 wt % oxide, respectively) and occasionally displays exsolution of ilmenite trellis and spinel blebs. Apatite and magnetite formed during a first stage with diopside or actinolite, monazite-1, and locally andradite-grossular. Progressive enrichment in REE led to the precipitation of minor to trace amounts of monazite-2, allanite, Y and Ti minerals and considerable amounts of carbonate and quartz. Locally, talc was formed by the late metasomatic fluids and replaces previous minerals. The early-formed minerals occur commonly as euhedral crystals or crystal fragments. Minor amounts of late sulphides were deposited locally within the oxide ore bodies.

2 DEPOSIT GEOLOGY

Host rhyolitic rocks, in part welded ash-flow tuffs, constitute the largest volume of the magmatic rocks throughout the study areas and are associated with basalts at Lakkeh Siah and at Gasestan. At Lakkeh Siah, the host rhyolites and the ore bodies display sedimentary features and occur within the volcano-sedimentary unit, CVSU. Early Cambrian dolomitic limestones, red sandstones, tuffites and shales occur outside the mineralized areas at Gasestan and Lakkeh Siah. The host rocks are intruded by strongly altered small bodies of diabase dikes and albitites.

3 MULTISTAGE METASOMATIC ALTERATION AND MINERALIZATION

In all three deposits mineralization was associated with an extensive complex, multistage regional and distal alteration of the host rhyolites. Metasomatites locally evolve to apatite bearing rocks (apatitites) and to apatite-REE–magnetite ores and share a common mineralogy.

3.1 Chogart deposit

The active Chogart mine is a large (450 Mt), Fe rich (60 %) podiform Fe oxide–apatite ore body, 1km long and 300m wide (NISCO 1980). The host rhyolitic rocks occasionally shows relics of fluidal texture. Apatite-rich rocks occur mainly within a breccia zone between the Fe oxide ore body and the host rhyolites, or as veins within the Fe ore body.

Dista/regional metasomatism at Chogart is characterized by alkali metasomatism that consists of K-feldspar and sericitization. K-feldspar metasomatism (Fig. 3) was followed by very minor amounts of albite indicating a clear phase separation. Albitionization, however, has locally converted the rhyolites to coarse-grained rocks that consist almost entirely of chequer albite. K-feldspar metasomatism was followed by ac-
tinolitization and minor diopside that are associated with traces of the metasomatic mineral suite REE-F-Cl apatite, Fe oxide, LREE minerals, titanite, rutile, Ca-thorite, zircon, Sr-barite, and late calcite (±Mg ±Fe). Monazite (Ce-La-Nd) is the most common REE mineral and can contain up to 6 wt% Th. Monazite formation was followed by xenotime, and by zoned allanite (Ce-La-Nd). Actinolite contains minor amounts of Mn, Na, and Ti and shows compositional variation during different metasomatic stages of formation and alteration.

The first stage of magnetite–apatite–REE ore formation was followed by deposition of calcite, quartz, and talc in open spaces. Apatite contains abundant monazite-1 (Ce-La-Nd) inclusions (Fig. 4A). Monazite-2 (Ce-La-Nd), allanite (Ce-La-Nd), xenotime, and a HREE phosphate mineral (probably synchysite) occur with the second-stage apatite, late calcite-quartz and locally talc. The late sulphide stage consists of pyrite and traces of chalcopyrite. No REE minerals are associated with the sulphide stage.

![Figure 3. Actinolitization following distal K feldspar metasomatism of the rhyolites at Chogart (light-colored fragments).](image)

### 3.2 Gasestan deposit

Incipient distal metasomatism of selected sheets within the welded ash flow tuffs at Gasestan has resulted in replacement of the feldspar phenocrysts by anhydrous (high temperature) haematite-rutile assemblage, Fe oxide, F-Cl apatite, monazite, zircon, and rutile (Fig. 4B), as well as the formation of disseminations and aggregates of these minerals and Sr-bearing barite along the flow lineation.

The Fe oxide ore lenses are aligned within a 500m, E–W trending actinolitized zone below distally metasomatized welded ash-flow tuffs. The iron ore contains abundant apatite that occurs as large (20–30cm) reddish crystals. Apatite exhibits growth- and patchy zoning due to variation in F/Cl and REE and is crowded with inclusions of monazite-1 (Ce-La-Nd). Monazite crystals are aligned along the C axis of the apatite suggesting their exsolution from the apatite structure.

Late carbonate and quartz fill contains apatite-2, monazite-2 (Ce-La-Nd±Th), zoned allanite (Ce-La-Nd), titanite and rutile. The Y minerals xenotime and synchysite are slightly later and replace the LREE minerals (Fig. 4C).

### 3.3 Lakke Siah deposit

The Lakke Siah deposit consists of a number of meter scale thick and smaller ore lenses and stratiform layers within the Lower Cambrian volcano-sedimentary sequence (CVSU). The host sequence is overlain by barren rhyolites displaying devitrified fluidal textures. These rhyolites are altered to sericite, and calcite. The ore lenses at the ore body No. II occur within a 250m thick body of actinolite rocks that locally grade to a “layered” (bedding?) metasomatite with abundant small, yellow, euhedral crystals and crystal fragments of yellow apatite and dark green diopside (Fig. 4D), and tiny, brown grains of andradite-grossular. Garnet grains are zoned and contain REE towards the rim (Fig. 4E). Late monazite-2 (Ce-Nd-La), and allanite (Ce-Nd-La) occur within the late calcite-quartz fill. Locally, whitish powdery, apatite-looking crystals in the magnetite ore are pseudomorphosed by talc (Mg2.85Fe0.15Si4O10(OH)2) and traces of minerals of the metasomatic assemblage monazite, xenotime, allanite, rutile, titanite, zircon, calcite, and quartz (Fig. 4F).

Magnetite occasionally contains inclusions of fluorite and a Ca-sulphate, probably anhydrite. Late chalcopyrite and pyrite were formed in minor amounts and replace magnetite.

### 4 DISCUSSION AND CONCLUSIONS

The Fe oxide–apatite–REE andapatiteite deposits of the Bafq district are similar to the global Fe oxide (P-REE-Th-U) rocks of hydrothermal origin (Hitzman 2000). Metasomatic alteration associated with the mineralization along the structural zone of Bafq and their intimate association with early Cambrian rhyolites indicates a tectonomagmatic control during this short time span. Despite the orogenic arc
setting for some Iranian rhyolites (Ramezani & Tucker 2003), a number of features such as the alkali metasomatism and similarities with “phoscorites” suggest some link between a rift-related magmatism and the mineralization at Bafq. Features such as the incipient alteration of the welded ash flow tuffs by a metasomatic suite of anhydrous minerals (high temperature!), suggest that the rhyolitic melt and the ore fluids might have coexisted at depth and may explain the common association of the apatite and Fe oxide ores with the rhyolites.

Figure 4. BSE images and a microphotograph (D) of the metasomatic mineral assemblages. (A) Abundant inclusions of the early stage monazite-1 in apatite-1. (B) Incipient distal alteration of the welded ash-flow tuffs, here represented by replacement of a feldspar phenocryst by Fe oxide, apatite, and haematite-rutile assemblage. (C) Allanite is associated with the late-stage quartz-calcite, interstitial to apatite. Later formed Y-minerals (possibly synchysite), are associated with talc alteration and fill cracks of apatite crystals. (D) Idiomorphic pyroxene inclusions in first-stage apatite. (E) Garnet displays REE enrichment towards the rim in apatite-actinolite rocks. (F) Late stage talc, rutile, and calcite replace apatite-1 crystals in the magnetite ore. act: actinolite, aln: allanite, ap: apatite, cc: calcite, grt: garnet, hem-rt: haematite-rutile, mt: magnetite, px: pyroxene, qtz: quartz, rt: rutile, sy: synchysite, tlc: talc.

The studied ore deposits show similar alteration and mineralization styles that extend throughout the whole Bafq province, indicating a large homogeneous fluid source at depth. Pyroxene, apatite, magnetite, and garnet formed earlier, probably in deeper crustal levels and were carried (in solid state!) to the surface by fluids which were enriched in LREE followed by minor Y and HREE, carbonate, silica, and some sulphides. Local variations within the metasomatic mineral suite were controlled by P–T and the mode of emplacement (synsedimentary versus epigenetic) of individual deposits.

ACKNOWLEDGEMENTS

Financial support for this study is provided by the “German Research Foundation” (DFG) and in cooperation with the Geological Survey of Iran, whose generous logistic support and field assistance are greatly appreciated.

REFERENCES


Petrographical study of Fe-REE mineralization in the Hongcheon area, South Korea

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ABSTRACT: The Hongcheon Fe-REE ore deposit contains ferroan dolomite, calcite, albite, K-feldspar, monazite, magnetite, haematite, columbite, fergusonite, strontianite, apatite and sulphide minerals. Magnetite, monazite and apatite formed early, and dolomite is both early and late. Nanometasomatism (fenites) is developed in the gneiss wall rocks. The mineral assemblages and chemical composition show that the Hongcheon Fe-REE ore deposit is part of a phoscorite intrusion, strongly differentiated from Fe-carbonatite melt.

KEYWORD: Hongcheon, South Korea, Fe-REE deposit, phoscorite, Fe-carbonatite

1 INTRODUCTION

Iron ore deposits of unknown age in the Hongcheon area have recently attracted interest due to their high REE contents. Our institute estimates 10 million tonnes of iron ore and 2.5% REE grade based on R2O3 from this area. We here present petrographical results on the mineral assemblage and chemistry of ore and gangue minerals.

2 GENERAL GEOLOGY

The area studied is located in the margin of the tectonic province of the Gyunggi gneiss complexes of the Korean peninsula which includes banded gneiss, biotite gneiss and biotite-hornblende gneiss. Carbonatite and alkaline ultramafic injection complexes occur in narrow and elongated sheet-like shape (20–50m width, 2500m total length) with norh-south trend within biotite-hornblende gneisses. The major minerals of the injection complexes are ferroan dolomite and magnetite, and accessories are monazite, strontianite, columbite, fergusonite, calcite, siderite, ankerite, chlorite, apatite, aegirine-augite, tirodite, acmite, pyrite, molybdenite and barite. The chemical formula of strontianite (microprobe analysis) is Ca0.02Sr0.84-0.98CO3, i.e. Sr is partly replaced by Ca. Reddish columbite without Ta is manganocolumbite, (Mn0.57Fe0.24Mg0.19)Nb2O6, and opaque columbite has ferrocolumbite composition, (Fe0.82Mn0.15Mg0.03)Nb2O6. Fergusonite has minor P and no Ta and its formula is (REE0.96Ca0.06Th0.03)NbO4. Mineral textures from microscopic observation prove that monazite and magnetite formed together with the carbonate minerals.

The mineralized carbonate rock with mag-
netite, monazite, strontianite, apatite, columbite and fergusonite has grades of 21.1% Fe, 2.4% REO, 1.8%\(\text{SrCO}_3\), 0.12% \(\text{Nb}_2\text{O}_5\), and 2.9% P.

The biotite-hornblende gneiss, the wall rock of carbonate injections, is altered to syenitic fenite (sugary albite and Na-tirodite) and feldspathic fenite (albite and haematite) by Na-metasomatism along the injection bodies.

3. GEOCHEMISTRY OF MINERALIZED CARBONATE ROCKS

Major elements of 12 samples of mineralized carbonate rocks have a more evolved composition compared to that of ferrocarbonatite in the triangular diagram of Na+K, Ca, and Mg+Fe\(_2\text{O}_3\) (Le Bas, 1987) (Fig. 1) and relatively high values of Fe\(_2\text{O}_3\), P\(_2\text{O}_5\), and Sr\(_\text{CO}_3\), and low contents of CaO and BaO in comparison to normal ferrocarbonatite (Woolley & Kempe, 1989).

Data from carbon and oxygen stable isotope analysis of dolomite and strontianite in mineralized carbonate rock shows \(\delta^{13}\text{C} = -3.89\text{~} - 9.31\%\text{o}\) and \(\delta^{18}\text{O} = -18.05\text{~} - 22.90\%\text{o}\) which implies an igneous origin (Fig. 3), but more data such as age of mineralization and metamorphism are necessary to clearly support the petrogenetic interpretation because regional metamorphism could cause depletion of \(^{13}\text{C}\) and \(^{18}\text{O}\).

4. CONCLUSION

The research results described above such as mineral assemblages of the mineralized zone, geochemical characteristics of major elements and REE, syenitic fenite and feldspathic fenite developed by Na metasomatism, ore mineral textures of intergrowth, corrosion features, exsolution and brecciation, and C-O stable isotope data indicate that the Hongcheon Fe-bearing carbonate rocks are phoscorites, i.e. a variety of Fe-carbonatite representing typical characteristics of the late differentiation stage of Fe-carbonatite melts.

The Hongcheon Fe-REE ore deposit is formed by late stage Fe-carbonatite melts and secondary hydrothermal overprint. Future studies on metamorphism and mineralization and secondary hydrothermal alteration processes are necessary to obtain more quantitative data.

REFERENCES


Wakita, H., Ray, P. and Schmitt, R.A., 1971, Abundance of the 14 rare-earth elements and 12 other trace elements in Apollo 12 samples: five igneous and
one breccia rocks and four soils Proc. 2nd Lunar Science Conf., pp. 1319–1329

Carbonatitic melt-fluid evolution: Evidence from inclusions in the Maoniuping REE deposit in western Sichuan, China

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ABSTRACT: Based on the results of petrography, microthermometry, LRM and SEM/EDS analysis of fluid, melt-fluid and melt inclusions, it can be concluded that the REE-forming fluid at Maoniuping is rich in K, Na, Ca, Ba, Sr, SO4, CO2 and REE, differing from that of porphyry copper deposits and hydrothermal gold deposits. The spectrum of melt, melt-fluid and fluid inclusions suggests a continuous evolution from carbonatite magma to hydrothermal fluid, and also suggests a magmatic source and unmixing of carbonatite melt and ore-forming fluid. The evolution process of the ore-forming fluid was from carbonatite melt, melt-fluid, high-medium temperature CO2-rich fluid to low temperature aqueous rich fluid. The fluid related to REE mineralization is a kind of supercritical CO2-H2O system. REE minerals precipitated from CO2-rich fluid at 219~362°C and 150-350 MPa. Phase separation of CO2 and aqueous fluid is the dominant mechanism for REE precipitation.

KEYWORDS: Maoniuping, carbonatite, melt-fluid inclusions, fluid inclusions, CO2-rich supercritical fluid, REE mineralization, China

1 INTRODUCTION

The Himalayan Mianning-Dechang (MD) REE belt, one of the most important ore-belts in China, is located in the western margin of the Yangtze craton in the East India-Asia collision zone. Five REE deposits, including Maoniuping, Dalucao, Lizhuang, Maidi and Muluo, have been found in this belt. The Maoniuping REE deposit is the largest of the five REE deposits and the third largest REE deposit in the world, after Bayan Obo in China and Mountain Pass in USA.

The Maoniuping REE deposit has abundant carbonate and hydrothermal minerals (such as calcite, fluorite, quartz, barite etc) related to REE mineralization. A large number of melt, melt-fluid and fluid inclusions were observed in the minerals (Niu et al. 1995,1996; Yuan et al. 1995; Yang et al. 2001; Xu et al., 2001, 2003; Xie et al. 2005). These inclusions are believed to have recorded a continuous carbonatitic melt-Fluid evolution for the REE ore system. Based on the petrography of inclusions, microthermometry, LRM analysis of aqueous, vapour and solid phases (daughter minerals and trapped minerals) in inclusions, and SEM/EDS analysis of solid phases in inclusions, as well as on integrating the results from former researchers, this paper discusses the origin and the evolution of carbonatite fluid and the REE mineralization process.

2 GEOLOGICAL OUTLINE

The Mianning-Dechang REE belt is genetically and spatially related to a belt of carbonatites and alkaline rocks.

The Maoniuping area is mostly covered by Yanshanian granite, rhyolite and a sequence of Devonian-Permian marine clastic to carbonate rocks. A series of NE-NNE trending faults controls the distribution and location of orebodies. The carbonatite-alkaline complex intruded the Yanshanian granite. The petrology, petrochemistry, isotope and REE compositions of the carbonatite-alkaline complex have been studied by many researchers (Yuan et al. 1995; Yang et al. 2001; Xu et al., 2001, 2003; Xie et al. 2005). These inclusions are believed to have recorded a continuous carbonatitic melt-Fluid evolution for the REE ore system. Based on the petrography of inclusions, microthermometry, LRM analysis of aqueous, vapour and solid phases (daughter minerals and trapped minerals) in inclusions, and SEM/EDS analysis of solid phases in inclusions, as well as on integrating the results from former researchers, this paper discusses the origin and the evolution of carbonatite fluid and the REE mineralization process.

Proceedings of the Ninth Biennial SGA Meeting, Dublin 2007

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Based on mineral assemblage, texture and structure of ores, crosscutting relationships of ore veins, and fluid inclusion data, five mineralization stages have been recognized: (1) Carbonatite stage (melt stage); (2) Pegmatite-coarse fluorite-quartz stage (melt-fluid stage), with the mineral assemblage of microcline, quartz, fluorite, phlogopite, biotite, aegirine-augite, magnesio-arfvedsonite, chevkinite, magnetcite, etc; (3) Barite-bastnaesite-calcite stage (CO₂-rich fluid stage), with the mineral assemblage of calcite + barite + celestine + bastnaesite. Two Cu-bearing intermetallic minerals were also detected by EPMA including copper and zinc cooperate (Xie et al. 2006). (4) Calcite stage (aqueous-rich fluid stage); (5) A supergenic oxidation stage. (Yuan et al. 1995).

3 INCLUSION RESULTS

3.1 Petrography of inclusions

Large numbers of melt, melt-fluid and fluid inclusions were observed in fluorite, quartz, calcite, barite and bastnaesite from stage 1 to 4. Based on their petrographic characteristics at room temperature and their characteristics on heating, the inclusions were grouped into three types and eight sub-types. They are described as follows:

1) Melt inclusions (M type); mostly composed of glass, daughter minerals, some with little volatile phase (Fig. 1b).
2) Melt-fluid inclusions (ML type, Fig. 1a). Most ML inclusions are composed of several solid phases (including net-like solid), aqueous phase and a bubble. They are very variable in size and in their liquid/vapour/solid ratios.
3) Fluid inclusions (L type): Five sub-types were distinguished on the basis of phase characteristics at room temperature and during heating.

AC sub-type (Fig. 2a) often occurs in calcite, quartz, barite and bastnaesite and minor in fluorite. These fluid inclusions are composed of aqueous and liquid CO₂, some with vapour CO₂ at room temperature. On heating, they homogenize to aqueous phase (AC-1) or critical phase (AC-2).

AV subtype often occurs in fluorite, quartz and calcite as secondary fluid inclusions as trails along the sewed fractures or in calcite from stage 4. This subtype of fluid inclusions is composed of aqueous and vapour phase, with low vapour/aqueous ratio (<20%). When heated, the fluid inclusions homogenize to aqueous phase.

ADC subtype is composed of one or more daughter minerals, aqueous and liquid CO₂ and is usually accompanied by AC and C fluid inclusions. This kind of fluid inclusions often occurs in barite, bastnaesite, quartz as primary fluid inclusions and minor in fluorite.

ADV subtype is composed of one or more daughter minerals, aqueous and vapour phase. These fluid inclusions are accompanied by AV fluid inclusions, and often occur in quartz, fluorite, bastnaesite, barite as secondary fluid inclusions.

C subtype is composed of liquid CO₂ or liquid and vapour CO₂. This kind of fluid inclusions often occurs in quartz, bastnaesite and barite and is accompanied by AC and ADC fluid inclusions.

The inclusion types vary with the minerals and ore-forming stage in the Maoniuping REE deposit, but the inclusion populations from different ore-forming stages show some regularity. From stage 1 to stage 4, the dominant inclusions vary from melt inclusions (M type) via melt-fluid inclusions (ML type) through high-medium temperature CO₂-rich fluid inclusions (AC, ADC, C type) to low temperature fluid inclusions (AV, ADV).

3.2 Microthermometric results

Melt inclusions: At room temperature, the aqueous phase is mostly absent, but on heating to about 700°C, the glass phase begins to melt and bubbles occur. At about 790-800°C, the melt inclusions homogenize to the melt phase.

Melt-fluid inclusions: Most exploded before homogenization, so, little homogenization temperature (Th) data were obtained. The homogenization temperatures of ML inclusions are 650-850°C in fluorite and 600-750°C in quartz.

Fluid inclusions: Most of AC fluid inclusions homogenized to critical phase and AV inclusions homogenized to aqueous phase. C type homogenized to liquid CO₂. AC subtype has a Th of 217~371°C, and the density of CO₂ was estimated as 0.636~0.982 g/cm³. ADC subtype has a Th of 224~477°C. AV fluid inclusions have the lowest Th of 101~226°C. C type inclusion have a density of CO₂ of 0.829~0.972 g/cm³. According to the density of CO₂ in C fluid inclusions combined with the homogenization temperature of AC and ADC fluid inclusions, the ore-forming pressure was estimated as 150-350Mpa based on the CO₂ system phase.
SEM/EDS and LRM results indicate that most daughter minerals are sulphate minerals. It is proved by LRM that SO$_4^{2-}$ is abundant in the aqueous phase of fluid and melt-fluid inclusions. The fluid is not a simple NaCl-(KCl)-H$_2$O-CO$_2$ system, so the salinity of fluid inclusions cannot be determined by ice melting or the point of CO$_2$ hydrate decomposition. Cooling measurements show that the triple point of pure CO$_2$ inclusions is -56.5$\text{°C}$ -58.5$\text{°C}$, a little lower than that of the pure CO$_2$ system. The coexistence of C, AC and ADC subtype fluid inclusions suggests unmixing of CO$_2$ and aqueous fluid.

### 3.3 LRM analysis of inclusions

In ML inclusions in fluorite and quartz, the aqueous phase is dominated by H$_2$O. The peak at 981-984 cm$^{-1}$ indicates the presence of SO$_4^{2-}$, which is the dominant anion in the aqueous phase. The solid phases are dominated by sulfate minerals including thenardite, gypsum, barite, celestite, etc. Carbonate and bicarbonate minerals were also detected by LRM.

For AC, ADC subtype fluid inclusions, the aqueous phase is also dominated by H$_2$O. The peaks at 981-984 cm$^{-1}$ suggest that SO$_4^{2-}$ is the dominant anion in the aqueous phase. The peak at 1066-1069 cm$^{-1}$ suggests the presence of CO$_3^{2-}$ in the aqueous phase. C subtype fluid inclusions and the bubbles in AC and ADC subtype fluid inclusions are dominated by CO$_2$; the spectrums show a strong peak at 1282 and 1386 cm$^{-1}$. The daughter minerals in fluid inclusions were also dominated by sulphate minerals including gypsum, celestite, barite and Glauber's salt daughter minerals. Nahcolite was also detected.

### 3.4 SEM/EDS analysis of daughter minerals in inclusions

EDS analysis showed that most daughter minerals are sulphate minerals, such as arcanite (K$_2$SO$_4$), aphaltose (NaK$_3$SO$_4$), Glauber's salt (Na$_2$SO$_4$) and gypsum (CaSO$_4$). Calcite was also detected. Sulphate and carbonate daughter minerals were also confirmed by LRM results. The abundance of K, Na-rich sulphate daughter minerals suggests a high K, Na, SO$_4^{2-}$ content in the ore-forming fluid. K- and Na-rich sul-
phate daughter minerals are rare daughter minerals reported before. K- and Na-rich sulphate daughter minerals have been reported by Fulignat et al. (2001) from the Mount Vesuvius carbonatite and by Williams-Jones et al. (2002) from the Amba Dongar carbonatite. Hence, sulphate daughter minerals rich in K and Na might be characteristic of inclusions related to carbonatite.

4 CONCLUSIONS

(1) Mineral association, SEM/EDS results of daughter minerals and LRM results show that the ore-forming fluid has a complex K-Na-Ca-Ba-Sr-REE-SO$_4$-CO$_2$-H$_2$O composition.

(2) The transitional spectrum of melt, melt-fluid and fluid inclusions suggests a continuous evolution from carbonatite magma to hydrothermal fluid, and also suggests a magmatic source and unmixing of carbonatite melt and ore-forming fluid. The evolution of the ore-forming fluid was from carbonatite melt, melt-fluid, high-medium temperature CO$_2$-rich fluid to low temperature aqueous fluid.

(3) The fluid related to REE mineralization is a kind of supercritical CO$_2$-H$_2$O system. REE minerals precipitated in CO$_2$-rich fluid and REE precipitation occurred at 219–362°C and 150-350 MPa. The phase separation of CO$_2$ and aqueous fluid is the dominant mechanism for the REE precipitation.

ACKNOWLEDGMENTS:

This study was supported by the National Nature Science Foundation of China (No. 40573035) and by the State Basic Research Program of China (No.2002-CB-412600).

REFERENCES


Rare earth element distribution in tourmaline and chlorite in tin deposits: Factors controlling REE fractionation in hydrothermal systems

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ABSTRACT: Tourmaline and chlorite from tin deposits of the Russian Far East have been studied by ICP-MS spectrometry to reveal REE distribution patterns and to constrain the parameters of mineralizing fluids in tin-bearing ore systems. The major factors controlling the fractionation of REE between fluid and mineral phases were found to be temperature, pH and Eh and also crystal chemistry peculiarities of minerals. Chemical complexation and sorption processes influence REE partitioning, which are expressed as concave-upward segments in chondrite-normalized patterns of minerals (tetrad effect).

KEYWORDS: rare earth elements, tourmaline, chlorite, tin deposits, Russian Far East

1 INTRODUCTION

Rare earth element (REE) geochemistry has been widely used for modeling of geochemical processes in magmatic, metamorphic and sedimentary petrology. REE are also of a considerable interest for the study of hydrothermal systems. We present here results of a study of REE distribution in tourmaline and chlorite and associated feldspar, biotite, apatite, fluorite and carbonate minerals from tin deposits situated in the Russian Far East (Priamurye and Primorye). Tourmaline and chlorite samples are from tin-bearing associations in granites, pegmatites, greisens, skarns, quartz-feldspar veins, and hydrothermal ores from deposits of the Komsomolsk region of Priamurye, and from several deposits in Primorye. To elucidate the role of crystallochemical factors for REE distribution in the mineral structure, tourmalines of various compositions: elbaite, dravite, Ca-bearing dravite, and shorlite were analyzed.

2 CASE STUDY

2.1. General characterization of deposits

The cassiterite-silicate-sulphide ore-magmatic systems studied are located within the Sikhote- Alin accretionary fold system which evolved from the Cretaceous to the Palaeocene through repeated alternation of settings of suprasubduction (Andean) and transform (Californian) continental margins. Tin deposits are confined to active continental palaeomargins which consist of folded interlayered sandstones, aleurolites, and clay shales intruded by dike bodies. The deposits are associated with multiphase series of granitoides from gabbros to leucocratic granites and are located at a considerable distance from these plutonic bodies. The ore bodies are stockworks, metasomatic mineralized zones and open-space filing veins. Tourmaline and chlorite are abundant. They are associated with cassiterite, quartz, sericite, and sulphide minerals. The cassiterite-tourmaline ores are typical of tin veins of the Komsomolsk ore district (Priamurye), while chlorite is a principal mineral in most commercial tin deposits of Primorye. In these magmatic-hydrothermal tin systems tourmaline and chlorite have a long-lasting history of crystallization. These minerals were found in mineral assemblages in granites, pegmatites, greisens, tin-bearing skarns, quartz-feldspar and cassiterite-quartz veins crystallized under different temperatures during different stages of these magmatic-hydrothermal systems.

3. ANALYTICAL PROCEDURE

30 samples of tourmaline, 40 samples of chlorite, and about 15 associated minerals have
been analyzed by an ICP - mass-spectrometer PQ2 Instruments (England). Feldspar, fluorite, biotite, chlorite were decomposed using a standard procedure. To digest tourmaline a special procedure was used. 50 mg of mineral powder were added to a mixture of H₂SO₄+HF acids in a microwave Milestone using the four-stage program “Turmalin”. The solution after digestion was evaporated to remove HF and H₂SO₄. A dry remnant was twice evaporated by H₂O to remove F-ions. Then 10 ml 26% HNO₃ was filled into measured retorts, an inner standard was added and the measurement of REE abundances was conducted.

3 RESULTS

4.1 REE distribution in tourmaline

Tourmaline composition from diverse mineral assemblages was found to be very variable both in total REE abundance and the chondrite-normalized REEₐ pattern. The total REE abundances in this mineral vary from 267 down to 0.28 ppm. LREE predominate in tourmaline (La/Yb=37.86-3.21) and most REE distribution patterns display a positive Eu anomaly (Fig. 1). Most samples have hump-shaped REE distribution patterns and only a few of them, as a rule, with a low REE content show a flat REEₐ pattern. Tourmalines were formed under various temperature conditions from 700-600°C for granites and pegmatites, 550-500°C for greisens and skarns, and up to 400-250°C for hydrothermal associations, based on thermometric data of fluid inclusions in minerals. This allows to infer that temperature is a major factor controlling REE fractionation between fluid and mineral. The influence of the alkalinity of solutions on total lanthanide concentration in tourmalines is evident because the minerals from quartz-feldspar veins crystallized under alkaline conditions have a higher REE concentration compared to tourmaline from quartz-muscovite greisens formed from an acid fluid. Some REEₐ patterns for tourmaline display the non-coherent (non-CHARAC) (Bau, 1996) REE behavior within tetrads La-Nd, Sm-Gd, Gd-Ho, and Er-Lu. Nd, Sm, Gd, Ho, Er break the smooth shape of the chondrite-normalized spectra.

4.2 REE in chlorite

The lanthanide concentrations in chlorites from various mineral assemblages range from 55 down to 1.73 ppm. All samples are rich in LREE (La/Yb=48.28-1.1). Three main types of REEₐ distribution patterns, two of which are hump-shaped and the third flat, were found. Most REEₐ patterns display Eu anomalies but a few show a positive Eu anomaly that could demonstrate different conditions of REE partitioning between a fluid and minerals. As a rule, chlorites with positive Eu anomalies have high total REE content, and flat patterns are more typical of low REE abundance (Fig. 2). Fluid inclusions studied in associated quartz (Bortnikov et al., 2005) and the chlorite geothermometer (Cathelineau, 1988) show that the crystallization temperature of chlorites ranges from 220°C up to 410°C. The temperature dependence of the total REE content in chlorites seems to be evident, because the high-temperature minerals (370-390°C) from a contact zone of diorite from the deep horizons of some deposits are characterized by a high REE abundance, while those from medium and low-temperature mineral assemblages have a low REE content.

4.3. REE distribution in associated silicates

REE distribution patterns obtained for silicate minerals associated with tourmaline and chlorite demonstrate the role of crystallochemical factors for REE partitioning among minerals. This is clearly seen in Ca-bearing minerals such as apatite, feldspar, fluorite, and carbonate. Thus, apatite, plagioclase, fluorite have a high REE content compared to coexisting biotite and orthoclase. However, in low-temperature Ca-bearing minerals such as carbonate, the Ca-ion does not positively influence the total REE content.

5 DISCUSSION

The comparative analysis of REE distribution in minerals studied demonstrates a clear relationship between REE abundances and temperature, Eh and pH of the mineralizing fluids. The strongest influence on total REE content has the temperature of mineral formation. High-temperature minerals formed at 700-380°C are considerably richer in lanthanides, while REE abundances in minerals of the hydrothermal stage of tin deposits (the crystallization temperature is 360-250°C) is considerably reduced. Redox potential and alkalinity are much important in REE fractionation. Both positive and negative Ce and Eu anomalies are controlled by Eh and pH (Sverjensky, 1984). These anoma
Figure 1. Chondrite-normalized REE<sub>n</sub> patterns for tourmalines from various tin-bearing assemblages.


Figure 2. Chondrite-normalized REE<sub>n</sub> pattern for chlorites from various tin deposits.

1 - quartz-cassiterite-chlorite vein in porphyry dyke, 2 – quartz-cassiterite-chlorite ore, 3 - 4 – cassiterite-quartz vein, 5 – chlorite-cassiterite-sulphide ore, 6-7 - chlorite-sulphide ore, 8 – tourmaline-cassiterite-chlorite association with carbonate (greisen stage), 9 – quartz-chlorite-sulphide vein, 10 – quartz-chlorite veinlet, 11 – quartz-chlorite vein with brown haematite.
lies found in the same minerals from various mineralization stages attest to the evolution of mineral-forming conditions. The positive Eu anomaly indicates the presence of Eu$^{2+}$ in a fluid and is evidence for crystallization of early stage minerals under reducing conditions. The predominance of Eu$^{3+}$ in minerals of late stages implies their deposition from an oxidized fluid. This evolution in fractionation of Eu could be influenced by mixing of magmatic deep fluids with meteoric waters (Bortnikov et al., 2005). Fluid inclusion studies (Bortnikov et al., 2005) and mineral compositions suggest that the REE were transported either as fluoride, chloride or boron complexes, or as a combination of these. A marked LREE enrichment of minerals implies LREE predominance in the co-existing fluid. Cl-bearing LREE complexes are stronger than HREE. Thus, REE are predominantly transported in the fluid as Cl-bearing complexes. The chemical complexation and sorption processes influence the partitioning of REE in aqueous media, which is shown by the lanthanide tetrad effect of minerals as concave-upward segments.

ACKNOWLEDGEMENTS

The work has been financially supported by Department of Earth Sciences of Russian Academy of Sciences (Program of Basic Researches “Superlarge Ore Deposits”).

REFERENCES


Element behaviour during episyenitization of the Kab Amiri granites, Eastern Desert, Egypt

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ABSTRACT: The granites of Kab Amiri underwent multistage hydrothermal processes. Late-magmatic alteration is indicated by low Zr/Hf and the tetrad effect visible in the REE patterns. At least two main stages of intensive post-magmatic hydrothermal alteration were involved. Episyenitization and/or albitization are the main alteration features of the first high-temperature stage. The high porosity resulting from quartz leaching during stage 1 led to percolation of low-temperature fluids at stage 2; the latter is characterized by K-metasomatism (illitization), vug filling by iron oxides and/or calcite. Almost all major and trace elements were enriched or depleted during one of the main alteration stages while Hf can be considered as immobile element during post-magmatic alteration besides Al₂O₃. The episyenite filled with calcite shows an enrichment in HREEs (LREE/HREE= 1.26) and displays a positive Ce anomaly. The recrystallization of REE-bearing minerals under such conditions could explain the development of a negative Ce anomaly in episyenites. Uranium anomalies are known at the surface in these porous rocks and they may represent major host for large hydrothermal uranium mineralization at depth.

KEYWORDS: granites, episyenite, albitization, illitization, uranium

1. INTRODUCTION

During the detailed geological studies of Kab Amiri granites, Eastern Desert of Egypt (ED), several types of alteration were recognized. One of the main alteration features is episyenitization. Special attention has been given to episyenites in the Hercynian granites of Central and Western Europe which act as hosts for U or Sn-W mineralization. Episyenites were also described from other parts of the world in granites of different ages. The elements behaviour during alteration processes including the episyenitization and other alteration types of the Kab Amiri granites will be discussed in this work.

2. GEOLOGICAL SETTING

The Kab Amiri granitic pluton is located in the ED between latitudes 26°17’ - 26°23’ N and longitudes 33°32’- 33°36’ E. A small granitic plug, 1.5 km SE of the main pluton, exhibits well developed episyenitic alteration (Fig.1).

Figure 1: Geologic map of Kap Amiri Episyenite body, central Eastern Desert, Egypt.
Two different phases can be distinguished by the field observations. The first phase is composed of porphyritic biotite coarse-grained granite and the second is equigranular two-mica medium to coarse-grained granite. The granitic plug SE of the main Kab Amiri pluton is a muscovite granite. There are two main perpendicular structural trends, NW-SE and NE-SW, which seems to control most of the tectonic and hydrothermal activities in the area with several reactivations. From the field observation four types of episyenites were recognized:

a) episyenites with free vugs, b) massive episyenites with very limited or no vugs (of limited local occurrence) and higher eTh (Av. 35ppm) and K (Av. 6 wt%) contents. They contain secondary iron oxides, and/or orthoclase & albite, c) episyenites with vugs filled by calcite, dominant in the western part of the main episyenitized zone. The highest radioactive spot, with the highest U/Th ratio is located at the contact between the episyenite with free vugs and calcite-episyenite, d) Specularitic episyenite exposed in the SE part of the main episyenite body, vugs have red-black colour due to iron oxide filling.

3. THE GEOCHEMICAL VARIATION AND MASS BALANCE CALCULATIONS

Kab Amiri granites are categorized as highly differentiated high K-calcalkaline (HKCA) magma (Gaafer, 2000; Abdel-Meguid et al., 2003). The most differentiated granites have high Nb, Th, U, Y and HREE contents, and lower quartz contents (resulting from possible incipient episyenitization). The porphyrytic coarse-grained granites are poorer in Nb, Th, and Y and much richer in Sr, Ba, Rb and LREE compared to the fine-grained phase and seems to represent a different magma. The episyenitized samples have a strongly peraluminous nature together with higher content of Nb, Rb and Th. At least part of this enrichment is related to the volume loss resulting from the leaching of quartz. But the high incompatible element contents of the episyenites correlate better with the geochemistry of the fine-grained granites than with the coarse ones.

Many alteration processes are developed with significant changes in the chemical composition involving most major, trace and rare earth elements which is first marked by a decrease of the Q1 parameter in the Q1-F1 diagram (Cathelineau, 1986) Fig. (2).

SiO₂ contents decrease from more than 75 wt% in most granitic samples down to 46.98 wt% in sample 30. To the opposite, in sample 16 the Q1 parameter increases in relation with greisenization. Samples with albitized feldspars are shifted toward a lower F1 parameter (sample 27: Na₂O = 10.2 wt%, K₂O = 0.67 wt%). While a shift toward higher F1 parameter denotes greisenization (sample 16: K₂O = 5.09 wt% and Na₂O = 0.3 wt%).

In order to avoid volume effects, in episyenitization phenomena, the isocon graphical method of Grant (1986) which is based on work of Gresens (1967) was applied. Al was used as an immobile element to estimate mass transfer and to show the enriched/depleted elements in the altered zones. The major oxides are plotted in weight percent and the trace and REEs are plotted in ppm. The scattered distribution of the elements each side of the isocon indicates that, most major and trace elements were mobilized to a variable extent.

The enrichment/depletion diagram (Fig. 3) for episyenite 6 indicates a volume loss (about 14%) due to quartz leaching (SiO₂ = 66.46 wt %) producing a vuggy granite. W, Y, Zn and REEs contents are depleted. The tetrad effect visible in the REE pattern of this sample has to be related to late-magmatic fluid-rock interaction (Irber, 1999).

In albitized episyenites (Fig. 4), a volume gain of nearly 20% is obtained from the isocon
The isocon diagram of the greisenized episyenites 16 indicates a slight volume loss (~16%). Hf, Sm, Ta, and Y are not mobile during greisenization (Fig. 5). This alteration has led to a strong depletion of Na₂O and weaker depletion of silica, Sn, Ba, Rb, La and Ce. The LREE depletion suggests monazite alteration.

In sample 30, partial to complete filling of the vugs by iron oxides, calcite and other secondary minerals, has led to other geochemical modifications. The isocon diagram (Fig. 6) indicates only a weak volume loss because the vugs left by quartz dissolution are totally filled
by iron oxide (Fe₂O₃ = 28.22 wt%). Fe₂O₃, V, Zn, W and Sn are enriched while REE and other elements are depleted.

4. CONCLUSION

Two main alteration processes can be distinguished in Kab Amiri granites; late-magmatic and post-magmatic hydrothermal alterations. Late magmatic alteration is detected in equigranular two-mica granite of Kab Amiri which shows non-CHARAC behaviour of some trace elements. The Zr/Hf ratio for some samples is well below the CHARAC field (26<Zr/Hf<46) according to Bau (1996) and the REE pattern displays a slight but significant tetrad effect (sample 6 in Fig. 3). Such trace element behaviour is shown also in the Nuweibi highly fractionated granites and attributed to late-magmatic fractionation processes by late magmatic fluids rich in strongly complexing agents such as F (Ali 2003).

Two main stages of post-magmatic hydrothermal alteration have been determined: episyenitization and albitionization. The formation of porous rock (episyenite) allows later hydrothermal/meteoric fluids to percolate and led to the deposition of secondary minerals. During second stage the vugs were occupied by albite or haematite with distinct element mobilities leading to the formation of different types of episyenite.

Most major and trace elements have been mobilized during post-magmatic hydrothermal alteration due to dissolution or replacement of the rock forming and accessory minerals, and crystallization of new mineral phases. The study of selected samples with largely dominant alteration types enabled the evaluation of specific mass transfers associated with each alteration event.

Kab Amiri granite pluton comprises two different magma types. The earliest coarse grained granite is intersected by multiple injections of the latest fine grained two mica granite at the periphery of the main pluton The fine-grained granite is generally associated with uranium anomalies and subjected to severe episyenitization followed by different alteration types. Episyenite bodies also exist within the main pluton beside the largest episyenite body located to the south. These alteration zones represent exploration targets for the discovery of uranium mineralization. The existence of two major tectonic directions crosscutting the area, of ore reservoir represented by episyenites and of uranium anomalies make this area highly favourable for the discovery of U-mineralization.

The realization of bore holes in selected sites are now necessary to detect the presence of uranium mineralized bodies at depth.

REFERENCES


Petrological and geochemical characterization of Ge-bearing coals from the eastern Rhodopes, Bulgaria

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ABSTRACT: The coals from Pchelarovo and Vulce Pole are perhydrogenated coals showing high sulphur content (3.2 - 6.2 wt%) and significant Ga and Ge contents (0 - 480 ppm) in organic matter (OM). The coals from Medenbuk could be perhydrogenated coals modified by weathering processes. They show low sulphur content (1.5 wt%), high homogeneous Ge contents in OM (~2500 ppm) and an unusual enrichment in Ge (up to 0.8 wt%) and V (2.8 wt%) in weathered zones of framboïdal pyrite. Sulphur isotopic study of pyrite and organic sulphur provides evidence of bacterial reduction of dominantly seawater sulphates. However taking account the geological context of the three basins, the introduction of volcanic fluids in the basins of Pchelarovo and Vulce Pole during their formation cannot be excluded.

KEYWORDS: coal geochemistry, germanium, sulphur isotopes, eastern Rhodopes, Bulgaria

1 INTRODUCTION

Coal is the main energy resource in Bulgaria and is the subject of numerous investigations on metal contents on the primary resource and on ashes after combustion in power stations. Coals from Pchelarovo, Vulce Pole and Medenbuk were previously studied for their Ge content (Eskenazy, 1996). Investigations on sulphur content and distribution, and on relationships between organic matter and metals are good indicators of the geological deposition. This abstract presents preliminary petrological and geochemical data of coals from the three coal deposits, in the aim to understand their conditions of deposition.

2 GEOLOGICAL SETTING

The Pchelarovo, Vulce Pole and Medenbuk coal deposits are located in the Eastern Rhodopes, resulting from the continental Macedonian - Rhodope - North-Aegean magmatic arc (Harkovska et al., 1998), formed after the late Cretaceous-Palaeogene collision of the Serbo-Macedonian and Rhodopes Massifs with the Pelagonian microplate. Coal-bearing sediments were deposited within intra–orogenic extensional basins during the final stage of continental collision in the Palaeogene.

2.1 Pchelarovo

The Pchelarovo coal deposit is located about 20km north of Kardzhali. Coal-sediments belong to the Pchelarovo depression quite close to the southeast of the Borovitsa volcanic area. The basement of the basin is composed of immature conglomerates and sandstones, reworking the metamorphic basement (Central Rhodopean dome and metamorphosed Palaeozoic basement). The basin is infilled by Palaeogene sediments composed of pyroclastic and volcanic rocks of Upper Eocene and Oligocene ages. The petrology of the sandstones intercalated with coal layers at Pchelarovo shows a high proportion of devitrified hyaloclastic components in the sediments, indicating that coal deposition is contemporaneous with explosive volcanism whose volcanic centers were close to the northeastern border of the Borovitsa caldera. An intercalated marl-calcareous layer with microfossils indicates a marine transgression. A previous study of advanced argillic alteration (AAA) in Bulgaria has shown that volcanic rocks of the area are strongly hydrothermally altered (Kunov, 1999). Complementary isotopic (S, O, H) data on alunite indicate that AAA is of magmatic-hydrothermal
origin with an important participation of external seawater-derived fluids (Lerouge et al., 2006). Coals occur as 5cm-thick vitrinite layers rich in pyrite (samples 6 to 9), or as thin seams (11-12). The sample 7 is characterized by small perpendicular fractures infilled by pyrite.

2.2 Vulce Pole

The coal samples were collected close to the Vulce Pole village in a tectonic depression 25 km long in east-west direction and 3-4 to 10 km wide, filled by Oligocene sediments. Coals occur as 10 to 50cm-thick seams (samples 29 and 31). The basement of the basin consists essentially of gneisses and amphibolites. Coal-bearing sediments of the basin are dominantly conglomerates and sandstones with intercalated volcanic tuffs and rare limestone at the bottom of the series, and clay layers at the top. The petrology of conglomerates and sandstones indicates immature sediments with a dominant contribution from the reworked basement (gneiss, granite) and an important component of devitrified volcanic clasts, suggesting that coal deposition is contemporaneous with explosive volcanic episode. Matrix of the elements is not abundant; carbonates are absent or rare, nodules of pyrite infill partially the porosity of the series with late circulation of H2S-bearing fluids. The volcanic centre close to the basin is the Madjarovo complex (120 km2) in the south, dated by the 40Ar/39Ar method on biotite and sanidine at around 32-33 Ma (Singer & Marchev, 2002). It induced intense magmatic-hydrothermal activity, marked by minor barren advanced argillic alteration and a well-developed epithermal adularia-sericite alteration associated with a base-metal-Au-Ag mineralization (Singer & Marchev, 2002).

2.3 Medenbuk

The coal sample (58) was collected from an outcrop of Palaeogene sediments, located 20km from Medenbuk. The basement of the basin is dominantly represented by gneisses and amphibolites of Proterozoic age. The coal-bearing sediments are close to the border and the basement of the basin; they are immature sandstones reworking exclusively components from the basement, consisting of gneisses, bioclastic-rich carbonates but also mafic rocks marked by presence of epidote, amphibole and clinopyroxene. The matrix is abundant and represented by micritic carbonates, strongly suggesting deposition under relatively deep marine conditions. The coal was present as small lenses, then partly reworked in a fracture. Nodules of pyrite are observed in sandstones directly above coal lenses.

3 RESULTS

3.1 Coal characterization

HI, OI, Tmax, S1 and S2 were analysed by Rock-Eval® RE6 pyrolysis according to standard methods. Vitrinite reflectance measurements were performed using a Leica DMR XP microscope under reflected light, following ICCP procedures.

![Figure 1: Location of Bulgarian coal samples in Van Krevelen’s HI-OI diagram.](image)

The coals from Pchelarovo are composed of dominantly collotelinite with minor humotelinite and semifusinite, whereas the coals from Vulce Pole and Medenbuk are composed of dominantly humotelinite with some collotelinite.

The vitrinite from the three basins shows high carbon contents (79-86 wt%), consistent with a bituminous high to medium volatile coal rank. However the vitrinite reflectance and Tmax values are low, rather indicating a sub-bituminous rank (Table 1). The coals from Vulce Pole and Pchelarovo are characterized by a bright green-yellow fluorescence and by abnormally high HI values and relatively low OI. These characteristics are typical of perhydrogenated coals (Jimenez et al., 1998).
The sample 9 from Pchelarovo has OI and HI values characteristic of humic coals (Fig. 1). The coal from Medenbuk is very different with a low fluorescence intensity high OI and low HI values. These characteristics may be interpreted by two ways. First, the sample is an immature humic coal. Second, it could be a perhydrogenous coal comparable to that from Vulce Pole and Pchelarovo, which could have been altered through hydrothermal processes or weathering. The presence of secondary gypsum and iron oxy-hydroxides in the coal lenses and the low fluorescence are in favor of the second assumption.

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<th>N° C %</th>
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<th>S2 (mg HC / g rock)</th>
<th>Tmax (°C)</th>
<th>Ro (%)</th>
<th>Mean Ro (%)</th>
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Table 1: Rock-Eval pyrolysis, vitrinite reflectance, and C-S data measured by EPMA with a 10 kV acceleration voltage and a current beam of 20 nA.

3.2 S, Ga, Ge and V distribution

Organic matter from the three coal deposits was analyzed for C, S, Fe and metal contents, using a Camebax SX50 electron microprobe.

S contents are high whereas Fe contents are low, showing that sulphur can be attributed to organic matter. Organic sulphur contents show that Medenbuk (1.5 wt%) is a medium-sulphur coal and Pchelarovo (3.2 – 6.2 wt%) and Vulce Pole (4.3 wt%) are high-sulphur coals. They may be compared with coals overlain by a marine roof in which most of the sulphur is derived from seawater sulphate.

Ge and Ga contents were measured in vitrinite of the three ore deposits, with a 20 kV acceleration voltage and a current beam of 20nA. The ranges of Ga content in the three ore deposits are quite similar: 0-260 ppm at Pchelarovo and Vulce Pole, and 0-330 ppm at Medenbuk. The ranges of Ge content at Vulce Pole and Pchelarovo are similar (0-480 ppm). On the other hand, Ge contents in OM from Medenbuk are high (2418 ± 1033 ppm, n = 12) and associated with significant V contents (0-1100 ppm).

Unusually high Ge and V contents (respectively up to 0.8 and 2.8 wt%) were measured in iron oxides (Fig. 2) resulting of the alteration of primary framboidal pyrites.

![Figure 2: Backscattered electron image of partially oxidized framboidal pyrites showing high Ge and V contents.](image)

3.3 Sulphur isotopes

Sulphur isotope analysis of pyrite, organic matter and secondary gypsum was performed using a CFIRMS system coupled with Flash EA and gas bench. Results are given in Table 2.

<table>
<thead>
<tr>
<th>N° observations</th>
<th>δ³⁴S (% CDT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pchelarovo</td>
<td></td>
</tr>
<tr>
<td>6 vitrinite</td>
<td>+10.0</td>
</tr>
<tr>
<td>7 Secant pyrite in coal</td>
<td>+2.9</td>
</tr>
<tr>
<td>8 Sub// pyrite in coal</td>
<td>+3.5</td>
</tr>
<tr>
<td>9 Sub// pyrite in coal</td>
<td>+4.1</td>
</tr>
<tr>
<td>12 vitrinite</td>
<td>+9.6</td>
</tr>
<tr>
<td>Vulce Pole</td>
<td></td>
</tr>
<tr>
<td>31 vitrinite</td>
<td>+2.2</td>
</tr>
<tr>
<td>34 patches of pyrite in sandstone</td>
<td>+5.6</td>
</tr>
<tr>
<td>36 patches of pyrite in sandstone</td>
<td>+10.2</td>
</tr>
<tr>
<td>38 patches of pyrite in sandstone</td>
<td>+6.5</td>
</tr>
<tr>
<td>Medenbuk</td>
<td></td>
</tr>
<tr>
<td>58 vitrinite</td>
<td>-12.1</td>
</tr>
<tr>
<td>58 Secondary gypsum in coal</td>
<td>-28.5</td>
</tr>
<tr>
<td>59 nodule of pyrite in sandstone</td>
<td>-30.2; -30.5</td>
</tr>
</tbody>
</table>

Table 2: Sulphur isotopic data on organic matter and sulphides from the three coal deposits.

3.3.1 Pchelarovo

Organic sulphur and syn-sedimentary pyrite have a relatively narrow range of δ³⁴S. Independent of the geological context, these values may be interpreted by two ways: 1) bacterial reduction of marine sulphates in a relatively closed system, and 2) input of magmatic-hydrothermal fluids in the basin during its formation. Taking into account the contemporane-
ous volcanic activity of the basin ($\delta^{34}S_{\text{fluid}} \approx 0-3 \%$, Lerouge et al., 2006) and the presence of marine sediments at Pchelarovo, the sulphur origin could be related to both circulation of volcanic-magmatic and seawater-derived fluids during the deposition of the sediments, with the basin evolving as a relatively closed system. The $\delta^{34}S$ of secant sulphides crosscutting the stratification is around $+3 \%$ and is not significantly different from the $\delta^{34}S$ of the syn-sedimentary sulphides, suggesting either a partial remobilization of the syn-sedimentary sulphides, or a persistence of circulation of the same type of fluids during sedimentation and diagenesis.

3.3.2 Vulce pole

The $\delta^{34}S$ of the pyrite infilling the porosity of sandstones varies between $+5.6$ and $+10.2 \%$ (CDT), whereas $\delta^{34}S$ organic matter is close to $+2.2 \%$. Values are heterogeneous and higher than the $\delta^{34}S$ of the magmatic fluids associated with the Madjarovo volcanic activity. The data cannot exclude the participation of magmatic fluids in the basin, but they preferentially indicate bacterial reduction of sulphates present in the fluids of the basin. The positive and heterogeneous values could result from evolution of sulphate-reducing bacteria in isolated micro-environments.

3.3.3 Medenbuk

The $\delta^{34}S$ of syn-sedimentary pyrite in coal can be deduced from the secondary gypsum produced by weathering of pyrite. The $\delta^{34}S$ value of gypsum is $-28.5 \%$, that is quite close to the $\delta^{34}S$ of the pyrite infilling the porosity of sandstone. The $\delta^{34}S$ of vitrinite is slightly higher than $\delta^{34}S$ of pyrite, as usual at Pchelarovo and most of coal deposits. This homogeneity of the $\delta^{34}S$ and the highly negative values are consistent with sedimentary sulphides resulting from the bacterial reduction of marine-derived sulphates in an open system for sulphates, and also in good agreement with petrological features of the studied samples.

4 DISCUSSION

The three coal basins were deposited during the late intra-orogenic extensional phase of the continental collision in the Palaeogene. Coals are rich in sulphur incorporated in organic matter and sulphides, and in metals. Coal from Medenbuk shows particularly high Ge content.

Sulphur isotopes in organic matter and pyrite are used to interpret fluid origins. The $\delta^{34}S$ values of organic sulphur and pyrite range from -30 to $+10 \%$ (CDT), consistent with sulphate bacterial reduction. However the complexity of the isotopic data requires to take into account the geological context. The three coal basins are different:

1) Depositional environment: The Medenbuk and Pchelarovo basins contain marine sediments just above coal seams. A part of sulphur (in organic matter and sulphides) results from the bacterial reduction of seawater-derived sulphates, in an open system at Medenbuk and in a closed system at Pchelarovo.

2) Contemporaneous volcanism: Pchelarovo and Vulce pole are close to volcanic centres, Medenbuk is far from any volcanism. Positive $\delta^{34}S$ values may be partly attributed to volcanic fluids involved in the basin at Pchelarovo and Vulce Pole.

ACKNOWLEDGEMENTS

This work was financially supported by the BRGM research projects and by the ECO-NET program (10161XM) between the BRGM (France), the Geological Institute of Sofia, Bulgarian Academy of Sciences (Bulgaria) and the University of Skopje (Macedonia).

REFERENCES


Singer, B., Marchev, P., 2000. Temporal evolution of arc magmatism and hydrothermal activity, including epithermal gold veins, Borovitsa caldera, Southern Bulgaria; Econ. Geol. 95, 1155–1164.
The occurrence of thallium in the Xiangquan thallium deposit in Anhui Province, East China

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ABSTRACT: Thallium commonly does not form independent ore deposits, and the study of the occurrence of thallium has been largely ignored. This paper presents data on the occurrence of thallium in the first example of a thallium-only epithermal deposit discovered in the northeastern margin of the Yangtze block, eastern China. The geochemistry and electron probe results show that most thallium is hosted by pyrite. In pyrite, some thallium occurs as tiny individual grains in fractures of pyrite and the remainder is in the crystal lattice of pyrite.

KEYWORDS: Xiangquan, thallium, pyrite, China

1 GEOLOGICAL SETTING

The Xiangquan thallium (Tl) deposit is located in the transition zone between the Yangtze Block and the North China Block. Mafic activity is minor in this region and sedimentary rocks predominate. The foreland fold-thrust belt trends northeast and consists of several thrust-detachment systems. The fold-thrust belt is divided into the eastern (Hanchao) and the western (Chouzhou) sub-belt by the Chu River fracture (Chang & Dong, 1996). The deposit occurs in the middle part of the Xiaolongwang Mountain anticline. Only the southwest limb of the anticline outcrops at surface.

The major stratigraphic units in the Xiangquan district are the Lower Ordovician Honghuayuan Group, Lunshan Group and Lower Silurian Gaojiabian Group (Wu, 2000). The host rocks of the orebodies are calcilutite of the Lunshan Group.

The orebodies are concordant with the sedimentary bedding of the country rocks. The thallium metal reserve at Xiangquan deposit is about 250 t (cut-off grade 100 ppm Tl). The gangue minerals include fluorite, quartz, calcite and barite. Hydrothermal alteration includes pyritization, silicification, fluoritization, carbonation, and baritization (Zhou et al., 2005, 2006, Fan et al., 2005).

2 THE ABUNDANCE OF THALLIUM IN ROCKS AND MINERALS

The Tl and other trace element contents of different types of ores, rocks and pyrite in the Xiangquan area are listed in Table 1. The Tl content of the Ordovician Honghuayuan Group and Lunshan Group is 0.596 ppm and 3.097 ppm, respectively. The country rock of the Tl ore body in the Lunshan Group has obviously higher thallium content, 5 times as high as the Honghuayuan Group and 3.7 times as high as the Clarke value of average sedimentary rock (Liu et al., 1984). The secondary silicified rock on surface shows a very slight enrichment of Tl (Table 1).

Tl concentration in ores varies from 213 to 2210 ppm. Pyrite has from 132 to 5667 ppm Tl. Based on the analysis of this work as well as analysis of five drill hole samples by the local geological company (Wu et al, 2000), it is found that the thallium content of the ore is positively related to the pyrite proportion. The Tl content increases from sparsely disseminated ore to densely disseminated ore, laminated ore, and to massive ore (Table 1). There is at least more than 1000 times of Tl enrichment between the ore and the host sedimentary rocks.

The concentrations of most of other elements (except As) in Tl ore are close to the host Lunshan Group sedimentary rock (Fig. 1).
These elements also do not show obvious enrichment in pyrite (Table 2) except As. Fan (2006) reported that the As content in the Tl-pyrite is between 2.64 and 7.52 wt%.

Based on the analytical data, we think that Tl has been enriched economically, and that most thallium is hosted in pyrite.

3 THE OCCURRENCE OF THALLIUM IN PYRITE

Since most of thallium is hosted in pyrite, we focus our study on the occurrence of thallium in pyrite. The pyrite at the Xiangquan deposit is mainly colloform pyrite inferred to be of digenetic origin. Colloform pyrite is all very fine grained (<10µm) and associated with quartz and clay minerals (Fig. 1). Most pyrite grains have thallium content less than 2000ppm and thallium is in the pyrite lattice those pyrite crystals (Fan, et al., 2005). In some pyrite in which thallium content is very high (>2%), we find thallium mineral grains which are generally submicroscopic (<10µm) and occur as individual minerals in the fractures in colloform pyrite. Bright points in Fig 2d. Most thallium minerals have grain size less than 1µm (Fig 2). But the exact composition of these thallium minerals can not yet be determined.

4 CONCLUSIONS

Our major conclusions are as follows:
1. Most thallium in the deposit is hosted in pyrite.
2. In pyrite, thallium occurs as tiny individual grains in fractures of pyrite and the remainder is in the pyrite lattice.

ACKNOWLEDGMENTS

This research is supported by the National Natural Science Foundation of China (Grant No. 40672062 and 40272048), Specialized Research Fund for the Doctoral Program of Higher Education (No. 20050359013) and the Anhui Provincial Excellent Youth Science and Technology Foundation (Grant No. 04045063).
We thank Prof. Chang Yinfo for his input during the study. Special thanks are due to Professor Bernd Lehmann, Institute of Mineralogy and Mineral Resources, Technical University of Clausthal, Germany, for his constructive advice and helpful comments.

REFERENCES


Fig 1 BSM image of pyrite in Xiangquan deposit  
(The zoom of image a, b is 500 and 1500)

Fig 2 Electron probe analysis points on pyrite  
(The zoom of image a, b, c, d are 100, 500, 1500, 3000 separately)
Mineralogic evolution of the Los Santos scheelite skarn deposit (NW Spain)

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ABSTRACT: The Los Santos skarn shows several chemical and mineralogical features common to many other W-bearing calcic mesozonal reduced skarn deposits. Early exoskarn consists of hedenbergite (Hd82-87), grossular (Grs53-73) and Mo-rich scheelite. The mineral assemblage which formed during the cooling of the system is very complex and is constituted mainly by subcalcic garnet, other hydrated silicates (amphibole, phlogopite, prehnite, epidote-clinozoisite, chlorite, white mica and zeolite) and metallic mineralization with Mo-poor scheelite. The aplitic granite is replaced by a calcic plagioclase, clinopyroxene and garnet endoskarn. Stockscheider, breccias, fractures and dikes indicate a forceful emplacement and over pressure associated with volatile exsolution from granite magma. This event probably could be related to the formation of the later skarn.

KEYWORDS: mineral chemistry, scheelite-skarn deposit, Los Santos

1 INTRODUCTION

The Los Santos skarn is the largest tungsten-bearing skarn of the Iberian Peninsula with current total resources of about 2.5 Mt with 0.58%WO₃ (Crespo et al. 2000). This skarn shows features similar to W-bearing calcic mesozonal reduced skarns elsewhere but also has its own characteristics. A chemical, mineralogical and petrographical study has been undertaken in order to characterize the paragenetic associations of the different stages of the Los Santos skarn formation.

2 GEOLOGIC SETTING

The W-bearing Los Santos skarn is located in the Central Iberian Zone of the Variscan Massif. Emplacement of granitoid bodies (granodiorites - monzogranites of the Ávila Batholith) during the late- to post- main Variscan tectonic events (Yenes et al. 1999), caused contact metamorphism of Later Vendian - Lower Cambrian metasedimentary rocks (Fig. 1) accompanied by intense metasomatism and development of the Los Santos skarn. The temperature of thermal metamorphism is estimated at 630-640°C and the pressure between 2.0 and 2.5 kbars (Timón et al. in press).

3 THE LOS SANTOS SCHEELITE SKARN

We distinguish between exoskarn and endoskarn referring to sedimentary and igneous protoliths, respectively. The exoskarn of the Los Santos deposit is irregular in shape and stratabound in the metasedimentary rocks. It is a hedenbergite exoskarn which replaced dolomitic marbles, calcic marbles and hornfelses of the Cambrian sequence. The endoskarn is less pronounced being developed on the aplitic granite and consists of a plagioclase-clinopyroxene-garnet skarn followed by an an-
orthitic plagioclase skarn. This aplite granite is only observed at the mine scale. Scheelite occurs in the calcic exoskarn and in the superimposed retrograde skarn. Magnesian exoskarn is devoid of mineralization as it occurs in similar settings (Costabonne; Guy 1979; Carro del Diablo; Casquet & Tornos 1984).

2.1 Exoskarn

The early exoskarn mineral assemblage consists of clinopyroxene, garnet and scheelite. From chemical analyses, the clinopyroxene can be classified as hedenbergite (Hd 82-87Di4-10Jh6-9), and the garnet as grossular (I) (Gr53-73Adr23-43Prp0-6Sp51.5). Grossular (I) appears as anhedral crystals with a brownish pleochroism and replacing hedenbergite. The scheelite (I) is abundant as fine (100-300 µm) and rounded crystals intergrown with the hedenbergite (Fig. 2a). The analytical data show that this scheelite type is Ce-rich (Ce2O3 ranging from 0.5 to 0.6 wt%) and is zoned, with MoO3-rich cores (0.2 to 0.3 wt% MoO3) and rims with 0.12 wt% MoO3 (Fig. 2b and c). The rim of scheelite (I) has a similar Mo content than that of the later scheelite (II). Allanite, with inclusions of uraninite, is an accessory mineral in the early exoskarn. Its microprobe profiles show a slight compositional zoning with decreasing REE and ThO2 outwards from 13.3 to 10.1 wt% REE, and from 1.23 to 0.85 wt% ThO2.

Later garnet intergrown with vesuvianite appears in millimetric to centimetric discordant veins hosted by the hedenbergite skarn. The chemical composition of garnet (II) ranges from Grs72-83Adr10-21Sp51.5-3.5Alm2-5 to Grs41Adr22Sp57.4-3.5Alm9. It is strongly anisotropic, shows pink pleochroism and an optical zoning under the microscope, which is due to the enrichment in Si, Ca, Fe2+ and Ti from core to rim of the crystals. Most of the garnet is subcalcic, with significant amounts of spessartine and almandine. This subcalcic garnet, according to Newberry (1983), is common in reduced tungsten skarns and is associated with leaching of early disseminated scheelite and redeposition as coarse-grained (up to 2 mm), xenomorphic, vein-controlled, Mo poor scheelite (II) (0.08 wt% MoO3). Garnet (II) also is associated with ferroactinolite (XMg=0.1-0.18), titanianite, apatite, quartz and pyrrhotite, löllingite-arsenopyrite, chalcopyrite, sphalerite, galena, native bismuth, bismuthinite, hedleyite, Bi-Pb-Ag sulphosalts, and electrum (Ag42).

In the succession of the retrograde alteration, clinozoisite, prehnite and chlorite occur. This mineral association shows a strong zonation that first reflects subcalcic garnet alteration to clinozoisite (XCa0.26-0.74; Fe/(Fe+Al)=0.4-2.0), clinozoisite to prehnite and finally to chlorite. Chlorite analyzed corresponds to chamosite and it has a (Fe/Fe+Mg) ratio between 0.76 and 0.9, and a Si content from 2.7 to 2.9. Quartz, calcite and white mica (aluminoceladonite and ferro-alumino-celadonite) are associated to the mineral assemblage described.

2.2 Endoskarn

The metasomatized aplite granite, previously affected by K-feldspatization, is transformed into an endoskarn containing calcic plagioclase-salite-ferrosalite clinopyroxene (Hd41-79Di17.51Jh2.7) ± garnet. Locally, there are aplite granite relics, containing zoned plagioclase (An83.47), K-feldspar, quartz, ilmenite, zircon, biotite and uraninite. Clinopyroxene and garnet are replaced by An85-88 and quartz. Later, this calcic plagioclase evolves to almost pure anorthite (An93.96). Generally, the anorthite formation is so intense that there is neither granite nor prograde endoskarn relics and a massif anorthosite skarn can be formed. The anorthite is pseudomorphed by zoisite (XEp=0.02-0.05). Zoisite is associated with Fe- and Al-rich titanite. Titanite, which forms crystalline aggregates developed from rutile and ilmenite, is associated with chlorite, probably derived from magmatic biotite. Fluorapatite is a common accessory mineral with 3.0 to 5.3 wt% F and 0.01 to 0.2 wt% Cl.

Aluminosilicates of the endoskarn are replaced by clinozoisite (XCa0.26-0.66), clinochlore (with a Fe/Fe+Mg ratio ranging from 0.48 and 0.51) quartz, calcite and aluminoceladonite (with a Fe/Mg+Fe ratio ranging from 0.05 to 0.39). Frequently, K-feldspar and plagioclase show a zeolitic alteration. Zeolites, which appear in cryptocrystalline aggregates and frequently envelop sulphide minerals, belong to the continuous isomorphic series from analcime Na/(Na+Ca)>0.5 to wairakite Na/(Na+Ca)<0.5.

2.3 Amphibole ± phlogopite skarn

Locally, when the metasomatic process affected the heterogeneous granite amphibole- and phlogopite-bearing assemblages with a high proportion of scheelite have been observed. Compositionally, the amphibole corresponds to hornblende whose Mg/(Mg+Fe2+) ratio ranges from 0.52 and 0.7. This magnesian
hornblende is transformed into phlogopite which has an $X_{Fe}$ of between 0.26 and 0.32 and $Al^{VI}$ of between 0.18 and 0.44. Quartz, apatite, titanite, sulphides and scheelite II are associated with hornblende and phlogopite in this type of skarn. The later mineral paragenesis of these zones consists of epidote, calcite, clinohlore and white mica.

3 CONCLUDING REMARKS

According to Newberry (1998) the relationships between plutons and W-skarns are frequently complex and the Los Santos skarn and its spatial and/or petrogenetic relationships with the granitic rocks associated are not an exception. There is an aplitic granite spatially associated with the Los Santos W skarn which is affected by metasomatic alteration (endoskarn described before). There is also a porphyritic biotite granite difficult to assign a genetic role because it not exhibits hydrothermal alteration.

The observations realized inside the Los Santos mine show that there is a stockscheider, defined in the sense of Nesen (1981), and other structures as dike swarms, breccia pipes, shatter breccias and abundant fractures. The endo-granite responsible for the stockscheider could be related to the heterogeneous granitic facies of the mine, with the amphibole ± phlogopite skarn and its ascent could have caused the opening of the system and the retrograde alteration of the skarn. This assumption is supported by fluid inclusion studies realized in magnesian hornblende and quartz from the amphibole ± phlogopite skarn which reveal boiling and immiscibility processes (Timón, unpubl. data).

The heterogeneous granite facies, which shows scheelite-rich metasomatic fronts overprinting the host-rocks (W concentration ~1020 ppm), could be a proof of high-permeability drainage zones wherever the metal-rich residual fluids circulated. The occurrence of zeolites, a typical mineral of geothermal systems, indicates that the hydrothermal fluid circulation probably communicated with the surface as in present-day geothermal systems (Bird et al. 1984).

Some of the mayor scheelite skarns in the world (King Island, Mac Tung, Cantung, Sangdong) are related to unexposed granite cupolas (Newberry 1998). An isotopic study realized in the Los Santos skarn by Tornos et al. (2001) suggests that part of the fluids probably derive from a deep but unexposed leucogranite.

ACKNOWLEDGEMENTS

This work was supported by the Comunidad Autónoma de Castilla y León (Research Project Ref. SA015A06)
REFERENCES


ABSTRACT: A detailed study of the rare earth element (REE) distribution patterns of the phosphates deposit of the Oshosun Formation within Dahomey Basin was carried out. The result of the study, which was based on the sum of the Light REE and the Heavy REE, indicate a higher value for the Light REE. Furthermore, the establishment of an index of La/Yb (chondrite normalized) fractionation, as well a Cerium deficit (Ce/Ce*) makes it possible to differentiate the lateral and vertical variation of the phosphate within the study area, which indicate similar palaeoenvironment. It was however established that the effects of weathering and diagenesis are minor compared with provenance, as provenance is the most important factor contributing to the REE content in the Tertiary Oshosun Formation.

KEYWORDS: Phosphate, Oshosun Formation, Rare Earth Element, Provenance, Tertiary

1 INTRODUCTION

In Nigeria, Phosphate hosted rocks are found in Dahomey Basin, part of Niger Delta and Sokoto Basin. Oshosun Formation is an important lithostratigraphic unit in the Dahomey Basin where significant phosphate has been reported (Fig 1). The phosphate deposit was first noticed in 1920’s during the construction of railway line that cut through Oshosun village, Southwestern Nigeria (Russ, 1924). The formation gently overlies the Ewekoro Formation with the maximum thickness of about 130m (Reyment, 1965).

The phosphatic beds in Oshosun Formation occur as nodules and are interbedded within the shales and the calcareous clays of the formation. The formation is composed predominantly of pale to grayish laminated shale (Adegoke et al., 1991).

This study is aimed at getting a clearer picture of the REE distribution in phosphates of Oshosun Formation, as REE are known to be more resistant to fractionation through weathering as well as diagenesis and metamorphism, when compared with other trace elements (Nance & Taylor, 1974).

2 GEOLOGICAL SETTING, LITHOSTRATIGRAPHY AND ANALYTICAL TECHNIQUES

2.1 Geological Setting

The Dahomey Basin is one of the several sedimentary basins on the continental margin of the Gulf of Guinea, extending from southeastern Ghana in the West to the Western flank of the Niger Delta. The area of study fall within the Eastern sector (Nigeria part) of the Basin (Fig 1). The basin was formed as a result of the
opening of the South Atlantic, during the Neo-comanian (Omatsola & Adegoke, 1980). Furthermore, deposition within the basin was initiated in fault-controlled depression on the basement complex (horst and grabens) during the Neoconian.

2.2 Lithostratigraphy

The main lithologic profiles of the phosphatised series identified in the Oshosun Formation are light grey shale and clay (Fig 2). The black shale identified in Oshosun probably belongs to the Imo Shale member because they are highly fissile and well laminated. The grey shale in the study area is moderately laminated with some phosphate nodules while the clay unit is light grey in color, soft and finely laminated.

2.3 Sampling and Analytical Techniques

The work was carried out within two different locations. Oshosun, longitude 3° 14’E latitude 6° 49’N, and Ebiti with longitude 3° 14’E, latitude 6° 48’. Three pits were dug and samples collected at approximately 0.3m interval. Five samples representative of all the lithology present in a pit were collected from each pit, thus, a total of 15 samples were collected. From this samples, REE were determined using the flux –fusion (FUS-ICP)-Atomic Emission Spectrometry (AES) and Mass Spectrometry (MS). The analysis was carried out at Activation Laboratory Ontario, Canada. The whole rock geochemical data generated was interpreted and used for the purpose of this study.

3 RESULTS

REE are effective indicators of depositional environment (Graf 1977, Lottermoser, 1989, Steiner et al., 2001). Understanding the REE geochemistry of and concentration process in a particular formation is usually a complex task. Furthermore, the degree of REE enrichment in a formation is a function of the concentration of REE in the host environment. The distribution pattern of Chondrite-normalised REE for Oshosun in Fig 3a, shows that the sum of LREE content is far higher than the HREE content. The $La_N/Yb_N$ ratio, which is used to determine the fractionation of REE in Oshosun ranges between 6.7-9.9. The Cerium deficit ($Ce/Ce^*$) is described by the distribution patterns of the REE, with an average value of 0.6. This is an indication that the negative Cerium anomaly observed with the distribution pattern is more attenuated. Furthermore, the REE patterns of the sample also show a gradual depletion with depth ranging from La to Lu. Results from Ebiti shows a similar trend in distribution patterns as that of Oshosun but has a higher value for LREE and HREE compared to Oshosun (Fig 3b). Another distinctive feature of Ebiti is the increasing value of REE with depth i.e. R10>R9>R8>R7>R6. This indicates that diagenesis has little effect or influence on the
The average value for the Cerium deficit in Ebiti almost equals that of Oshosun. The \( \text{La}_{\text{N}}/\text{Yb}_{\text{N}} \) ratio ranges between 6.9 to 11.3.

Generally, REE distribution from the study pits shows remarkable semblance, though with varying concentrations. This is attributable to effective mechanical mixing taking place in the sedimentary environment. The Cerium deficit values (0.5-0.7) for the study pits are an indication of a reducing environment. Generally and independently of location, the REE distribution pattern of the phosphate nodules from the three pits show a LREE content far higher than HREE and the \( \text{La}_{\text{N}}/\text{Yb}_{\text{N}} \) ratio is between 2.9 to 6.8. Also, the \( \text{Ce}/\text{Ce}^* \) deficit values of 0.5-0.6 indicate a reducing environment.

### 4 CONCLUSION

The lateral and vertical similarities in the REE distributions and concentrations patterns of the Tertiary Oshosun (Pits1-3) sediments is indicative of a close relationship between palaeogeography as well as palaeo-environment. Furthermore, the single most important factor contributing to the REE content in the study area is the Provenance (Fleet, 1984; McLennan, 1985). Thus during transportation and distribution, REE are chiefly transported as particulate matter carrying with it the chemistry of the source. The \( \text{Ce}/\text{Ce}^* \) values established a reducing environment for the sediments. The \( \text{La}_{\text{N}}/\text{Yb}_{\text{N}} \) fractionations show a general lateral variation from Oshosun to Ebiti. Thus the environment of deposition can best be described as a transgressive and regressive shelf and shore zone.

### 5 REFERENCES


Fig 3. REE patterns for the Oshosum Formation.

Fig 4. REE patterns for the phosphate nodules from the three pits used for this study.

MINERALIZATION ASSOCIATED WITH BASIC & ULTRABASIC ROCKS

EDITED BY:
Variation in PGE tenor in sulphides of the Merensky Reef: Implications for the Genesis of the Reef

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The University of the Witwatersrand

Gordon Chunnett
Anglo Platinum, Johannesburg

Judith Kinnaird
The University of the Witwatersrand

ABSTRACT: The variations in PGE tenor have been studied over 42 profiles through the Merensky Reef in the Northwestern, Southwestern, and Eastern lobes of the Bushveld complex. The data indicate that sulphides segregated in situ from at least 2 separate influxes of magma, and that the later influxes thermally eroded, either partially or completely, cumulates deposited from earlier influxes.

KEYWORDS: PGE, Platinum, Palladium, fractional sulphide segregation, Bushveld Igneous Complex, Merensky Reef

1. INTRODUCTION

The Bushveld Complex is the largest known mafic igneous, extending as a series of lobes for 430km east-west and 250km north-south, with an average thickness of 8km. The Platinum-group Elements (PGE) occur in 3 principal geological units, the Merensky Reef (32% of total proven and indicated reserves), the UG-2 chromitite (58%) and the Platreef (9%) (Anglo Platinum, Impala and Lonmin annual reports, 2004). In both the Merensky Reef and Platreef, the PGE are closely associated with sulphides that are thought to be of primary magmatic origin and to have scavenged the PGE from the magma with which they are associated. This study is concerned with the PGE tenor (PGE concentration in 100% sulphides) of the sulphides of the Merensky Reef, how this varies both vertically and laterally, and the implication that this has on the genesis of the Reef. The Merensky Reef is present at approximately the same stratigraphic level in both Western and Eastern lobes of the Complex (approximately 2 km above the base), but shows significant variation within itself and in terms of how it relates to the underlying strata on both a local (1-2km) and regional (100-300km) scale. In order to obtain a comprehensive overview of how variations in tenor occur both locally and regionally over the Reef, 42 separate drill intersections have been sampled at either 10 or 20 cm intervals from well below known mineralization through the Reef to 2-3m into the overlying pyroxenite. Because 10 or 20cm sampling was too coarse an interval to document variations in thinner types of Reef (<50cm), underground samples covering the whole of the Reef were collected from 5 locations and sampled at 2cm intervals. This study also includes documentation of 24 intersections through the UG-2, and 820 samples documenting 4 profiles through the Platreef, amounting to a total of 2500 samples. The UG-2 and Platreef data are not discussed here.

2. VARIABILITY OF THE MERENSKY REEF

Cawthorn (2004) has noted that the Merensky Reef is composite, and was likely the result of several pulses of magma. This is illustrated in a simplistic manner in Figure 1. Starting at the SE end of the south-western part of the western lobe of the Bushveld in the Lonmin Eastern Platinum mine, one finds that two pyroxenite units occur at the level of the Merensky Reef. These comprise a lower unit (referred to as the Pre-Merensky cyclic unit), 10m thick, with intermittent chromite, and a weak peak in PGE values at the base, overlain by the Merensky cyclic unit. The contact is marked by a thin, intermittent seam of chromite and patches of pegmatitic pyroxenite below this level. The
principal PGE values are associated with visible interstitial sulphides that occur both in the basal 60-100cm of the Merensky cyclic unit and in the upper 60-100cm of the underlying Pre-Merensky unit. Farther west, near the western limit of the Lonmin Western Platinum mine, the Pre-Merensky cyclic unit, the Pre-Merensky cyclic unit has narrowed to 1-4m. Mineralization occurs primarily in the lower 100cm of the Merensky unit and the upper 20-40cm of the Pre-Merensky unit. Still farther west, in the shafts operated by Anglo Platinum, the reef is variable, ranging from 60cm downward in thickness (Thick, Normal and Thin Reef facies). As shown in Figure 1, in some areas the Reef comprises a single chromite seam at the contact overlain by pyroxenite (Contact Reef). In others the Reef undulates with a wavelength of 1 to several meters, and alternates between Thin Reef and Contact Reef facies. These variations are thought to be due to the variable erosion of the Pre-Merensky cyclic unit by the influx of magma that gave rise to the Merensky unit.

2. VARIATIONS IN PGE TENOR AND IMPLICATIONS TO THE GENESIS OF THE MERENSKY REEF

The PGE are highly chalcophile elements and, once a discrete sulphide phase (normally liquid sulphide) develops in a magma, partition into the sulphide, leaving the magma depleted. Despite the high sulphide liquid-silicate magma PGE partition coefficients, subsequent sulphides segregating from the same magma reflect the PGE depleted nature of the magma. The decrease in the PGE content of successively segregating sulphides is exponential. Three possible hypothetical examples of this effect are illustrated in Figure 2.

Figure 2A illustrates the variation in Pt ($D_{sul/sil/magma}$ assumed to be $10^4$) assuming that sulphides segregate and accumulate at the base of cumulates resulting from crystallization of a fresh, sulphide-saturated batch of magma. Figure 2B shows the same effect, but assumes that the magma is carrying a basal load of pre-segregated sulphide. Figure 2C is the same as Figure 2B, but illustrates the effect of a second, fresh influx of magma following the first.

The results of some of the profiles obtained in this study are illustrated in Figure 3A-C. The hatched area indicates the amount of sulphide that would be expected in an igneous cumulate with 10-40% interstitial magma, if this magma were just sulphide saturated. Thus sulphide contents to the right of this area would indicate cumulus sulphide liquid, and those within it would be unlikely to represent samples containing cumulus sulphide. Figure 3A shows variations in Normal Reef from the Rustenburg area. The two chromite seams are 10cm apart, so that an underground sample equivalent to that sampled from core at 20cm intervals was sampled at 2cm intervals to provide greater detail. An upper maximum in PGE tenor occurs at the Upper Chromite seam, while a second maximum is present 4 cm below the lower chromite. The upper maximum shows a marked exponential upward decay. Figure 3B shows Contact Reef, in which only one chromite seam is present. The maximum tenor occurs in the 20cm sample containing the chromite, and there is an
exponential upward decay throughout the overlying 1 m of pyroxenite. The sulphide tenors in the Eastern Platinum Reef also show an exponential upward decay. There is no indication of a “bottom load” of sulphide with a constant tenor as illustrated in Figure 2B in any of the profiles.

In the case of the Rustenburg Normal Reef (Fig. 3A), significant sulphide occurs below the lower chromite seam (which is thought to represent the base of the Pre-Merensky pyroxenite) – these sulphides are interpreted as having soaked down into the underlying anorthosite after having segregated from the magma responsible for the Pre-Merensky cyclic unit. The pegmatitic pyroxenite between the two chromite seams is believed to be all that is left of the Pre-Merensky unit, most of which was thermally eroded by the subsequent influx of magma responsible for the Merensky unit. The upper chromite seam marks the base of the Merensky unit. The exponential decay in PGE tenor in the sulphides within and above this chromite seam is interpreted as the result of fractional segregation from this magma.

In the case of Rustenburg Contact Reef (Fig. 3B) all traces of the Pre-Merensky cyclic unit have been eroded away, no sulphides have penetrated the underlying anorthosite, and the picture is that to be expected as a result of fractional segregation of sulphide from Merensky magma.

In the case of profile TN72 (Fig. 3C) from Eastern Platinum Mine, the vestiges of the chromite seam noted in the figure mark the contact between the Pre-Merensky and Merensky Cyclic Units. The sulphides occur in the basal 60 cm to 1 m of the Merensky pyroxenite but extend as much as 1 m into the top of the Pre-Merensky pyroxenite. Our interpretation is that the upper part of the Pre-Merensky pyroxenite was still hot when the Merensky magma was intruded, and that the dense sulphides from this magma sank into the underlying unit to occupy intercumulus space. Nevertheless, the upward exponential decay in PGE tenor is still preserved.

Two further aspects require comment. The first is that in Figures 3 B and C, and in many other of our profiles, there is an increase in PGE tenor in sulphides occurring 50cm to 2m above the base of the Reef. This is thought to be the result of a gentle influx of fresh magma, that mixed with the existing magma, refreshing it in PGE. The second aspect is that in many of our profiles, including those shown in Figures 3 B and C, there is an increase in PGE tenor in rocks that underlie zones containing cumulus sulphide. The reason for this is not fully understood, but may be due to PGE-enriched magma seeping into the chamber before the event that triggered sulphide saturation. Overall, the profiles support the concept of the emplacement of magma that then achieved sulphide-saturation in situ.

3. ACKNOWLEDGEMENTS

We are grateful to Anglo Platinum for supporting the research expenses of this project and for permission to present this talk.
Figure 3: Examples of the variation in Pt and Pd tenor and wt% sulphide in profiles through (A) Normal Reef, (B) Contact Reef and (C) Reef where the underlying Pre-Merensky Pyroxenite (see text) is 10m thick.
The Ni-Cu-PGE bearing Platreef in the northern limb of the Bushveld Complex

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ABSTRACT: The Platreef in the northern limb of the Bushveld Complex, is the third largest PGE resource on Earth. It is predominantly a pyroxenitic PGE-Cu-Ni-bearing package, between the Transvaal metasedimentary footwall and the Main Zone hangingwall, which is believed to have been emplaced as a series of sills. The Platreef has been equated with the Merensky Reef but it differs from the Merensky Reef as it occurs at the base of the magmatic succession rather than within a layered sequence 2 km from the floor, it is much thicker, has greater petrological variability, has more Cu and Ni sulphides than the Merensky and UG-2 layers, a lower overall PGE grade and Pt/Pd ratios.

KEYWORDS: Bushveld Complex, Platreef, Ni-Cu-PGE mineralization

1. THE PLATREEF

The Platreef is regarded as the dominantly pyroxenitic PGE-Cu-Ni-bearing layer, between the Transvaal metasedimentary footwall and the Main Zone hangingwall in the northern limb of the Bushveld Complex. The northern sector has an Archaean granite footwall, the central sector has a footwall of Malmani dolomite whilst the southern sector is has a lithologically variable floor of Duitschland formation shales and dolomites and Timeball Hill quartzites (Figure 1). The Platreef comprises a wide range of basic and ultrabasic facies which range from dunite to anorthosite with feldspathic pyroxenite the predominant lithology. It is variable in thickness along strike reaching >400m in basins in the southern sector to < 50m in the north (Figure 2).

2. GEOCHEMISTRY

Geochemical data from the southern sector suggest that the Platreef is a complex intrusive body comprising three or four feldspathic pyroxenite sills each with a distinctive chemistry. Each package is characterised by difference in Mg#, SiO$_2$/Al$_2$O$_3$ and CaO/Al$_2$O$_3$ ratios, trace element abundances and Pt:Pd and Ni:Cu ratios. Compositional breaks in major

Figure 1 The northern limb of the Bushveld Complex showing the location of the Platreef (after van der Merwe, 1978)
and trace element chemistry between the different pyroxenite packages are supported by changes in mineral chemistry. The more primitive feldspathic pyroxenite with the highest Cr content and Mg# occurs towards the top of the succession whereas pyroxenites lower in the succession show varying degrees of interaction with floor rocks and hornfels xenoliths resulting in inhomogeneous textures, variability in composition even on a metre scale, increased incompatible elements and migration of sulphur from shale to magma.

3. MINERALIZATION

Good PGE grades and massive sulphides occur at the base of individual pyroxenite packages or in serpentinites. In the mineralized zones, sulphides may reach <30 modal % in some intersections. These are dominated by pyrrhotite, with lesser pentlandite and chalcopyrite, minor pyrite and traces of a wide compositional range of sulphides. In the southern sector, mineralized zones have Cu grades of 0.1-0.25% and Ni 0.15-0.36%. Massive sulphides are localized, commonly, but not exclusively towards the contact with footwall metasedimentary rocks. Magmatic sulphides are disseminated or net-textured ranging from a few microns to 2 cm grains of pyrrhotite and pentlandite with chalcopyrite and minor pyrite. Much of the sulphide is associated with intergranular plagioclase, or quartz-feldspar symplectites, along the margins of rounded cumulus orthopyroxenes. The PGE’s occur as tellurides, bismuthides, arsenides, antimonides, bismuthoantimonides and complex bismuthotellurides. PGM are rarely included in the sulphides but occur as micron-sized satellite grains around interstitial sulphides and within alteration assemblages in serpentinitized zones. The Pt:Pd ratio differs through the Platreef with a higher Pd:Pt ratio at the base and a higher Pt:Pd ratio generally at the top to give an overall 1:1 ratio for the Platreef as a whole. PGE grade may be decoupled from S and base metal abundance. Hydrothermal remobilization has modified the original distribution and mineral chemistry.

4. SULPHUR ISOTOPE DATA

Clearly the Platreef is highly enriched in sulphur compared with other PGE-rich layers like the Merensky Reef or the UG2 chromitite. The entire length of the Platreef has been contaminated by crustal sulphur to some degree (Sharman-Harris, 2006). Contamination was probably from volatile-rich fluids released from metasedimentary crustal xenoliths and floor or roof during metamorphism. It is unlikely that
the sulphur was incorporated by whole rock assimilation of xenolithic metasedimentary material as there is no geochemical evidence for major and trace element contamination close to xenoliths (Kinnaird, 2005).

In the southern sector, heavy signatures (δ³⁴S +4 to +7‰) which indicate country rock contamination from pyrite-bearing Duitschland shales closest to the footwall or to metasedimentary xenoliths, with lighter values (δ³⁴S +2‰), closest to that expected for pure magmatic sulphur, near the top. In contrast, for the northern sector of the Platreef, where sulphur isotope data also indicates that there has been a contribution of sulphur from an external source, the sulphide mineralization occurs in the top half of the Platreef associated with the occurrence of altered sulphur-bearing Malmani dolomite rafts that collapsed from the roof into the magma during the emplacement of the Platreef. The main sulphide concentrations are associated with these xenoliths with low concentrations close to the base where the footwall is sulphur-poor granites. In the central sector, sulphur has most likely come from sulphur-rich dolomites and evaporites from the Malmani dolomites. Oxygen isotope studies also support the presence of local crustal contamination in the system. Elevated δ¹⁸O values (+6 to +9‰ for plagioclase, and +6.5 to +8.5‰ for pyroxene) in cores with a footwall of Duitschland Formation indicate a crustal oxygen component within the Platreef package.

5. CORRELATION OF THE PLATREEF WITH THE EASTERN AND WESTERN LIMBS OF THE BUSHVELD

The Platreef has been equated with the Merensky Reef (e.g. White, 1994) but it differs from the Merensky Reef in that it occurs at the base of the Bushveld succession rather than within a layered sequence 2km from the floor, it is much thicker (<400m compared with 1m), has greater petrological variability (dunite to anorthosite in the southern sector) has more Cu and Ni sulphides than the Merensky Reef and UG-2 chromitite, a lower overall PGE grade in the mineralized zone which is typically 4g/t where footwall is dolomite, but commonly 1-2 g/t elsewhere compared with grades of 4-6g/t over 1m for the Merensky Reef and UG2. Pt/Pd ratios also vary; for the Merensky Reef and UG2 south of the Steelpoort Fault the ratio is typically around 2, whereas for the Platreef quoted Pt/Pd ratios vary through the Platreef.

The Platreef has distinct affinities to the upper Critical Zone of the eastern and western limbs of the Bushveld with the uppermost package having the closest similarities to the Merensky Reef in terms of whole rock Mg#, chromite compositions, pyroxene chemistry, and Pt:Pd ratio of 2. However, the whole Platreef package cannot be directly correlated with the Merensky Reef, only the uppermost unit.

South of the Planknek Fault, part of a major lineament system, the Thabazimbi-Murchison Lineament (TML) which has been active since the Archaean, the stratigraphic succession in the northern limb, is much more readily correlated with the succession of the eastern and western Bushveld limbs rather than with the Platreef sequence to the north. However the Main Zone which was intruded post Platreef-post Critical Zone is recognizable on both sides of the TML although it is thinner in the northern limb than in the Bushveld as a whole. As it intruded, it incorporated at the base enclaves of Platreef pyroxenite and metasedimentary xenoliths of country rock that originally formed the roof to the Platreef. This has resulted in a laterally persistent ‘disturbed’ and contaminated Main Zone.

6. CONCLUSIONS

It is envisaged that the Platreef was intruded as a series of sills into the Transvaal metasedimentary sequence. As further pulses followed, some metasedimentary material was detached from the floor and later magma flowed under or over these layers. Some of the later pulses also interfingered with the early Platreef pulses. These intrusive pulses are suggested to be equivalent to the upper Critical Zone elsewhere in the Bushveld Complex, although the well-developed chromitite layering of the Critical Zone does not occur. Later Main Zone norites/gabbronorites also intruded the Platreef pyroxenitic packages as sills, sometimes incorporating metasedimentary rocks from the top of the Platreef. The unit between the Main Zone gabbronorites is thus a complex zone of interfingered lithologies, including some Main Zone. This whole package is collectively called the Platreef. A crustal contribution of sulphur has been important to the formation of Cu-Ni sulphides.
ACKNOWLEDGEMENTS

We would like to thank Anglo Platinum, Platreef Resources (Ivanhoe Mines) and CCIC for financial support for this research. We thank all members of the research team especially Johan Kruger, Tony Naldrett, Dave Hutchinson, Victor Mothetha, Nesbert Nyama and Libby Sharman Harris. We would also like to thank the NRF/THRIP for matching funding for this project. In addition we would like to acknowledge the interest and support from a variety of people including Chris Lee, Gordon Chunnett, Grant Cawthorn, Barry Jones, Marc Prefontaine, Gernot Wober, Albie Brits, Mark Whitehead, Jeff White, Terry Holohan, Dave Holwell, Iain McDonald, Boz Wing, Sarah Penniston Dorland, Keith Roberts and Ludmila Zhitova.

REFERENCES


White, J. A. 1994. The Potgietersrus Prospect - Geology and Exploration History. XVth CMMI Congress, South Africa, SAIMM and GSSA.
Microtomographical, Microstructural and Geochemical Analysis of the Merensky Reef (Bushveld Complex, South Africa): Implication on the Formation of the Reef

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**ABSTRACT:** The 3-D distribution of the base-metal sulphides (BMS), the analysis of platinum-group elements and base metals (in both BMS and the whole rock) and the study of platinum-group minerals in the Merensky Reef of the Bushveld Complex allow us: (i) to establish the phases concentrating the PGE, (ii) to evaluate the role of the sulphide liquid on the PGE collection and (iii) to evaluate the processes which may have triggered the formation of the Merensky Reef. In the silicate rocks, the PGE were only collected by an immiscible sulphide liquid which percolated downward in the silicate rocks. In the chromitite layers, the collection of the PGE may have happened in two steps: some PGM crystallised from the magma during the chromite crystallization and before the sulphide saturation; subsequently an immiscible sulphide liquid formed and collected the remaining PGE. The liquid then percolated downward through the cumulate pile until was arrested at a relatively impermeable chromitite layer.

**KEYWORDS:** platinum-group elements, sulphide, platinum-group mineral, laser ablation ICP-MS

1 INTRODUCTION

Large mafic and ultramafic layered intrusions such as the Bushveld Complex (South Africa) may contain layers enriched in platinum-group elements (PGE) and Au, referred to as “reefs”. The Merensky Reef of the Bushveld Complex is the second largest PGE resource in the world (Cawthorn, 1999). Several processes have been proposed to explain the enrichment of the PGE and other metals in these layered intrusions: (i) the direct crystallisation of PGE from the magma as platinum-group minerals (PGM) (Hiemstra, 1979); (ii) the collection of the PGE by an immiscible sulphide liquid which interact with a large volume of silicate magma (Campbell & Naldrett, 1979; Naldrett et al., 1986); (iii) remobilization of the PGE by upward migrating magmatic fluids enriched in Cl (Boudreau & Mc Callum, 1992; Willmore et al., 2000), (iv) the collection of PGE by chromite (Capobianco & Drake, 1990; Capobianco et al., 1994).

In many reefs the PGE in reefs are found associated with base metal sulphides (BMS) and/or as PGM. The aim of the present study was to better understand the role of the sulphide liquid in PGE reef formation. First, we have investigated the physical processes which can trigger or explain the distribution of BMS in the reef. The distribution and quantification of the BMS in a slab of Merensky Reef was determined in 3-D using X-ray Computed Tomography (X-ray CT-scan). The relationship between the BMS distribution and the microstructures was studied by examining oriented polished thin sections cut from the samples (Godel et al., 2006). Secondly, we have also investigated the geochemical processes which may have occurred during the formation of the cumulate pile (Godel et al., *Submitted to Journal of Petrology*). We have attempted to establish which minerals host the PGE in the reefs. First, we have determined the concentration of PGE, Re, Ag, Au, Cd, Ni, Cu and Co in the BMS by laser ablation ICP-MS and the whole rocks within the different lithologies of the Merensky Reef. Then a detailed image analysis of the platinum-group mineral distribution was carried out. These data allow the calculation of a PGE mass balance in the reef. The details of all the methodologies are given in Godel et al. (2006) and Godel et al. (*Submitted to Journal of Petrology*).
Integration of the results (both physical and geochemical) allows us to evaluate the implication of each of the above processes to propose a possible model for the formation of the Merensky Reef.

2 GEOLOGY AND PETROGRAPHY

The Merensky Reef is found in the Upper Critical Zone of the Bushveld Complex. The reef is a stratiform layer containing 5-10 ppm of PGE (Barnes & Maier, 2002; Cawthorn, 2002). The studied sample consists of a slab of normal Merensky Reef from Frank Shaft, Rustenburg Platinum Mine (western lobe of the Bushveld Complex).

The sample is composed, from bottom to top, of: (i) a basal anorthosite; (ii) an ~1 cm of chromitite which undulates on a centimetre scales; (iii) a coarse-grained melanorite of ~10 cm thickness; (iv) a second layer of chromitite of ~1 cm thickness (v) a melanorite. All lithologies contain visible BMS (pentlandite, pyrrhotite and chalcopyrite). These BMS are described and studied in details below.

3 RESULTS

3.1 Migration of sulphide liquid

The 3-D images show that the BMS are present in both the chromitite layers and the melanorites, but are rare in the underlying anorthosite. These results are confirmed by the petrographic observations. In the melanorite, up to 5.5 % BMS are distributed along palaeovertical networks. These networks terminated in the underlying chromitite and the BMS more abundant just above the chromitite layers.

The microstructural analysis has shown that all lithologies exhibit high temperature crystal deformation features (indented contacts of orthopyroxene, deformation twins in plagioclases, undulose extinctions, sub-grain development). BMS are located along pyroxene grains boundaries and form a vertical network along faces of the crystals. All the deformation features are consistent with a palaeovertical maximum principal compressive stress (σ1) that is responsible for compaction during cumulate pile formation. During the compaction vertical dilatencies along silicate grain boundaries may have formed and may have been filled by sulphides.

Dihedral angle measurements in the Merensky Reef sample indicate (Godel et al., 2006) that the sulphide liquid showed variable physical behaviour depending on the nature of the host rock. In the melanorite, the sulphide liquid may have been interconnected (angle <60°) and could have percolated downward in the cumulate pile. In contrast in the chromitite where the BMS occur as droplets, sulphide melt connectivity is negligible and percolation of the sulphide liquid was limited. Thus, the chromitite may have impeded percolation of sulphide liquid.

3.2 Geochemistry

The BMS consists on average of ~44 wt% of pentlandite, ~37 wt% of pyrrhotite and ~19 wt% of chalcopyrite. The chromitite layers and the immediately underlying silicate rocks are richer in chalcopyrite (25-30 wt%) than the silicate rocks overlying them (9-14 wt%). Furthermore, the chromitite layers are enriched in PGE relative to the silicate rocks by a factor of more than 5. In the BMS, the PGE content varies slightly as a function of the stratigraphy. The BSM in the chromitite contain twice as much PGE than those of the silicate rocks. Thus, although some of the strong enrichment in PGE of the chromitite can be partially explained by a PGE enrichment of the BMS, some other PGE phases must be present.

The mass balance calculation shows that in all lithologies, most of the PGE (~65% to 85%) are hosted by PGM (essentially Pt-Fe alloy, Pt-Pd sulphide and Pt-Pd bismuthotelluride). These PGM are in many cases associated with BMS (included in or located at the contact between the BMS and the silicates). The remaining PGE are found in solid-solution within the BMS. Pentlandite is the principal host of the PGE (containing up to 600 ppm), particularly Pd and Rh. Pentlandite and pyrrhotite preferentially host Pd, Rh, Os, Ir, Ru and Co. Silver and Cd content is highest in the chalcopyrite. In contrast, Pt and Au do not partition into the BMS and only occur as PGM and electrum.

4 DISCUSSION

Several models for the formation of the PGE enrichment in the Merensky Reef may be considered.

(i) The PGE observed in solid-solution of the BSM or as PGM were initially host by an immiscible sulphide liquid which interacted with silicate magma to collect the PGE. In these case the whole rock content may be modelled
using the equation of Campbell & Naldrett (1979). In the silicate rocks, the PGE can all be accommodated in a sulphide liquid which interacted with a large volume of silicate magma (R-factor up to 45 000). In contrast, in the chromitite layers, it is not possible to explain the PGE enrichment by considering only the model of collection of the PGE by a sulphide liquid, an additional crystallisation of PGM or other processes are needed to explain the enrichment of the chromitite layers in IPGE.

(ii) The PGE were mobilized by an upward migrating fluid enriched in Cl which saturated the intercumulate liquid (e.g. Boudreau & Mc Callum, 1992). The BMS and the PGE precipitated where the intercumulate liquid is fluid undersaturated. Contrary to our observations, this model implies that the rocks below the reef are depleted in PGE. Furthermore, the PGE enrichment in the upper chromitite layer is difficult to explain as the the fluid would be depleted in PGE as it reaches this layer. As no experimental data are available of the solubility of all the PGE in magmatic fluids, it is actually not possible to test the hypothesis.

(iii) PGE enrichment of the chromitite layers may have occurred by means of sulphur loss. In this case, ~75 to ~80 % of the initial sulphide may have been removed to achieve a 5 to 10 times enrichment of IPGE. Some Pd and Au may have also been removed. However, it is not clear to us why the S removal would only occur in the chromitite and not in the overlying silicate rocks.

(iv) Some of the IPGE may be hosted in solid-solution within chromite (Righter et al., 2004). However, it implies that the partition coefficients for the IPGE and Rh were considerably higher than those determined experimentally.

(v) Borisov & Palme (1997) calculated that Fe-bearing mafic magma become saturated in Pt-Ru and Ir-Fe alloys at 0.4 to 14 ppb (values comparable with Bushveld magma). Thus, the high values of IPGE in the chromitite layers may be due to crystallisation of Fe-PGE alloys prior to sulphide melt saturation. However, the PGM found in the chromitites are in many case associated with BMS and only few PGM are included in chromite. This observation would imply that the PGM would have subsequently been absorbed by the sulphide liquid.

5 CONCLUSION

Integration of the above results and considerations allows us to propose the following model for the PGE enrichment in the Merensky Reef at Rustenburg Platinum Mine.

A new magma entered the chamber and mixed with the resident magma, chromite, orthopyroxene and PGE alloys formed and accumulated on the top of the existing protoanorthosite forming a layer enriched in chromite and PGE. The fractionated melt became saturated in an immiscible base metal sulphide liquid which collected the remaining PGE by interaction with a large volume of silicate magma. As further magma entered the chamber. It triggered the liquefaction of the cumulate pile which resulted in an enhanced compaction, improved downward migration of the sulphide liquid and the upward migration of the S-undersaturated interstitial silicate liquid. On cooling, this S-undersaturated liquid interacted with the BMS resulting in the formation of Pt-Fe alloy and Cu-Pd rich sulphide liquid by desulphurisation. As the Cu-Pd rich sulphide liquid have a higher wetability against silicates and oxides, it may have migrated through the chromitite and dissolved some of the PGE alloys formed earlier. Then, as temperature decreased, the MSS exsolved pyrrhotite and pentlandite and the ISS exsolved chalcocite and cubanite. The PGM (Pt-Pd bismuthotellurides, Pt-Pd sulphides and laurite) exsolved from these BMS and migrated grains boundaries.

REFERENCES


ABSTRACT: The Platreef is the main PGE bearing horizon of the Northern Limb of the Bushveld Complex, South Africa. In order to determine the role crustal contamination played in the formation of sulphides within the Platreef a new technique is being applied. Mass independent fractionation of sulphur isotopes is a process that occurred only in the Archaean atmosphere. Non-zero $\Delta^{33}S$ values therefore indicate the presence of crustal sulphur. A deposit wide study is currently being conducted on sulphides from the Platreef. Initial results show non-zero $\Delta^{33}S$ values in Platreef sulphides, indicating a crustal sulphur contribution to the formation of sulphide mineralization.

KEYWORDS: Platreef, sulphur isotopes, sulphide mineralization

1 INTRODUCTION

The Platreef is the main Platinum Group Element (PGE) bearing horizon of the Northern Limb of the Bushveld Complex. It is the world’s third largest PGE deposit after two other PGE horizons within the Bushveld Complexes (the Merensky Reef and the UG2). The reef itself comprises a series of pyroxenites, gabbro-norites and norites that contain xenoliths/rafts of footwall rocks. The Platreef is irregularly mineralized with PGE, Cu and Ni, and has a greater abundance of sulphides than the Merensky Reef. The main base metal sulphides within the Platreef are pyrrhotite, pyrite, pentlandite, and chalcopyrite. Extremely varied platinum group minerals occur as tellurides, bismuthotellurides, antimonides and arsenides.

The focus of this study is the relative enrichment in sulphides within the Platreef when compared to the rest of the Bushveld Complex. By understanding the processes and sources of sulphur that led to the formation of sulphides we gain a better understanding of the formation and the role of contamination in the Platreef as a whole. We use a new isotopic tracing technique to determine the role of crustal sulphur in the formation of sulphide mineralization in this deposit. Conventional sulphur isotope analyses ($\delta^{34}S = [^{34}S/^{32}S]_{\text{sample}} / [^{34}S/^{32}S]_{\text{standard}} -1$) can suggest the presence of crustal sulphur in nominally magmatic sulphide deposits but their effectiveness is limited by two requirements: (1) a crustal source characterized by large isotopic fractionations; and (2) a significant addition of crustal sulphur to the deposit. However, multiple sulphur isotope analyses ($\delta^{33}S = [^{33}S/^{32}S]_{\text{sample}} / [^{33}S/^{32}S]_{\text{standard}} -1$) may offer a more sensitive monitor of crustal sulphur.

During the Archaean Eon (>2.45 Ga), the lack of an oxygenated atmosphere likely allowed for the mass-independent fractionation of sulphur isotopes during atmospheric photochemical reactions. This isotopic anomaly can be identified by $\delta^{33}S$ measurements, and is quantified by $\Delta^{33}S$ ($= \delta^{33}S_{\text{measured}} - \delta^{33}S_{\text{predicted}}$, where $\delta^{33}S_{\text{predicted}} = [\delta^{34}S_{\text{measured}}+1]^{0.515}-1$). Under current working models for the Archean sulphur cycle, mass-independent fractionation is fundamentally a surface process; any recorded occurrence of a non-zero $\Delta^{33}S$ value, therefore, conclusively indicates the presence of sulphur that cycled through the Archean atmosphere. This property implies that multiple sulphur isotope analyses provide a definitive and sensitive tool for identifying crustal sulphur contributions in Archean ore deposits.
2 REGIONAL GEOLOGY

2.1 The Transvaal Supergroup

The Transvaal Supergroup was deposited between 2.67 and 2.07 Ga (Eriksson et al., 2001). The Supergroup comprises the Wolkberg, Chuinespoort, and Pretoria Groups. The Duitschland Formation marks the base of the Pretoria Group and disconformably overlies the Chuniespoort Group. The upper part of the formation is dominated by fine-grained laminated shales and marls; thick dolomite beds are more common in the upper part of the formation. The Duitschland Formation overlies the Penge Iron Formation which is composed predominantly of quartz-, magnetite- and hematite-rich rocks interlayered with minor carbonaceous shale beds. The Malmani subgroup, which underlies the Penge Iron Formation, reaches a maximum thickness of 2400 m, and comprises limestone, chert-rich, and chert-poor dolomite.

2.2 The Northern Limb

The northern limb of the Bushveld Complex is a slightly sinuous, north-west striking sequence with a length of 110 km (Armitage et al., 2002), and is typically divided into a southern, central, and northern sector (Figure 1). The Platreef is the major PGE-bearing horizon of the northern limb, and occurs at the base of the layered rocks. It is observed as being a highly inhomogeneous body, comprising different rock types including pyroxenites, parapyroxenites, feldspathic pyroxenites (pyroxenites with >10% interstitial plagioclase), serpentinites, gabbronorites and norites.

The Platreef has a transgressive relationship with underlying footwall rocks, which results in footwall rocks that are younger to the south. In the north, the footwall comprises Archaean granites, followed by the Malmani Subgroup, Penge Formation, Duitschland Formation, and Timeball Hill Formation respectively going southwards, all of which are part of the Transvaal Supergroup (Figure 1). The Platreef also contains a variety of xenoliths of altered footwall material, including hornfels rafts that most likely have shale protoliths, and calc-silicate rafts, which were originally dolomites.

The base- and precious-metal mineralization of the Platreef is unevenly distributed, and occurs over a zone that is up to 400m thick. In the southern sector, sulphide minerals occur throughout the succession. Generally, these occur as centimetre to millimetre-sized blebs and interstitial grains of pentlandite, pyrrhotite and chalcopyrite. A wide range of accessory minerals are also present including sphalerite, galena, molybdenite, pyrite, chalcocite, and covellite among others. Where present, zones of massive sulphides rich in chalcopyrite are found close to the footwall contact. More compositionally complex sulphides are associated with felsic melt phases that pervasively infiltrate the package soon after its partial or complete crystallization (Hutchinson & Kinnaird, 2005).

3 SULPHUR ISOTOPE ANALYSIS

3.1 Conventional Sulphur Isotopes

Conventional sulphur isotope analyses have been conducted on samples along the length of the Platreef, and have yielded a wide range of interpretations. Buchanan et al. (1981) and Buchanan & Rouse (1984) proposed that crustal sulphur contributed to the formation of sulphide within the Platreef but suggested that this sulphur came only from anhydrites within the
Malmani Subgroup. Manyeruke et al. (2005) concluded that crustal sulphur had contributed to the formation of sulphides on the Farm Townlands in the southern sector of the Platreef but did not propose a source. Sharman-Harris et al. (2005) and Sharman-Harris (2006, unpublished MSc thesis) identified crustal contamination in both the southern and northern sectors of the Platreef, especially associated with the presence of footwall xenoliths, and proposed that local-scale contamination added sulphur to the Platreef, with sources varying depending on footwall.

In contrast, Liebenberg (1968, unpublished DSc. thesis) and Hulbert (1983, unpublished DSc. thesis) both concluded that no crustal sulphur had been added to the Platreef system and that formation of sulphides was a purely magmatic process. Similarly, Holwell & McDonald (2006) proposed that in the northern sector of the Platreef on Farm Overysel there has been no crustal sulphur contribution to the formation of sulphides.

It is clear that conventional sulphur isotope analyses provide an equivocal view of crustal contamination within the Platreef. This arises in large part because strictly igneous processes can lead to some isotopic variability around the canonical magmatic $\delta^{34}S$ value (~0‰). Therefore a more sensitive line of evidence is required to document the presence of crustal sulphur within the Platreef.

3.2 Mass Independent Fractionation

The near ubiquitous presence of anomalous sulphur isotope fractionation in Archean sedimentary rocks suggests that the Archean sulphur cycle was unique in Earth history. Most sulphur-bearing compounds younger than ~2.45 Ga have isotopic compositions that are characterized by $\Delta^{33}S$ values of ~0‰. The transition from significant to near zero $\Delta^{33}S$ values is thought to be due to a change in the Earth’s atmospheric chemistry (Farquhar & Wing, 2003). Mass independent fractionation of sulphur has been experimentally demonstrated during the ultraviolet photolysis of sulphur dioxide (Farquhar et al., 2000). These results have been incorporated into a conceptual model of the Archean sulphur cycle in which the presence of non-zero $\Delta^{33}S$ values is attributed to vanishingly low atmospheric oxygen levels (Farquhar et al. 2000). Within this working model, any non-zero $\Delta^{33}S$ values reflect the presence of sulphur that passed through the atmosphere at some point in its history. A corollary is, therefore, that sulphur with a primary magmatic origin will not be mass-independently fractionated, and should retain near zero $\Delta^{33}S$ values.

A detailed multiple sulphur isotope study has been conducted on the part of the Transvaal Supergroup covering the top of the Malmani Dolomite through the Penge and Duitschland Formations in the area of Farm Duitschland (located approximately 20km south-east of the town of Mokopane) (Baker, 2006, unpublished MSc. thesis). Farm Duitschland was chosen as the site of this study as it is situated outside of the contact metamorphic aureole of the northern limb. This enables us to study the footwall of the Platreef, without having to account for metamorphic effects. A major break in both $\delta^{34}S$ and $\Delta^{33}S$ values occurs between the Lower and Upper Duitschland Formations (Figure 2), placing the hypothesized change in Earth’s atmospheric chemistry between the time of deposition of these formations.

As the magma that formed the Platreef intruded into the Transvaal Supergroup, crustal sulphur assimilated from Lower Duitschland or older strata should transfer a mass independent fractionation signature into the Platreef sulphides. The presence of non-zero $\Delta^{33}S$ values would conclusively indicate the presence of crustal sulphur within the Platreef, and may also constrain which lithologies contributed sulphur to the ore-forming system.

4 RESULTS

An ongoing multiple sulphur isotope study is being conducted on samples taken from drill core in the southern, central and northern Platreef. In the southern sector non-zero $\Delta^{33}S$ values (~0.4–0.6‰) have been found in sulphides from the lower half of the Platreef package. In the top half of the package in this area $\Delta^{33}S$ values are closer to zero (~0.2‰). Metamorphosed calc-silicate footwall of the Platreef in the southern sector also has low $\Delta^{33}S$ values (~0.1–0.2‰). In ore sulphide from the central sector of the Platreef, $\Delta^{33}S$ values up to 2.6‰ are present.

5 CONCLUSIONS

The initial results of this ongoing study definitely demonstrate that crustal sulphur is present in the ore sulphides of the lower portion of the Platreef package. Non-zero $\Delta^{33}S$ values in-
Figure 2: Diagram showing multiple sulphur isotope data for the Transvaal Supergroup, and the southern sector of the Platreef, against a simplified stratigraphic column.

dicate that some proportion of the sulphur in the Platreef was a participant of the Archaean atmospheric sulphur cycle. In the southern sector of the Platreef this sulphur most likely came from pyritic shales of the Lower Duitschland Formation. However, the direct footwall of the Platreef in this area is most likely Upper Duitschland Formation, raising questions about the structural setting of the footwall, and the method of emplacement of the Platreef. We are collecting further data to confirm our initial findings. As it stands, our measurements indicate that sulphide mineralization within the Platreef was not induced by a strictly local source of sulphur neither from the parental magma nor from the direct footwall.

ACKNOWLEDGEMENTS

The authors would like to thank AngloPlatinum, Ivanhoe Platinum, and Hunter Dickinson for providing access to samples for this study. Research was supported by the USGS Mineral Resources External Research Program and Ivanhoe Platinum.

REFERENCES


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ABSTRACT: The concentrations of the platinum-group elements (PGE), Ni, Cu, Co, Re, Au and Ag have been determined in the base-metal sulphide (BMS) and the whole rocks of the J-M Reef of the Stillwater Complex. In addition we performed detailed image analysis of the platinum-group minerals (PGM). Palladium and Pt are the more abundant PGE in our samples (average Pd/Pt ratio of 3). Palladium is mainly partitioned in pentlandite whereas Pt is almost exclusively found as Pt-alloy and do not partition in any BMS. The other PGE are largely found in the BMS. Our modelling results indicate that a sulphide liquid may have initially controlled the PGE, but that sulphide removal (desulphurization) may have occurred and concentrated the PGE in the remaining BMS (and by analogy in the rocks). In addition, in highly mineralized samples Pd may have been added to the system by aqueous fluid which has triggered the alteration of the base-metal sulphides to magnetite and the formation of skaergaardite.

KEYWORDS: platinum-group elements, sulphide, skaergaardite, laser ablation ICP-MS, parental magma

1 INTRODUCTION

The Stillwater Complex (Montana, U.S.A) is a layered ultramafic to mafic intrusion which contains several layers enriched in platinum-group elements (PGE). Amongst them the J-M Reef contain the highest Pt+Pd grade (~18 ppm) of all known PGE reefs (Zientek et al., 2002). The Stillwater Complex is altered and has been affected by several hydrothermal processes (Czamanske & Loferski, 1996) which may have modified the base-metal and the PGE content (Polovina et al., 2004).

Previous authors (Cabri et al., 1984; Li & Ripley, 2006; Polovina et al., 2004) reported high concentration of Pd in pentlandites (~1870 up to ~98 000 ppm) from the J-M Reef. Polovina et al. (2004) in their characterization of the postmagmatic alteration of the J-M Reef and its possible implications on the PGE mineralization concluded that the least altered samples contain the highest Pd content and that Pt and Pd may have been leached out of altered pentlandite by low-temperature (~250-300°C) hydrothermal fluids. No data are available for the other PGE.

In the current work, we have attempted to determine which phases host the PGE in order to consider and evaluate the possible processes which have triggered the formation of the J-M Reef. The first aim of the study was to determined by LA-ICP-MS the PGE, Re, Au, Ag, Co, Cd and Zn content in the base-metal sulphides (pentlandite, pyrrhotite and chalcopyrite) and the whole rock of the J-M Reef to establish

(i) whether the base-metal sulphide (BMS) are the principal phases concentrating these elements;
(ii) whether these elements preferentially partition into a specific BMS and:
(iii) whether their contents vary as a function of host lithology and/or alteration.

Secondly, a detailed (backscattered electron images and geochemical) analysis of the platinum-group minerals (PGM) has been made to determine which PGM are present in our samples and what are their textural relationships with other phases such as BMS and/or alteration minerals. The details of all the methodologies are given in Godel & Barnes (submitted to Chemical Geology).
GEOLOGY AND PETROGRAPHY

The Stillwater Complex is 2705+/-4 Ma old (Premo et al., 1990) and is intruded into middle to late Archean metasediments. The layered rocks are divided into five series, from bottom to top: the Basal, the Ultramafic, the Lower Banded, Middle Banded and the Upper Banded series. The samples studied in this work are from the J-M Reef package. The J-M Reef is associated with the olivine-bearing cumulate (OB-1) of the Lower Banded series. It is a disseminated PGE-enriched sulphide mineralization which has the highest grade of all known PGE reef in the world with an average of 18 ppm of Pt and Pd (Zientek et al., 2002).

Twelve samples from the J-M Reef “package” (footwall, reef and hanging wall) from the East-Boulder Mine were studied. They consist of anorthosite, norite, leuconorite, troctolite and olivine melagabbro-norite. Four samples of the reef contain visible BMS and were taken for the in-situ analysis of sulphides. The BMS occur as interstitial phases between primary silicates (olivine, pyroxene or plagioclase) and/or as tiny grains (usually composed of chalcopyrite) closely associated with alteration silicates (chlorite-tremolite-actinolite). In some samples, secondary magnetite has replaced the BMS at the contact with silicates.

RESULTS

3.1. PGE in the whole rocks

Only minor PGE (~10 to 140 ppb) were found in the footwall and hanging wall samples of the J-M Reef which contain only a small amount of sulphur (~140 to 400 ppm). In contrast, the reef samples enriched in BMS contain higher values of PGE (49 up to 419 ppm). Palladium and Pt are the principal PGE found in these rocks and represent ~60 to ~83% and ~23% to 40% of the total PGE content, respectively. The S, Ni, Cu and PGE contents follow the same trends. This probably reflects the fact that the BMS are the principal phases initially controlling these elements. Palladium is the PGE which is the most enriched in these samples. The Pd/Pt ratio is lowest (0.3) just below the reef. It increases strongly in the reef samples (1.3 to 5.2, average 3) and it decreases upward in the hanging wall (from 2.9 to 1). Similarly, the high Pd/Ir ratio and the mantle normalized metal patterns in the reef indicate that Pd is more strongly enriched in the reef relative to surrounding rocks than the other PGE.

3.2. PGE and other metals in BMS

All the BMS (pentlandite, pyrrhotite and chalcopyrite) contain PGE. Pentlandite is the principal BMS host of the PGE (value ~350 ppm up to more than 28 000 ppm). In the pyrrhotite and the chalcopyrite, the values are lower and vary from ~2 to 150 ppm. Palladium is the PGE which is the most partitioned in the BMS, it represented ~98% of the PGE found in pentlandite and ~63 to 95% of those found in pyrrhotite and chalcopyrite. As predicted by the partition coefficient between the sulphide liquid and the monosulphide-solid solution (MSS), Co, Rh, Ru, Ir, and Os partitionned in the exsolution product of the MSS the pyrrhotite and the pentlandite. As predicted by the partition coefficient, Ag, Cd and Zn are concentrated in chalcopyrite which is the exsolution product of the intermediate solid-solution (ISS). Palladium is essentially concentrated in pentlandite and contrary to that predicted by the partition coefficient is not partitioned in the chalcopyrite. It probably indicates that some Pd was redistributed during the exsolution and/or alteration processes. In contrast, Pt and Au are not partitionned in any BMS.

3.3. PGE mass balance

The results of the whole rock and the in-situ PGE analysis of the BMS were used to calculate the percentage of each PGE in each BMS.

In all samples, the Pt and Au content found in these BMS represent <0.1% of the whole rock content. These elements are found as PGM and electrum (see description below). For Pd, Ir and to a lesser extend Os, the proportions of each element in each BMS vary from ~23% to ~73%. In all rock types, a far smaller proportion (~3 to ~23%) of Os is found in the in-situ sulphides. Rhodium and Ru proportion in BMS are higher (~75 to 100%) in the olivine-bearing rock than other lithologies (~10 to 80%). These results indicate that phases other than BMS accommodate the remaining Ru, Rh, Pd, Ir and Os and almost all the Pt and Au.

3.4. PGM and their textural associations

Backscattered (BSE) image analysis of four sections representing the reef samples was carried out to find, measure and analyse (qualitative or quantitative analysis) these PGE rich
phases. Eight types of PGM were found: (i) Pd +/-Pt telluride; (ii) Pd +/- Pt sulphide; (iii) Pt-Fe alloy; (iv) Ru-Ir-Os sulphide; (v) Pd electrum; (vi) Pd-Pb alloy; (vii) Pd-Cu alloy and (vii) native Pd. The proportion of each PGM varies as a function of the section. The Pd-Cu alloy (Skaergaardite) and native Pd were only found in one section and represent almost all (except 2 grains of Pt-Fe alloy and 2 grains of Pd +/-Pt telluride) the PGM found in this section. Skaergaardite is in many cases associated with secondary magnetite (included in magnetite or located at contact between magnetite and silicate) and also occur as small veinlets which crosscut the BMS. On the other three sections, more than 850 PGE-rich phases were found. Palladium +/- Pt sulphides (braggite, cooperite and vysotskite) and Pt-Fe alloy (isoperplatinum) are the most common PGM, they represent respectively ~59 area% and ~23.5 area% of the PGM found. Palladium +/- Pt telluride (telluropalladinite, keithconnite with minor moncheite, merenskite and kotulskite) represent ~12 area% of the PGM. Zvyagintsevite (Pd-Pb alloy), laurite (Ru-Ir-Os sulphide) and Pd electrum are less abundant (~2.9 area%, ~1.1 area% and ~1.9 area%, respectively). If we consider all the PGM, most of them are found associated with the BMS: located at contact between silicate and BMS (42.5%), included in BMS (23.5%) and to a minor extended located at the boundary between BMS and magnetite (1.8%). The remaining PGM are in many cases surrounded by alteration silicates (26%) or associated with secondary magnetite (6.4%).

4 DISCUSSION

According to the results above, it is clear that the PGE are in many cases found associated with the BMS (as solid-solution in sulphides or as PGM closely associated with them). Contrary to the Bushveld Complex, no well defined parental magma is proposed for the Stillwater Complex but some authors considered that the magmas present at Stillwater had similar composition to those of the Bushveld Complex (Barnes & Maier, 2002 and references therein). In contrast, for all PGE, the calculated composition of the possible parental magma is too high (up to 10 times for Pd) than the composition observed for the Bushveld Complex or most basalt lavas. Although some lavas may contain high values of Pd (Hamlyn et al., 1985), the calculated Stillwater values are higher than most of the basalt and it is probable that Pd and to a lower extent minor Pt may have been remobilised by post-sulphide liquid. Thus, other processes may have occurred to collect and/or concentrate the PGE.

Secondly, we use the S/Se ratio to calculate the sulphide removal and make the assumptions that the PGE (whole rock contents) were not removed by the fluid but were concentrated in the remaining BMS. For Ni, Cu, Co, the IPGE and in many cases for Pt, the calculated values for the possible parental magma of the J-M Reef are similar to those of the tholeitic basalt proposed for the parental magma of the Bushveld complex (Barnes & Maier, 2002 and references therein). In contrast, for Pd the calculated values range from ~18 ppb up to 115 ppb for the highly mineralized samples. Although some lavas may contain high values of Pd, the calculated Stillwater values are higher than most of the basalts and it is probable that Pd and to a lower extent minor Pt may have been remobilised by post-sulphide liquid PGE collection processes and superimposed on the sulphide “PGE signature”.

Finally, the PGM analysis suggests that Pd was mobile and possibly added to the system during alteration processes leading to the oxidation of the BMS to magnetite. Thus, we consider that some of the whole rock Pd was added by different processes to those found in BMS and that they have undergone the same S removal and PGE enrichment than previously de-
scribed. We obtain for most rocks an estimate of magma values ranging from ~12 to ~31 ppb of Pd. These values are close to the parental magma proposed for the Merensky Reef of the Bushveld Complex and to those found in basalts. However, for the highly mineralized sample the calculated Pd content is still high (~80 ppb). Palladium may have been remobilized by fluid and then may have interacted with nickel sulphides to form Pd highly enriched pentlandite.

5 CONCLUSION

Our modeling results suggest that the PGE enrichment of the J-M Reef may be summarized into different steps:

(i) an immiscible sulphide liquid interacted with a large volume of magma with PGE composition close to high Mg basalt and collected the PGE. The PGE-rich sulphide liquid percolated downward in the cumulate pile until it reached a layer with a permeability too low to allow it to further migrate.

(ii) during cooling, magma chamber instabilities triggered the partial desulphurisation of the BMS, the enrichments of the remaining BMS in PGE and the formation of Pt-Fe alloy.

(iii) in some part of the reef, a fluid deposited Pd (possibly removed from the underlying cumulate pile) and altered the BMS to magnetite. During this step, Pd may crystallise as Pd alloy and/or substitute to Ni in pentlandite to form a high-Pd bearing pentlandite.

The variability of the Pd grade observed along the J-M Reef probably reflects the different contribution of each process in different part of the reef.

REFERENCES


ABSTRACT: In multi-stage, open-system, magmatic environments metal-rich sulphide liquids can be developed from smaller relative amounts of silicate magma than in single-stage, closed systems. Moreover, if the sulphide liquid is progressively dissolved by subsequent magma batches, rules and limits inherent in closed systems and open systems that lack dissolution begin to break down, allowing strong metal enrichment and decoupling of PGE from base metals. This provides an interesting mechanism that could explain high-grade Ni-Cu (± PGE) massive sulphide deposits, strongly PGE-enriched disseminated sulphide deposits, and other examples that lie between these extremes. Ultimately, it may provide a route towards a unified magmatic model for this diverse family of deposits.

KEYWORDS: Magmatic Sulphides, Geochemistry, Ore Deposits, Nickel, PGE, Models

1 INTRODUCTION

It is now generally recognized that the simple, static, separation of liquid sulphides from silicate magma is unlikely to generate metal-rich sulphide deposits. Dynamic, multistage magmatic environments, in which sulphides are exposed to multiple batches of magma, may be an important requirement (e.g., Naldrett, 1999). The importance of conduit systems is well-established for the Noril’sk deposits of Siberia and the Voisey’s Bay deposit of Labrador, amongst other examples. Lava tubes and rivers (i.e., extrusive conduit systems) are important for the formation of sulphide deposits hosted by komatiitic volcanic rocks (e.g., Naldrett, 1999).

Despite growing appreciation of the importance of such dynamic magmatic environments, most geochemical modelling of magmatic sulphide enrichment assumes closed-system, single-stage conditions, after Campbell & Naldrett (1979), who first outlined the influence of the silicate magma to sulphide liquid mass ratio (R-factor, or R) upon Ni, Cu and PGE contents. In simple terms, large R results in metal-rich sulphide liquids, as more magma is processed for metals, whereas small R results in metal-poor sulphides, because the supply of metal is limited. In any closed system the metal content of a sulphide liquid will always be less than a limiting value, which is the product of the initial magmatic concentration (X) and the sulphide/silicate distribution coefficient (D). Sulphide liquids typically achieve half the limiting concentration when R=D, and approach it when R = 10D. For chalcophile elements that have very high D and very low magmatic concentrations (e.g., PGE), enormous relative quantities of magma must be processed for sulphide liquids to attain economic metal values.

Many PGE deposits contain small amounts of highly enriched sulphides, which have high PGE to base-metal ratios indicating enormous R. However, it is not easy to visualize physical environments in which a sulphide liquid can equilibrate with a mass of silicate magma that is as much as a million times greater. It is largely because of this problem that several disparate models, some of which partially involve hydrothermal processes, are proposed for these PGE-rich deposits. In contrast, orthomagmatic models are widely accepted for sulphide-rich deposits dominated by base metals. We currently do not have a “unified model” that links these end-member types of magmatic sulphide ore deposits.

2. OPEN-SYSTEM MODELS

Multistage open-system models are exemplified by proposals for the huge Noril’sk deposits
of Siberia (Naldrett et al., 1995). These suggest that early metal-poor sulphide liquids were exposed to a continued flux of magma in conduit systems. These later magmas were not depleted in metals, and progressively enriched the sulphide liquids. The depletion and rebound of magmatic Ni, Cu and PGE concentrations are preserved in the chemostratigraphy of the associated flood-basalts. Similar models have been applied to the Voisey’s Bay deposit in Canada, and to other base-metal-rich magmatic sulphide deposits (e.g., Naldrett, 1999).

These models have an important implication. Sulphide liquid formation is by definition anomalous, and most mafic magmas are sulphur-undersaturated at emplacement. Thus, any continued flux of mafic magma in such an open system could partially redissolve any earlier-formed sulphide liquid. This issue has not been addressed in detail, and it has important implications. These were explored through a formal mathematical treatment, and applied to two natural examples by Kerr & Leitch (2005).

The results of this research are summarized here, without reference to equations and theoretical premises. This paper seeks instead to outline and explore the implications of such processes for the interpretation of geochemical patterns, and discuss the potential for development of unified genetic models for the diverse family of magmatic sulphide deposits.

3. SIMPLE MULTISTAGE UPGRADING

Simple Multistage Upgrading is defined as interaction between a fixed mass of sulphide liquid (formed in step 1) and multiple equal-sized batches of silicate magma, in which the magmatic metal content remains fixed. Modelling using simplified equations (Kerr & Leitch, 2005) shows that variations in $D$ and $R$ control the behavior of the system. $R$ is here defined as the mass ratio of each magma batch to the sulphide liquid, as opposed to cumulative $R$, which indicates the total mass of magma.

Simple multistage upgrading proves to be more efficient than single-stage, closed-system segregation, especially in situations where $R$ is small (<100), i.e., in which many small batches of silicate magma are processed. This case can be described with a simple formulation termed the conduit equation, which predicts the interaction between a sulphide liquid and a continuous flux of magma. For a typical base-metal (e.g., Ni; $D = 500$) larger individual magma batches reduce the efficiency of metal extraction, but it is always more efficient than in the closed system. For a typical PGE (e.g., Pt, $D = 10\,000$), the actual size of the magma batches is essentially irrelevant. Conduit-type simple multistage upgrading can significantly reduce the amount of magma that must be processed to achieve a given metal content in the sulphide liquid. For example, using $D=500$ and $X=100$ ppm for Ni, sulphide metal contents of 4.6% Ni (equivalent to Voisey’s Bay) can be achieved with one-fifth of the total amount of silicate magma required in a closed system. For the PGE, the advantages could be as much as tenfold, although the total amount of silicate magma required remains large.

Despite its efficiency, simple multistage upgrading shares one crucial limitation with a closed-system situation. i.e., the concentration of a metal in the sulphide liquid cannot exceed the limiting value of $DX$.

4. MULTISTAGE-DISSOLUTION UPGRADING

Multistage-Dissolution Upgrading differs from the simpler case in that each incoming magma batch dissolves a fixed proportion of the sulphide liquid formed in the first step. As outlined above, it is a more likely natural process. Element behavior is sensitive to $R$ and $D$, as in the simple case, but is crucially dependent on the loss factor ($L$), which is defined as the proportion of existing sulphide liquid redissolved in each step. As the mass of sulphide liquid diminishes, the mass of incoming magma batches also shrinks, because $R$ is held constant. This is a reasonable assumption, because there must be limitations on how much magma a given mass of sulphide can react with.

The simplified general equation for multistage-dissolution upgrading is interesting in that it produces two radically different sets of results, depending on relative values of $D$, $L$ and $R$ (Kerr & Leitch, 2005). In simple terms, if $L < R/D$, sulphide metal contents will stabilize at a limiting value, but if $L > R/D$, they will grow at progressively increasing rates, with no limiting value. This latter situation is dubbed runaway upgrading. The two cases are separated by the special case where $L = R/D$, which generates growth at a fixed rate. The contrasting behaviors of a base metal (Ni) and a PGE (Pt) are shown in Figure 1 (Kerr & Leitch, 2005).

This divergent behavior has important impli-
cations, because values of $D$ vary much more than values of either $L$ or $R$. Runaway upgrading will occur in situations where $D$ is very large, and will thus apply to the PGE, unless $L$ is extremely small. Conversely, base-metals, for which $D$ is moderate, will generally stabilize at a limiting value, unless $L$ is very large. Copper is especially interesting, because its $D$ is intermediate between those for Ni and the PGE, and its behavior is not readily predictable.

A crucial feature of this multistage-dissolution upgrading is that it can result in sulphide metal contents above the limits inherent in closed-system segregation and simple multistage upgrading. Even in cases where sulphide metal contents stabilize, the limiting values are greater than $DX$, and rise progressively as $L$ increases. The mass of sulphide liquid decreases in such models, but significant amounts of sulphide (50% to 5%) remain when these high Ni and PGE contents are attained (Figure 1).

The mechanism that permits such high concentrations can be imagined qualitatively as remittance of a small fraction of the metal to the magma as the sulphide liquid dissolves. This raises the magmatic metal content, which in turn allows sulphide metal contents to remain high, or continue to grow, depending upon operative $D$. For high $D$ elements (PGE), far smaller amounts of metal are remitted.

Multistage-dissolution upgrading effectively breaks the “R-factor barrier”, because it facilitates the generation of metal-rich sulphide liquids from much smaller amounts of silicate magma than previously envisaged. In ideal circumstances, the process could reduce the amount of magma that must be processed by as much as two orders of magnitude.

5. DISCUSSION AND APPLICATION

These geologically reasonable processes permit efficient extraction of metals from silicate magma by sulphide liquids, and earlier estimates of $R$ predicated on closed-system behavior may be exaggerated. If redissolution of sulphide liquid occurs, sulphide metal concentrations can rise above limits suggested by estimates of primary magmatic metal contents and $D$ values. Clearly, multistage open-system processes could be vital in forming high-grade magmatic ore deposits. In multistage-dissolution upgrading, the base-metals (moderate $D$) and the PGE (very large $D$) will become decoupled, because the latter are no longer subject to limiting values, unless dissolution is very slow. Amongst the base-metals, the behavior of Cu is inherently difficult to predict, and the use of ratios such as Cu/Pd or Ni/Pt to constrain $R$ is suspect. More importantly, the process could generate strongly PGE-enriched sulphide liquids with high PGE/base-metal ratios, like those inferred for many PGE deposits. The decoupling of individual PGE (e.g. Pd vs Pt) is

![Figure 1. The contrasting behaviour of a base-metal (e.g., Ni; part a) and a PGE (e.g., Pt; part b) during multistage-dissolution upgrading. Parameters for models are listed in charts. Both simulations assume that $L$=0.05 (5%), i.e., 5% of the sulphide liquid is dissolved by each incoming magma batch. Left-hand Y scales indicate metal content of sulphide liquid, and right-hand Y-scales indicate metal content of outgoing silicate magma. Note that the maximum sulphide metal contents permitted by closed-system, single-stage fractionation are 5% Ni and 100 ppm Pt, respectively. Figure modified after Kerr & Leitch (2005)](image)
more difficult, but is possible in situations where dissolution rates are very slow.

Multistage enrichment (± dissolution) is suspected to play a role in the development of sulphide-rich base-metal-dominated deposits associated with komatites (e.g., Raglan) and mafic intrusions (e.g., Voisey’s Bay). The degree of dissolution in such environments is likely modest, albeit difficult to constrain. Komatites are the most Ni-rich amongst host magmas, and represent one of the few environments in which closed-system segregation might be effective. However, komatiitic environments were extremely dynamic, and such magmas would be strongly sulphur-undersaturated. Large “cloud-like” disseminated deposits containing Ni-rich sulphides (e.g., Mount Keith) may be remnants from protracted cannibalization of earlier low-grade sulphides by voracious magmas.

The Noril’sk deposits of Siberia include sulphide bodies that are strongly enriched in Ni, Cu and PGE. These compositions correspond well to those predicted from more extensive dissolution of sulphides, such that 50% to 17% of the original mass remains (Kerr & Leitch, 2005). The total amount of silicate magma that must be processed is much less than for any closed-system model. It is suggested, after Naldrett et al. (1995) that variable multistage-dissolution upgrading occurred in conduit systems through which large amounts of magma passed. As Noril’sk is one of the world’s largest deposits, enormous quantities of sulphide liquid may have been consumed. As the known deposits account for only 12% of the metals estimated to be missing from the huge volumes of metal-depleted lavas, this is clearly permissible. Sulphide-poor, disseminated, reef-type PGE deposits (e.g., Bushveld, Stillwater) correspond to predicted residual sulphide liquids from extensive, protracted redissolution. Under such conditions, the PGE experience runaway upgrading. Such sulphides could represent the end-products of multistage-dissolution upgrading in conduit systems. If this is so, the sulphides must subsequently have been injected into higher-level magma chambers. In this context, there is evidence for earlier low-grade sulphide liquids at Stillwater. However, the models would apply equally well to the sudden development of a sulphide liquid within the upper chamber, followed by its settling through a sulphur-undersaturated magma column. This idea fits the original proposals of Campbell et al. (1984), but requires far less silicate magma.

These open-system sulphide liquid segregation and enrichment models offer the promise for unified models based largely upon magmatic premises. Although they do not preclude hydrothermal overprints (notably in PGE deposits, they may resolve some of the questions that have bedevilled orthomagmatic models.

REFERENCES


Controls on the emplacement and genesis of the MKD5 and Sarah’s Find Ni-Cu-PGE deposits, Mount Keith, Agnew-Wiluna Greenstone Belt, Western Australia.

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ABSTRACT: The Mount Keith Ultramafic unit (MKU) of Western Australia is one of the most highly NiS-endowed komatiite belts in the world. The internal architecture of the MKU is made up of adcumulate-textured pods and lenses, which are flanked by thinner meso- and orthocumulate-textured units, overlain by pyroxenitic and gabbroic horizons. The internal architecture of the MKU and the transitional contacts between the various komatiite units, coupled with the significant lateral variation between the Mount Keith Ultramafic Complex and Sarah’s Find, suggests that the MKU has experienced variations in magma flux during its emplacement and assembly history. The nickel-sulphide ore typology and style vary greatly along the strike extension of the Mount Keith Ultramafic unit. Basal massive nickel-sulphide mineralization generally occurs in the thinner meso- and orthocumulate-textured units, whereas stratabound disseminated NiS mineralization is hosted in the adcumulate-textured pods. We hypothesize that the formation of basal massive and stratabound NiS deposits is due to the localized coalescence of entrained sulphide blebs. In fact, the very low PGE content of the initial liquid of the Mount Keith Ultramafic unit suggests that the initial magma pulse that penetrated through the dacite host-rock had already equilibrated with sulphides at depth and/or carried entrained immiscible sulphide blebs. We argue that upon emplacement, the intruding magma experienced a significant thermal shock at the contact with water-saturated volcaniclastic breccias. Accordingly, the sudden chilling would have increased the viscosity of the magma, possibly to the point where it was no longer able to sustain the suspension of the immiscible sulphide liquid. As a result, the sulphide blebs coalesced and formed the basal massive sulphide NiS mineralization at the base of the sill (i.e. Sarah’s Find). A prolonged episode of focused high volume magma flow within the sill resulted in the emplacement of thick, lens-shaped accumulations of olivine adcumulate. Local variations in intensive parameters other than crustal assimilation (e.g. T, fO2, fS2) may be principally responsible for sulphide-supersaturation and controlled the local distribution of stratabound disseminated nickel-sulphide mineralization, generally localized within the core of the thicker dunite lenses.

KEYWORDS: Komatiite, nickel-sulphide, NiS, platinum-group element, PGE, Archaean

Mount Keith is situated in the northern part of the Agnew-Wiluna Belt, which forms part of the northern section of the Eastern Goldfields Province of the Yilgarn Craton of Western Australia (Burt & Sheppy 1975; Naldrett & Turner 1977; Hill et al. 1990; Dowling & Hill 1992; Barnes et al. 1988).

The Agnew-Wiluna Belt (AWB) comprises a ca. 2.7 Ga sequence of felsic-to-intermediate volcanic and volcaniclastic rocks, sulphidic cherts, carbonaceous shales, and laterally variable komatiites including cumulates, thin spinifex-textured units and komatiitic basalts. The AWB is one of the most highly Ni-endowed belts in the world, and contains several world-class Ni-Cu-(PGE) deposits, including two of the largest known komatiite-hosted ore deposits at Mount Keith and Perseverance (Fig. 1).

The Mt Keith (MKD5) nickel-sulphide deposit is one of the largest komatiite-hosted NiS deposits in the world and is hosted by a distinctive spinifex-free cumulate-rich ultramafic horizon/unit termed the Mount Keith Ultramafic.
The Mount Keith Ultramafic shows significant variation along its lateral extent. The internal architecture is made up of adcumulate-textured pods and lenses, which are flanked by thinner meso- and orthocumulate-textured units, overlain by pyroxenitic and gabbroic horizons. The lateral and vertical changes in the geometry and internal architecture reflect variations in the lithological association and emplacement conditions along the strike extent of the belt. Disseminated NiS occurs interstitial to former olivine crystals, and is concentrated in the lensoidal areas. The MKD5 Ni Deposit represents the greatest accumulation in the thickest lens. The thicker lenses (i.e. Pods in Fig. 2) display a complex internal stratigraphy, comprising several textural and compositional units (Rosengren et al. 2004), representing the product of a complex emplacement history. Conversely, the thinner portions of the MKU (i.e. Constrictions in Fig. 2) have a simple internal stratigraphy, with relatively large proportions of pyroxenite and gabbro at the upper margins.

The chilled margins of the Mount Keith Ultramafic unit contain ~1200 ppm Ni. Olivine cumulates average ~2500-3500 ppm Ni, with few exceptions (Ni>4500 ppm) reflecting occurrence of minor nickel-sulphides, whereas pyroxenites and gabbros generally contain respectively ~1500-2000 and ~100-1000 ppm Ni. Olivine cumulates generally contain low Cr concentrations (~2500 ppm Cr), with the rare presence of chromite-rich intervals containing anomalously high values (>5000 ppm Cr). The distribution of rare earth elements divides the internal stratigraphy of the Mount Keith Ultramafic unit into two groups. The chilled margins and the internal units of the Main Adcumulate domain display LREE-enriched patterns [(La/Sm)n > 1-3] and negative Eu, Hf, Zr, Nb and Ti anomalies. Conversely, the internal units in the Western Mineralized zone generally display flat chondrite-normalised REE patterns and only minor negative Nb anomalies.

The pattern of PGE distribution varies greatly along the strike extent of the Mount Keith Ultramafic unit. The chilled margins display relatively low absolute concentrations [PGE (excl. Os) ~16 ppb] and relatively fractionated patterns, with subchondritic Pt/Pd ratios (~1.5), and superchondritic Pd/Ir ratios (~3). The PGE trends in the thick adcumulate-textured pods containing widespread NiS mineralization display positive correlation with sulphide abundance, whereas fractionated pyroxenites and gabbros in the thinner domains display highly depleted PGE concentrations and generally show compatible PGE trends.

The nickel-sulphide ore typology and style vary greatly along the strike extension of the Mount Keith Ultramafic unit. Basal massive nickel-sulphide mineralization (e.g. Sarah’s Find) occurs in the thinner meso- and orthocumulate-textured units, whereas stratabound disseminated NiS mineralization (e.g. MKD5 Ni Deposit) is hosted in the adcumulate-textured pods. We hypothesise that the very low PGE content of the initial liquid of the Mount Keith Ultramafic unit suggests that the initial magma pulse that penetrated through the dacite host-rock had already equilibrated with sulphides at depth and/or carried entrained immiscible sulphide blebs. We argue that upon emplacement, the intruding magma experienced a significant thermal shock at the contact with water-saturated volcaniclastic breccias. Accordingly, the sudden chilling would have increased the viscosity of the magma, possibly to the point where it was no longer able to sustain the suspension of the immiscible sulphide liquid. As a result, the sulphide blebs coalesced and formed the basal massive sulphide NiS mineralization at the base of the sill (Fig. 2). Prolonged fo-
cused high volume magma flow within the sill resulted in the emplacement of a thick, lens-shaped accumulation of olivine adcumulate (Fig. 2). Local variations in intensive parameters other than crustal assimilation (e.g. T, fO\textsubscript{2}, fS\textsubscript{2}) may be principally responsible for sulphide-supersaturation and controlled the local distribution of stratabound disseminated nickel-sulphide mineralization (e.g. MKD5 Ni Deposit), generally localized within the core of the thicker dunite lenses.

ACKNOWLEDGEMENTS

This work is part of the PhD theses of Marco Fiorentini and Nic Rosengren. We acknowledge discussions with Paul Duuring, Mark Bailey, Wolf Maier, Steve Barnes and Peter Lightfoot that have greatly improved the scope and the quality of the work. This study also formed part of the multi-disciplinary AMIRA P710 project on the Agnew-Wiluna Greenstone Belt. We would like to acknowledge the support of AMIRA and industry sponsors (WMC Resources, Inco, MPI and Lionore). In particular, we acknowledge discussions on komatiite geochemistry with Dr Mary Gee (University of Western Australia) and on PGE analytical methods with Dr Marcus Burnham (Geoscience Laboratories). Professor Reid Keays and Dr Bruce Schaefer (Monash University) are kindly thanked for their analytical support for PGE analyses with the Carius tube method.

REFERENCES


Rosengren NM, Beresford SW, Gruguric BA, Cas RAF (2005) An intrusive origin for the komatiitic dunite-hosted Mount Keith nickel sulphide deposit, Western Australia. \textit{Econ Geol} 100: 149-156.
ABSTRACT: The Flying Fox nickel deposit is located in the Forrestania greenstone belt of Western Australia. The nickel ore bodies are characterized by five phases of deformation, regional amphibolite facies metamorphism, multiple phases of magmatism and hydrothermal alteration which resulted in remobilized and structurally modified nickel ore shoots.

KEYWORDS: nickel, sulphides, komatiites, deformation

1 INTRODUCTION

The Flying Fox nickel sulphide deposit is located in the Forrestania greenstone belt, a typical Archean greenstone succession in the western part of the Yilgarn Craton. The local geological succession is characterized by five phases of deformation, metamorphism, magmatism and hydrothermal alteration that have modified the overall ore body geometry and contributed to the unusually high grades that can reach 21% nickel in places. The average grade of nickel increases with depth from 4.1% at the T0 ore body to 5.9% at the T5 ore body and the deposit has an overall current probable ore reserve of 1.16 million T with 74,000 T of contained nickel.

3 FLYING FOX NICKEL DEPOSIT

The Flying Fox deposit is located in ca 2.9 Ga supracrustal rocks that are intruded by multiple granite stocks (of currently unknown age).

3.1 Lithostratigraphy and Metamorphism

The lithostratigraphy at Flying Fox is divided into three major domains (oldest to youngest): (i) footwall metasedimentary quartz-rich schists intercalated with minor basalts; (ii) Ultramafic-mafic volcanic succession - lowermost differentiated ultramafic package hosting the ore-bodies overlain by up to four separate undifferentiated ultramafic and mafic volcanic sequences. These sequences contain quartz-rich interflow sulphidic sedimentary rocks; and iii) Eastern hangingwall metasedimentary shale and pelitic schists. These rocks are metamorphosed to mid- to upper-amphibolite facies with estimated peak metamorphism at 655°C±30°C and 4.0±1.0kb (Porter & McKay 1981).

Three different intrusive events have been identified at the Flying Fox deposit: (i) early adamellite intrusions that cross-cut the stratigraphy but contain the interpreted S1reg foliation; (ii) later intrusion of granite stocks that
cross-cut $S_{\text{1reg}}$ foliation and include two pulses of granodiorite, a biotite rich granite and a felsic granite, followed by late stage pegmatites; and (iii) E-W trending Proterozoic dolerite dyke that cross-cuts all lithostratigraphic units.

3.2 Deformation History

Five deformation events at the Flying Fox deposit have been identified from more than 100 diamond drill core with a total length exceeding 50km:

- $D_{\text{a}1\text{reg}}$: Previous work has interpreted that E-W compression resulted in the Forrestania syncline which strikes N-S and gently plunges 10°-20° to the north. The eastern limb dips 60°-90° to the west and the western limb dips 40°-70° to the east. Flying Fox is located on the western limb with $S_{\text{1reg}}$ foliation dipping 60° to the east.
- $D_{\text{b}1\text{FF}}$: continued E-W compression resulted in co-axial flattening of footwall metasedimentary rocks-sulphide/ultramafic contact and the uppermost basalt package-hangingwall-metasedimentary rocks contact resulting in a $S_{\text{2FF}}$ foliation that dips 80°-85° to the east.
- $D_{\text{c}1\text{FF}}$: ENE-WSW compression resulted in non-coaxial shearing of the $D_{\text{b}1\text{FF}}$ structures that locally display shear zone indicators (e.g. rotated augens, S-C fabric) which show east block down giving a normal sense of movement.
- $D_{\text{d}1\text{FF}}$: ESE-WNW compression resulted in shallow angle thrusts dipping 5°-10° to the southeast with displacement of up to 200m (based on plunge of the lineations and displacement of ore body and stratigraphy). The event formed $S_{\text{1FF}}$ foliation which dips 5°-10° to the southeast and crenulated the $S_{\text{1reg}}$ foliation.
- $D_{\text{e}1\text{FF}}$: during E-W extension two normal ductile-brittle faults formed at the T0 and T4 ore bodies and are interpreted to be the result of dilation of granites against the footwall metasedimentary rocks and ultramafic contact and “smeared” sulphides along this contact.
- $D_{\text{f}1\text{FF}}$: during E-W extension late stage brittle normal faulting occurred and included: (i) reactivation of $D_{\text{c}1\text{FF}}$ to $D_{\text{d}1\text{FF}}$ structures; (ii) E-W striking sub-vertical set dipping 80° towards 345° interpreted to be the result of dolerite dyke intrusion; and (iii) NW striking set dipping 75° towards 210° interpreted as conjugate to $D_{\text{e}1\text{FF}}$ faults.

3.3 Mineralization

Five ore bodies (T0, T1/T2, T4 and T5) have been identified at Flying Fox (Fig 2) from which four styles of mineralization have been identified: (i) disseminated sulphides – located in cumulate rocks stratigraphically above the massive sulphides; (ii) massive to breccia sulphides – located at the contact between the cumulate package and footwall metasedimentary rocks: in places they are located off-contact into the footwall metasedimentary rocks; (iii) stringer and vein sulphides – located off-contact in the footwall metasedimentary rocks and granite stocks; and (iv) breccia sulphides – located in the felsic granite stocks as a matrix.

The sulphides are comprised of nickeliferous pyrrhotite, pyrite and only minor chalcopyrite. All sulphides (except sulphides that make up the disseminated style) have been subject to at least one phase of remobilization.

3.4 Hydrothermal Alteration

The first phase of hydrothermal alteration resulted in seafloor alteration of basalts. The
<table>
<thead>
<tr>
<th>Events</th>
<th>$\sigma_1$</th>
<th>Deformation</th>
<th>Metamorphism</th>
<th>Magnatism</th>
<th>Representative Structure</th>
<th>Nickel Mineralisation &amp; Remobilization</th>
<th>Hydrothermal Alteration</th>
</tr>
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<tbody>
<tr>
<td>$D_{FF}$</td>
<td></td>
<td>Previous work interpreted that E-W compression forms the (a) the Foretrastian splay ∼ N-S striking (b) the foreland upfold fold: S$_{um}$ (defined by metamorphic minerals) western limb: striking NS, dipping 60°</td>
<td>Metamorphism 1 (MM): Equilibrium assemblages: Mb act-plg-biot-chl, U: trem-mn4F oliv-chl-sym-tat-tal-cum, Sld: qtz-plg-bio-chlt-msc-ser-amp-plg-car</td>
<td>Late-syn D$<em>{um}$: apline dikes (contain metamorphic S$</em>{um}$ fabric) bst cross-cuts stratigraphy</td>
<td></td>
<td>Primary nickel mineralisation synchronous with cumulate lava emplacement</td>
<td>Seafloor alteration of Mafic rocks (∼ chl-car-hem?)</td>
</tr>
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</table>
| $D_{str} 
\equiv 
\equiv$ | | Continued E-W compression results in coaxial flattening along: a) footwall metasomatism and ultramafic rocks contact; and b) hangingwall metasomatism and a thin sheet of rock contact forming S$_{um}$: N-S striking structures which dip 80°-85° towards the E. | Continued MM. | | | | Dio and car halo around T1 and T5 ore bodies (more pronounced in T5 ore body); fuc in footwall metasomatism rocks; qtz clasts in massive S; secondary (hydrothermal?) pyt overgrowing massive S qtz/plg veins in footwall metasomatism rocks close to ore bodies |
| $D_{FF}$ | Slight rotation of n results in normal movement along D$_{um}$ structures. Movement vector determined by: (a) Car and plg augen's in Sld; (b) S-C fabrics; and (c) Lineations (kinematics more pronounced in the hangingwall of the S-C fabrics) | Continued MM. | | | | |
| $D_{FF}$ | | Characterised by NNE-SSW striking shallow thrusts dipping 5°-10° towards the SE, resulting in development of S$_{um}$ foliation. Tilt block moved NNW based on: (a) lineations (amp and sil rods) ∼ S$_{um}$; 5° towards SE, and L$_{um}$: 5°SE; and (b) displacement of stratigraphy and ore (displacement up to several hundred metres); or evidenced in Sld (S$_{um}$-in situ calcite calcite | Retrograde metamorphism (MM) → late to post D$_{um}$; Mb: chl U: spg-mag-tat Sld: ser/mec-epd-sau-car | Intrusion of Grg stocks → Gd 1 followed by Gd 2 then mafic Grg followed by felsic Grg. Peg intruded as the last phase of magmatism based on cross-cutting relationships; evidence of S$_{um}$ and S$_{um}$ foliation related to drag | | Second remobilization of S occurs at intersection of D$_{um}$ and S (including baran S in metasomatism rocks) which resulted in local smearing of S also observed in ems where py remobilized in fold-hinge and nose of subhorizontal fold axis (i.e. S$_{um}$-in situ calcite calcite) |
| $D_{FF}$ | | Normal ductile brittle faults formed as Grg pooled at triple points (creating T0 and T4 ore bodies) ∼ striking NNW, dipping 60° to the E (Figure 1 in representative structures); Stratigraphy near T1 and T5 ore bodies show back rotation near D$_{um}$ fault planes which is not compatible with kinematics of these low angle thrusts ∼ interpreted to be relaxation during D$_{um}$ as no kinematic evidence to support change in transport direction (Figure 2 in representative structures) | | | Third remobilization of event of nickel via Grg entrapment → Grg entrain a block of massive S and form T3 pipe; entrain $S$ into the magma and $S$ form a matrix to the Grg, Grg dilutes at triple points and smears S down D$_{um}$ faults forming T0 and T4 ore bodies | Marker qtz vein between T0 ore body and footwall metasomatism rock contact; plag phenocrysts in Grg altered to epid and ser; qtz clasts in massive S |
| $D_{FF}$ | Brittle faults: (a) brittle reactivation of D$_{um}$ to D$_{um}$ structures; (b) E-W striking subvertical set (80° towards 345°) related to EW trending dolerite dyke intrusion; and (c) NW striking set dipping 75° towards 210° (which may be conjugate to D$_{um}$ faults) | | E-W trending dolerite dyke intrusions (on a regional scale) pre-syn E$_{um}$ | | | chl-car-ser coating D$_{um}$, brittle faults |

Table 1: Integrated chronology of events at the Flying Fox Deposit (Abbreviations: act=actinolite, amp=amphibol, an=anthophyllite, bio=biotite, car=carbonate, c/o=cumulation cleavage, chl=chlorite, cum=cummingstonite, dio=diopside, en=enstatite, epd= epidote fuc=fuchsite, gar=garner, Gd=Gd-granulite, Grg=Grg, hem=hematite, Mb=mafic rocks (tholeiite), mgs=mafic gneiss, msc=mafic craton, oliv=olivine, oliv-musc=olivine olivine, plag=plagioclase, pyt=pyrite, ph-phlogopite, qtz=quartz, sau=sauvsite, ser=sericite, sil=sillimanite, spg=serpentinite, tal-talc, trm-trondhjemite, Um-ultramafic rocks, $S$=sulphides).
second phase of hydrothermal alteration is related to fault zones evident by a marker quartz vein at the contact between T0 ore and footwall mafic rocks, diopside and carbonate (calcite) alteration of ultramafic rocks adjacent to D1FF structures and secondary pyrite overgrowing massive sulphides. The third phase of alteration is defined by chlorite-carbonate-sericite alteration zones surrounding D2FF structures.

An integrated descriptive model for the Flying Fox deposit is shown in Table 1. The first deformation event (D0FF) is defined as magmatic nickel mineralisation and is characterized by seafloor alteration of the basalts. Interpreted regional isoclinal folding occurred during D1reg and was accompanied by regional prograde metamorphism (MM1). The first nickel remobilization event occurred during D1bFF and D2FF where increased temperatures (likely > 600°C) reverted sulphides to MSS. The MM1 waned post D2FF and retrograde metamorphism likely occurred post D3FF. The second sulphide remobilization event is interpreted during D3FF where sulphides were smeared locally along D3FF fault planes. The granitic stocks intruded post D3FF, exploited D3FF structures, “entrained” sulphides and locally remobilized them (third remobilization event). During D4FF granite magma pooled at two triple points - defined by Weinberg et al (2004) as zones of high differential stress and low mean stress. The two triple points at the Flying Fox deposit are identified at the intersection of the D3FF structures with the metasedimentary/ultramafic rock contact where granite magma dilated down “smearing” sulphides along the contact creating brittle-ductile faults that form the T0 and T4 ore bodies (fourth remobilization event). Backrotation of the stratigraphy between D3FF fault planes is interpreted to be the result of relaxation during E-W extension. The D3FF event is defined by brittle faulting and reactivation of the D1FF to D3FF structures which may be caused by the intrusion of the dolerite dyke.

5 CONCLUSIONS

The Preliminary investigations have demonstrated that the Flying Fox deposit has experienced a complex history which has resulted in up to four phases of sulphide remobilization that has significantly controlled the overall geometry of the ore bodies.

ACKNOWLEDGEMENTS

Special mention to Western Areas NL for their financial support and John Miller for advice related to structural events.

REFERENCES


Footwall-type Cu-Ni-PGE Mineralization in the Broken Hammer Area, Wisner property, North Range, Sudbury Structure

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ABSTRACT: We report results from two main footwall-type Cu-Ni-PGE occurrences (Broken Hammer Zone and the South Zone) on the Wisner Property. The observed mineralization includes massive sulphide veins, disseminated/replacive mineralization and silicate-quartz dominated veins. All assemblages are dominated by chalcopyrite, millerite, magnetite and/or pyrite, quartz and hydrous silicates, which are accompanied by PGM and other trace phases. Drilling dataset of both occurrences revealed systematics of metal distribution and highlighted differences between the two studied mineralization. Most of the features observed in the two occurrences are in agreement that a high salinity, relatively high temperature (400-500°C) magmatic-hydrothermal system was responsible for Cu-Ni-PGE deposition, and there is no proof for the initial emplacement of a fractionated sulphide melt.

KEYWORDS: Sudbury, Cu-Ni-PGE ore, platinum-group minerals, fluid inclusions

1 INTRODUCTION

Footwall-type Cu-Ni-PGE deposits are the main focus of recent exploration in the Sudbury camp due to their higher Cu and precious metal contents in comparison to the magmatic sulphide orebodies situated along the lower contact of the Sudbury Igneous Complex (SIC). The most well-known footwall-type orebodies occur in the Onaping-Levack area of the North Range (McCreedy East and West, Strathcona Copper and Deep Copper Zones), but important deposits are also found along the East Range (Fig.1.)

The origin of these vein-type, Cu-PGE-rich footwall deposits has been debated for many years. One kind of models argues that hot, highly saline hydrothermal fluids driven by the heat of the cooling SIC leached out metals from contact mineralization and re-deposited them in brecciated footwall units (Farrow et al. 1997; Molnár et al. 2001; Farrow 2005). Others favour an initial emplacement of a highly fractionated sulphide liquid into the footwall, followed by later redistribution of metals by hydrothermal fluids (Morrison et al. 1994; Li & Naldrett 1993; Jago et al. 1994).

In this study we report results from main footwall-type Cu-Ni-PGE occurrences (the Broken Hammer and South zones) of the Wisner property, which were all discovered by the Wallbridge Mining Company Ltd. in 2003 and 2004.

Fig.1. Geological map of the Sudbury Structure. Major contact and footwall orebodies and the location of the studied area are indicated.
2 GEOLOGY OF THE STUDIED AREA

Footwall rocks on the Wisner property belong to the Archean Levack Gneiss Complex and several later intrusions. These include granitoids of the Cartier Batholith, diabase dikes of the Matachewan dike swarm, and the Wisner Gabbro intrusion. All these footwall rocks suffered intense brecciation at the 1.85 Ga Sudbury Impact Event.

Discoveries are situated in intensely Sudbury brecciated zones of the footwall 1300 and 700 meters (Broken Hammer and South Zone, respectively) north of the present SIC-footwall contact. Mineralization has been classified into three groups: (1) massive sulphide veins, (2) disseminated/replacive mineralization and (3) silicate-quartz dominated veins. The distribution of sulphide and silicate-quartz dominated veins shows strong structural control. At the Broken Hammer Zone a very dense stockwork of these veins has a major NE-SW trend. Another structural orientation (SE-NW) is also important in controlling Cu-Ni-PGE bearing vein systems, especially at the South Zone.

3 PETROGRAPHY

3.1 Massive sulphide veins

At Broken Hammer, sulphide veins (up to 30 cm width) are especially found within the most intensely brecciated zone, and follow the main strike of the hydrothermal stockwork (NE-SW). The ‘Big Boy’ vein is a shallow dipping sulphide vein (up to 1m in width) following the orientation of a Sudbury Breccia zone (WNW-ESE).

Sulphide veins are dominantly made up of chalcopyrite, which hosts various amounts of magnetite, sulphides, quartz and hydrous silicates. Millerite is the main Ni-bearing phase, which shows an increased abundance in distal sulphide veins. Other accessory sulphides are: pyrite, pentlandite, sphalerite, galena. Bornite, covellite and violarite mostly occur as late, replacive phases. Narrow (up to 3 cm) sulphide veins at South Zone have similar mineralogy, although they contain octahedral pyrite instead of magnetite.

Quartz and hydrous silicates are important constituents of sulphide veins; their amount is quite variable, however it is mostly around 20-30 vol.%. These phases (epidote, actinolite, biotite) often occur as euhedral, isolated inclu-

3.2 Disseminated/replacive ore

High grade Pd+Pt+Au (TPM) assemblages are also found disseminated in Sudbury Breccia and footwall rocks, or form pervasive replacements in them. This type of mineralization often occurs with no connection to sulphide veins, but is confined to lithological changes. Amount of sulphides in these assemblages is highly variable; it can be as low as several percents, and yet in most cases this style of mineralization is highly PGE-bearing. At South Zone, this is the main style of Cu-Ni-PGE mineralization.

Disseminated and replacive mineralization is mineralogically similar to sulphide veins, however, assemblages are dominated by hydrous silicates, which enclose the sulphides.

3.3 Silicate-quartz dominated veins

Veins dominated by actinolite, epidote, chlorite and quartz containing various amounts of sulphides and haematite are very abundant within the mineralized zone of both localities. They often have anomalous TPM contents up to several g/t.

4 PLATINUM-GROUP MINERALS (PGM) AND OTHER TRACE PHASES

In massive sulphide veins and disseminated ore, PGM and other trace metal phases are located within sulphides and hydrous silicates and at their grain boundaries (Fig.2). Most commonly they can be observed in the form of composite grains consisting up to 5 phases, but nearly euhedral grains of single phases also occur.

Within the composite grains wittichenite (Cu$_3$Bi$_3$S$_3$) is the most abundant phase accompanying precious metal minerals and is found as an outer rim towards chalcopyrite, or forming symplectite with merenskyite (PdTe$_2$) (Fig. 2A). Cassiterite is another common phase in these assemblages, while melonite (NiTe$_2$), telluobismuthite (Bi$_2$Te$_3$), tetradymite (Bi$_2$Te$_2$S) and clausthalite (PbSe) were only found in few
The most common Pt-mineral at Broken Hammer is sperrylite (PtAs₂), which always forms very large (up to 2 mm) euhedral grains within chalcopyrite groundmass, and is never found in the composite grains. At South Zone sperrylite was not observed, and the dominant Pt-mineral is moncheite (PtTe₂). Dominant Pd-bearing phases at both occurrences include merenskyite (PdTₑ₂), and unknown Pd-sulphide (CuPdBiS₃) and michenerite (PdBiTe) (Fig. 2A). The unknown phase is present in almost every massive sulphide and disseminated ore sample from both localities and occurs within composite grains, or as individual, irregular grains up to 200 µm. In this phase Pd might be substituted by up to 2.8 wt.% Ni, and is most probably the Pd-equivalent of mückeite (Cu-NiBiS₃) (Watkinson et al. 2005).

Other precious metal minerals found in only few samples include: kotulskite (PdTₑ), sopcheite (Ag₄Pd₃Te₄), Au-Ag alloy (Au₆₅Ag₃₅), hessite (Ag₂Te), naumannite (Ag₂Se), bohdanowiczite (AgBiSe₂).

5 METAL DISTRIBUTION

Depending on sulphide content, the concentration of Cu in massive sulphide vein grab samples can be as much as 35 wt.% The concentration of Ni is much more variable; it is mostly under 0.05 wt.%, but gets as high as 5 wt.% in distal millerite-rich veins. Sulphide veinlets at South Zone have Ni-contents of 0.2-0.6 wt.%. Concentration of Pd in veins is quite constant (around 20-40 g/t in grab samples), but the distribution of Pt and Au shows nugget effect. Thus TPM contents in grab samples vary between 20-70 g/t, and there is no correlation with the percentage of sulphides.

TPM contents of disseminated ore may also reach 50 g/t, regardless of the amount of sulphides. As sulphides are, in general, slightly disseminated to semi-massive, the relative precious metal grade is often much higher than in massive sulphide veins [Cu/TPM values usually under 1000, in comparison to values of more than 5000 (mostly well above 10000) for massive sulphide veins].

Deposit-scale metal distribution was investigated using drilling dataset from Wallbridge Mining Company Ltd. Both occurrences show strong Cu-enrichment (average Cu/(Cu+Ni) values of 0.81 and 0.84) typical for Sudbury footwall deposits. Average Pt/(Pt+Pd) values of 0.43 and 0.48 are also comparable to values of other footwall deposits in the Sudbury camp. Pd concentrations show strong positive correlation with Cu and S values, and with the following trace elements (in decreasing order): Te, In, Sn, Cd, Bi, Zn. The correlation coefficients of Pt are very different for the two studies areas. At Broken Hammer, Pt is only well correlated with As, and shows no correlation with other metals, including Cu, Ni and Pd. In contrast, Pt shows similar correlation patterns to Pd at the South Zone. The systematics in correlation coefficients are well understood considering the platinum-group mineralogy of the two occurrences.

6 FLUID INCLUSION STUDIES

During fluid inclusion petrography of samples from the various Cu-Ni-PGE mineralization types we could distinguish three inclusion generations according to their phase compositions at room temperature.

**Type IA saturated aqueous inclusions** have polyphase (Laq+ V+ S_halite+ SX₁±SX₂) composition and always contain an oval shaped green daughter mineral, with dark outline and weak anisotropy (referred as SX₁) (Fig. 3A). Type IA inclusions are primary in quartz of massive sulphide and silicate-quartz dominated veins, and in the newly formed parts of recrystallized rock forming quartz in disseminated ore.

**Type IB saturated aqueous inclusions** also have polyphase Laq+ V+ S_halite+ SX₂ compositions, but they do not contain the green SX₁ phase (Fig. 3B). They are primary in quartz of silicate-quartz dominated veins.
Type II unsaturated aqueous inclusions have a liquid + vapor (L\textsubscript{aq} + V) phase composition at room temperatures (Fig. 3C). Type II inclusions occur in fracture-related fluid inclusion trails of quartz in all studied assemblages, thus are referred as late secondary in these samples.

In type IA inclusions, the last phase to dissolve was always the green SX\textsubscript{1} phase, which gave total homogenization temperatures of 415 to 492°C. Dissolution temperatures of halite (223-363°C) correspond to 33-44 wt.% NaCl eq. salinity of this fluid type.

Total homogenization of type IB inclusions was achieved by dissolution of halite between 219 and 371°C. These dissolution temperatures correspond to salinities of 29-44 wt.% NaCl eq. In cases where freezing of inclusions could be achieved, eutectic melting temperatures range from -50 to -75°C, while final melting of ice occurred between -43 and -62°C. Type II secondary inclusions always homogenized to liquid between 105 and 157°C. Eutectic melting in the range of -50 to -54°C and ice melting temperatures of -13 to -30°C, hence salinities were calculated for CaCl\textsubscript{2}-H\textsubscript{2}O model compositions and values are between 17-25 wt percent CaCl\textsubscript{2} eq.

7 CONCLUDING REMARKS

During this study we outlined characteristics of Cu-Ni-PGE mineralization observed at newly discovered occurrences of the Wisner property. Mineralization in this segment of the footwall of the SIC has not been known before.

Our fluid inclusions studies revealed three fluid generations, which are very similar to those described from well-known footwall-type deposits in the Onaping-Levack area (e.g. Li & Naldrett, 1993; Molnár \textit{et al.}, 2001). Polyphase fluid inclusions being primary in Cu-Ni-PGE bearing assemblages represent a highly saline (30-40 wt.% NaCl eq.) magmatic-hydrothermal system with a high temperature (min. 450-500°C) and a lower temperature (min. 300-350°C) stage.

In our opinion most of the features observed in the two studied occurrences are in agreement that magmatic-hydrothermal processes were responsible for Cu-Ni-PGE deposition, and there is no proof for the initial emplacement of a fractionated sulphide melt.

ACKNOWLEDGEMENTS

Authors thank the support of the Canada-Hungary Science and Technology Agreement (project CAN-02/04) and NSERC grant No. No.7874 to D.H.W., Wallbridge Mining Company Limited and Xstrata Nickel.

REFERENCES


Origin of large and unique PGE-Cu-Ni deposits of large igneous provinces: evidence from Northern Siberia and Fennoscandian Shield

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ABSTRACT: The problem of the origins of large and unique PGE-Cu-Ni sulphide ore deposits, related to mafic-ultramafic intrusions, is discussed using examples of three large igneous provinces on Russian territory: the Phanerozoic Siberian traps (Noril’sk district), and two Palaeo-proterozoic examples on the Fennoscandian Shield namely (1) the early Palaeoproterozoic Baltic LIP (Monchegorsk district) and the middle Palaeo-proterozoic Jatulian-Ludikovian LIP (Pechenga district, Kola Peninsula). It is shown that development of such deposits was linked in combination with favourable geological-petrological factors.

KEYWORDS: large igneous provinces; layered mafic-ultramafic intrusions; sulphide PGE-Cu-Ni ore deposits; Noril’sk, Pechenga, Monchegorsk

1 INTRODUCTION

Large igneous provinces (“LIP’s”) are widely represented in geological history of the Earth from the Palaeo-proterozoic to the Cenozoic. The most important type of their ore mineralization are large, and often unique, sulphide PGE-Cu-Ni ore deposits related to mafic-ultramafic intrusions. However, despite of the huge sizes of these provinces, such deposits are very rare. Why is this? We will discuss this problem using examples from the Phanerozoic Siberian and from two Palaeo-proterozoic Fennoscandian large igneous provinces on Russian territory.

2 PERMIAN-TRIASSIC SIBERIAN TRAPS

The Siberian trap province (240-250 Ma) is formed mainly by tholeiitic basalt sheets and sill-like mafic, rarely mafic-ultramafic intrusions and is the largest known example on the planet. In the NW of the platform, in the Noril’sk district, this province contains the unique sulphide PGE-Cu-Ni ore deposits (Talnakh, Oktyabr’skoe, Noril’sk I and Vostochno-Noril’skoe) (Duzhikov et al., 1988). Such deposits are practically absent across all the other extent of the Siberian traps or, in the best case, have sub-economic importance.
rites, pyroxenites and chromitites. Within the bottom exocontact thick (up to 300m) metasomatic zones are developed within the sedimentary wall rocks. Sulphide Cu-Ni-PGE mineralization is present in various styles: (1) disseminated mineralization in picritic and tachytic gabbro-dolerites; (2) massive sulphides, which form large bodies, up to 40 metres in thickness which may extend as replacive masses into underlying metamorphic and metasomatic rocks; (3) veinlet disseminated mineralization between bodies of massive sulphides; and (4) low sulphide PGE mineralization within chromitite-bearing olivine gabbro in the upper sections of the intrusions.

3 PALAEO-PROTEROZOIC “LIP’s” OF THE FENNOSCANDIAN SHIELD

Palaeo-proterozoic Cu-Ni-PGE mineralization is linked in this region with two large igneous provinces: (1) the middle Palaeo-proterozoic, located within the Pechenga structure on the Kola Peninsula (Escola, 1963), and, (2) the large layered intrusions of the early Palaeo-proterozoic Baltic igneous province of the siliceous high-Mg (boninite-like) series (SHMS) (Sharkov et al., 1997).

The Pechenga mineralization, dated at 1.98Ga, is associated with minor coarsely layered mafic-ultramafic intrusions injected within metasediments of the “Productive Pile” of the Pechenga Formation. Parental magmas of these intrusions were ferropicrites similar to lavas seen in the upper parts of the Formation. Sulphide Cu-Ni mineralization is represented by disseminated, veinlet-disseminated, breccia-like and massive sulphides (Gorbunov et al., 1999). Disseminated sulphides are typical for the central and upper parts of the intrusions whilst veinlet-disseminated occur near to the bottom; breccia-like and massive ores confined to tectonic zones along the lower endocontacts of the intrusions.

According to isotopic data, the sulphide mineralization has a complicated genesis as they show evidence of primary-mantle material as well as material remobilized as a result of metamorphic and metasomatic processes.

Large mafic-ultramafic layered intrusions with PGE-Cu-Ni deposits form parts of a large igneous SHMS province which evolved from 2.5 to 2.35Ga. These intrusions are located in the eastern part of the Baltic Shield. They were mainly formed during initial stages of Palaeo-proterozoic rifting, and are usually found at elevated shoulders of rifts which are infilled by boninite-like volcanics of an equivalent age. On the Kola Peninsula they evolved in the surroundings of the Pechenga-Varzuga rift zone and are also represented by the Monchegorsky and the Imandra complexes as well as in the Pana-Fedorova Tundras and on Mount General’skay. In Russian Karelia such intrusions are found in the north (Lukkulaisvaara, Tsipringa and Kivakka) and in the south where the largest in the Europe, the Burakovka massif, exists. (Sharkov & Smolkin, 1998). These intrusions are formed by rhythmic alternation of dunites, harzburgites, bronzitites, norites, gabbronorites and anorthosites and have compositions close to the classic layered intrusions such as the Bushveld and Stillwater.

Despite the general similarity in rock composition and in their overall morphology and cross-section, each of these intrusions have their own individual features in structure and sulphide mineralization. The most diverse mineralization is seen in the Monchegorsky complex, where economic Cu-Ni sulphide ores, chromites and PGE are known; in the Burakovka complex - chromites and PGE; in the Mount General’skaya complex - Cu-Ni-PGE; and at Fedorovo-Pansky and Lukkulaisvaara - low sulphur PGE mineralization.

Detailed studies of these intrusions have shown that replenishment of fresh magmas from underlying transitional chambers played an important role in their origin. However, only some of new magmas were enriched in mineralizing components. For example in one such reef-type deposit as the “Sopcha ore bed” in the Monchegorsky layered pluton, a horizon of thin-layered peridotites 2-3 meters thick contains rich sulphide disseminations, whose origin can only be explained by injection of a new pulse of fresh magma injected along the temporary base of the intrusive chamber.

4 DISCUSSION AND CONCLUSIONS

A question that continually arises is why are only rare portions of the replenished magmas metalliferous? We suggest that this is linked to features relating to the origins of the siliceous high-Mg magmas. Judging by isotopic and geochemical data, such magmas formed as a result of large scale assimilation by mantle-derived melts of Archaean crustal material. We believe
that the buoyancy and migration of the high-temperature mantle-derived magma body through the crust was by the zone refinement principle, which is by melting of the roof accompanied by crystallization at the bottom (Sharkov et al., 1997).

From such a point of view, the reefs appearance was linked with assimilation by such magma bodies of Archaean supracrustal rocks, enriched in metallic components (PGE, Ni, Cu, etc) and chlorine- and sulphur-bearing fluids and brines, which favoured the mobilization of such elements and their fixation in mineral form. Such supracrustal rocks could be komatiites, black shales, sulphide-bearing metasediments, etc. If such rocks were absent from the upward path of the ascending magma bodies, reefs are also absent, which are seen well in numerous examples of barren layered intrusions composed by similar rocks throughout the world, but without sulphide mineral deposits.

To summarize, it is necessary to stress that in spite of the widespread development of similar magmatic rocks over a vast territory, in all cases only one large occurrence of sulphide PGE-Cu-Ni mineral deposits occurs. These occurrences are characterized by combination by at least three similar features:

1. long term formation of the structures where ore deposits located (more than 300Ma in the case of Noril’sk district, where faults were inherited from the Neoproterozoic rift zones; and about 600Ma in the case of the Pechenga structure which located on the place of the late Archaean greenstone belt and evolved during the early Palaeo-proterozoic);

2. presence beneath them of ancient highly-depleted mantle where the PGE had accumulated in residuals during former multiple episodes of melting;

3. presence of the S- and Cl-bearing sediments in these places: Neoproterozoic and Palaeozoic evaporites in the Noril’sk region; early Palaeo-proterozoic and Archaean sulphide-bearing metasediments into the Pechenga structure and in it’s basement, as well as metamorphosed sulphide-bearing metasediments of the Archaean Kola Fm, which enclose the Monchegorsky pluton. Probably, it was not only the wall-rocks of the intrusions, but also rocks assimilated during the ascendancy of the magmatic chambers, as demonstrated by Grinenko & Hanksi (2003) using the Keivitsa ore deposits in Finland using oxygen and sulphur isotopy.

Thus, the type of tectonomagmatic activity is not the only reason for appearance of large and unique PGE-Cu-Ni mineral deposits, but it is also necessary to exist other factors, especially those mentioned above. In places, where such a combination is absent, no large mineral deposits form, in spite of the similar characteristics of the magmatic activity. Moreover, in the case of large mafic-ultramafic layered intrusions it is necessary to take into account that the appearance of platiniferous reefs is unpredictable, because it depends on PGE-bearing horizons existing in the crust on the path of the ascending magma body. So cross-sections of each large layered intrusion should be studied carefully during prospecting works as reef could be found in any location.

ACKNOWLEDGEMENTS

Work was supported by grant RFBR # 04-05-64581

REFERENCES


Syntectonic gabbro-norite-hosted Ni-Cu-(Co) mineralization in the western Mesoproterozoic Namaqua Province, South Africa: a new Ni-Cu district?

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ABSTRACT: Exploration in the western Namaqua Province has located noteworthy massive sulphide Ni-Cu-Co mineralization occurring as several small, flattened and attenuated bodies associated with an orthomagmatic gabbro-norite host rock. Textural and geochemical characteristics suggest that the deposits are the result of a sulphide-rich, calc-alkaline basaltic magma that syntectonically intruded a multiphase deformed and ultra-metamorphosed supracrustal sequence. Similarities to the cupriferous mafic rocks of the O’kiep Copper District indicate a common magmatic source and the possible existence of a peripheral Ni-Cu district.

KEYWORDS: magmatic, massive sulphide, Ni-Cu-Co, mesoproterozoic

1 INTRODUCTION

The considerable increase in metal prices, in particular in that of copper and nickel, over the past number of years, has initiated renewed interest in the exploration for magmatic Cu and Cu-Ni deposits in the western Namaqua Province South Africa.

Several small Ni-Cu-(Co) deposits occur south of the well-known O’kiep Copper District in south-western Namaqualand and are the focus of an extensive exploration program presently in progress. Copper and nickel soil geochemistry anomalies and small gossans, supported by positive ground magnetic and electromagnetic geophysical surveys were tested by core drilling. At this stage a total of some 8000m of drilling has outlined a shallow resource of 4mt massive sulphide mineralization with a grade of ~0.9% Ni, ~0.20% Cu and 400ppm Co.

The aim is to introduce these relatively unknown deposits with respect to their geometry, mineralogy and geochemistry. Of particular interest will be to compare them to the well-studied suite of cupriferous basic rocks of the Koperberg Suite in Namaqualand from a genetic and exploration point of view.

2 GEOLOGICAL SETTING

The deposits occur in the southern part of the Bushmanland Subprovince of the Namaqua Province. Granitic and charnokitic orthogneisses enclose remnant belts of highly metamorphosed supracrustal rocks of the Namaqualand Metamorphic Complex, the southern extension of the 1200Ma Kibaran orogenic episode of central Africa (Thomas et al., 1994). This episode is characterized by polyphase tectonism, regional metamorphism and large scale plutonism.

In the area where most of mineralization occurs the supracrustals have been subjected to ultra-metamorphism (P 5kbar and T >850°C) and consist of calcareous, pelitic, semipelitic, quartzose, quartzo-feldspathic and mafic units. These have been deformed into east-west trending interference patterns in which broad domal structures feature prominently (Albat 1984). During the c. 1100Ma peak metamorphic event the western Subprovince was intruded by small, mafic dyke-, sill- and plug-like bodies, some of which are cupriferous (O’kiep Copper District). Although several very low grade nickel deposits have been investigated in the past, there are no operating nickel mines associated with mafic rocks of Kibaran age.
3 THE NI-CU-CO DEPOSITS

3.1 Local geology

The best nickel-copper resources discovered thus far are located near Kliprand. On surface these are indicated by gossan cappings associated with attenuated and flattened mafic bodies of the Nuwefontein Suite, which occur over a strike length of several kilometres (Fig. 1). Regional observations confirm that the mafic bodies are possibly pre- but clearly syntectonic and have been affected by the pervasive regional metamorphism and deformation. The mafic rocks can be classified as meta-gabbro-norites (Le Maitre, 1989) and where mineralized are hosted by a narrow zone of banded migmatitic biotite-garnet paragneiss. The gabbro-norite bodies are flattened, folded and orientated parallel to the migmatite banding, suggesting structural control during emplacement and subsequent deformation. Consequently some of the more closely spaced mineralized bodies could represent a larger dismembered sill. The migmatite zone has also been late tectonically intruded by a megacrystic charno-enderbite which contains a diversity of supracrustal xenoliths but also mafic rocks of the Nuwefontein Suite clearly demonstrating their temporal relationships.

3.2 The host rock

The gabbro-norite-sulphide relationships are illustrated in Figure 2. Most of the sulphide lenses are located at the structural base of the gabbro-norite. Contact relationships are clearly gradational ranging from massive at the base to disseminated sulphides in the mafic host rock.
Deformation of the ore lenses is common and resulted in the concentration of plastic sulphides such as pyrrhotite in fold hinges (Fig. 2).

The host rock is mainly a medium-grained gabbro-norite consisting of plagioclase (An_{45-55}), orthopyroxene (En_{53-62}), clinopyroxene (Wo_{45-En_{35-Fs_{20}}}) and phlogopite with minor quartz, apatite and opaque minerals. Where clinopyroxene is absent the rocks contain less phlogopite and have a noritic composition and when orthopyroxene is absent they are dioritic. Glimmerite is locally developed. Mineral textures are equidimensional, interlobate and granoblastic. Deformed phlogopite and plagioclase twins as well as serrated grain boundaries that meet in equal angle triple boundaries, indicate that the mafic bodies have been affected by tectonism and recrystallized during metamorphism.

The ore mineral assemblage is dominated by massive magnetic pyrrhotite hosting exsolved cobaltian pentlandite flames and irregularly shaped chalcopyrite blebs (Fig. 4). Euhedral pyrite mostly surrounded by pyrrhotite is a minor constituent with accessory sphalerite, rare cubanite and mackinawite. Outside the ore zone, ilmenite is by far the most abundant opaque mineral. Ore textures indicate sulphide mobility the result of deformation and prograde metamorphism.

The effects of possibly Pan-African retrograde metamorphism (Clifford et al., 1995) are displayed by the alteration of pentlandite to violarite and pyrrhotite to a fine-grained mixture of marcasite and pyrite. Pyrrhotite alteration is visible as typical birds-eye textures developed along its basal cleavage planes.

Textures of both the silicate and ore assemblages indicate that these rocks have been subjected to regional metamorphism after emplacement.

4 GEOCHEMISTRY

A major and trace element lithochemical study representative of the Nuwefontein Suite (Kliprand) and excluding sulphide mineralized gabbro-norite, was conducted by Hamman et al. (1996). They showed that the suite is confined to the hypersthenic rock series and has a calc-alkaline character. The Al and Fe enriched nature of the gabbro-norite was suspected as having a connection to anorthosite complexes and their parent magmas based on the interpretation of Adirondack gabbros (Olson and Moore 1990). Mantle normalized multi-element diagrams show that the Suite has geochemical characteristics of calc-alkaline basaltic magma (Hamman op cit; Saunders et al., 1980). Sulphur isotopic composition of pyrrhotite from both the massive and disseminated ore showed $\delta^{34}$S ratios which vary in a narrow range from -2.2 to -3.6‰. Sulphur derived from the mantle has an isotopic composition very similar to meteorite sulphur and according to Ohmoto (1986) it is highly unlikely that magmas which originated from the upper mantle would produce igneous rocks with $\delta^{34}$S ratios outside the range of -3 to +3‰. Despite the observed effects of metamorphism and deformation the sulphur isotope composition of the gabbro-norite hosted ore, has remained remarkably close to those of the mantle range indicating very limited oxida-
tion or devolatilization.

5 DISCUSSION

The small gabbro-norite associated Ni-Cu-Co-bearing massive sulphide bodies have the characteristics of orthomagmatic deposits associated with mafic and ultramafic intrusions (Naldrett, 2004). The gravity induced accumulation of almost massive pyrrhotite with minor pentlandite, chalcopyrite and pyrite towards the base of its host rock is one of the typical features of such deposits. Although the complex structural setting of the gabbro-norites precludes the positive identification of the original attitude of the pre- to syntectonic sill-shaped intrusions, the gradational contact between the disseminated and massive sulphides would suggest a similar but modified relationship. This would imply a similar genesis where sulphide concentrations are the result of accumulation of dense immiscible sulphide droplets derived from sulphur-saturated to over-saturated calc-alkaline basaltic magma.

Hamman et al. (1996) have compared mafic rocks of the Nuwefontein Suite to those of the Koperberg Suite of the Okiep Copper District located to the north. They concluded that the suites are mineralogically and geochemically very similar and are possibly genetically related sharing a common magmatic source. The predominance of low sulphur copper deposits and absence of massive sulphide Ni-Cu mineralization in the latter is explained by a two stage emplacement model. The early gabbro-norite phase intruded as sills and dykes together with Ni-Cu-Co massive sulphide mineralization mainly in southern Namaqualand. This was followed by a later phase of magma accumulation and fractional crystallization to produce anorthosite cumulates towards the top and low sulphur hypersthene-copper-sulphide-magnetite liquid-cumulate mixtures towards the floor of the chamber. Tectonically induced sequential intrusion of the differentiates produced early barren anorthosite phases followed by later more mafic cupriferous bodies in the O’kiep Copper District.

This model has important implications with respect to the exploration potential for magmatic nickel deposits in the southern Bushmanland Subprovince. A common magmatic source could imply the existence of a Ni-Cu district of similar dimensions to that of the well known O’kiep Copper District. Indications are that such a district would be geographically peripheral to the latter and located in areas where deeper crustal level have been exhumed.

REFERENCES


ABSTRACT: Os-rich alloy grains from two localities (Ingaringda and Burlakovsky placers) within the southern part of the Guli clinopyroxenite-dunite massif (Maimecha-Kotui Province, Russia) have been studied by a number of modern techniques (SEM, EMPA and LA MC ICP-MS). Os-rich alloy grains divided into six morphological types are controlled by their chemical composition (i.e., osmium and iridian osmium) and partly by the Os isotope composition. The Os isotope composition of Os-rich alloys at Ingaringda and Burlakovsky, with a narrow range of subchondritic $^{187}$Os/$^{188}$Os values, is consistent with a highly productive single-stage formation of Os-rich minerals. Calculated $^{187}$Os/$^{188}$Os model ages of osmium and iridian osmium constrain the age of ultramafic protoliths in the northern part of the Siberian Craton indicating that this event took place in the Late Proterozoic.

KEYWORDS: osmium, Os isotope composition, Guli massif, Siberian Craton

1 INTRODUCTION

The Guli clinopyroxenite-dunite massif, like other clinopyroxenite-dunite massifs, e.g. Kondyor and Inagli (Malitch, 1999), is situated at the periphery of the Siberian Craton. The presence of economically important platinum-group element (PGE) placers in spatial association with ultramafites is a specific feature of these massifs. This contrasts with dunite-harzburgite (ophiolite-type) complexes that do not have economic placer deposits. The unique features of the Au-PGE placers at Guli are, (1) the dominance of Os-rich alloys over other platinum-group minerals (PGM) and Au, and, (2) the considerable potential resources of noble metals, particularly osmium (Malitch et al. 1998; 2002).

In this contribution, we for the first time, focus on mineral chemistry of distinct morphological types of Os-rich grains from two localities within the Guli massif, for which Os isotope composition has been obtained by laser-ablation attached to multiple collector inductively coupled plasma mass spectrometry (LA MC ICP-MS). This investigation forms part of more extensive study that aims to place Os-isotope constraints on the origin of clinopyroxenite-dunite complexes (Malitch 1999).

2 GEOLOGICAL BACKGROUND AND SAMPLE LOCATION

The distinctive feature of the Guli ultramafic massif, located in the Maimecha-Kotui province of northern Siberia, is its considerable size. It is controlled by the Taimyr-Baikal and Enisei-Kotui palaeo-rift structures. Dunite (Fo$_{85-91}$) predominates, forming a crescent-shaped, plate-like body 30km long and 10 to 15 km wide covering an area of approximately 450 km$^2$, which dips 15° to 20° to the northwest. Vein-type bodies of chromitite are abundant at the southern peripheral part of the massif. Wehrlite and magnetite-rich clinopyroxenite form dikes, stockworks and lenticular bodies within the dunite.

The main geological characteristics of the Guli massif, the world’s largest clinopyroxenite-dunite massif, and associated placer deposits have been summarized by Malitch & Lopatin (1997) and Malitch et al. (2002).

This study is based on 165 Os-rich alloy grains (size range between 0.25 and 0.5mm), which were collected during prospecting in the area of the Ingaringda River at two localities in the southern part of the Guli massif. 117 grains investigated were derived from Quaternary sediments of the Ingaringda River (i.e. from...
prospecting line 365), whereas 48 grains were collected from the Burlakovsky stream (prospecting line 2), the left tributary of the Ingaringda River.

3 ANALYTICAL METHODS

After investigation by scanning electron microscopy (SEM) and electron microprobe analysis (EMPA), the Os-rich alloy grains were measured by laser ablation (LA) and multiple collector inductively coupled plasma mass spectrometry (MC ICP-MS) at Technical University of Mining and Metallurgy (Freiberg, Germany) and All-Russia Geological Research Institute (St. Petersburg, Russia). Technical details of the method and principal factors that influence the accuracy of LA MC ICP-MS analyses are presented elsewhere (Becker & Dietze 2000; Junk 2001; Malitch 2004a; b).

4 RESULTS AND DISCUSSION

4.1 Granulometry and morphology of Os-rich grains

The granulometric composition of Os-rich grains at Ingaringda and Burlakovsky is determined by five size classes (in mm): 0.25-0.5 (56 and 63 %, respectively), 0.125-0.25 (33 and 29 %), 0.5-1.0 (9 and 7 %), >1 (about 1 and 0 %), <0.125 (around 1 % each), implying that the size range 0.25-0.5 mm dominates the PGM budget of placer deposits.

By morphology Os-rich grains were divided into six types. Well preserved euhedral crystals are characteristic of type 1, whereas type 2 consists of partly preserved euhedral crystals that also show irregular shapes. Both types are dominated by a grey colour and a metallic appearance. Type 3 and 4 are formed by subhedral to unhedral crystals and rarely as mineral aggregates composed by irregularly shaped minerals of grey colour, frequently with yellow tone (i.e. type 3) or dark brown colour (i.e. type 4). Type 5 grains consist of well preserved mineral aggregates (up to 4-5 crystals) dominated by grey colour and metallic luster (similar to type 1), whereas type 6 forms polyphase aggregates, up to hundreds of crystals that show features similar to type 2, 3 and 4. Among Os-rich grains (Table 1) type 2 and 3 dominate at Ingaringda (36.52 and 29.56 %, respectively), whereas type 5 and 2 are predominant at Burlakovsky (47.92 and 33.34 %, respectively).

Table 1. Distribution (%) of Os-rich alloy morphological types (grain size 0.25-0.5 mm)

<table>
<thead>
<tr>
<th>Type</th>
<th>Ingaringda (n=115)</th>
<th>Burlakovsky (n=48)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>9.57</td>
<td>8.33</td>
</tr>
<tr>
<td>Type 2</td>
<td>36.52</td>
<td>33.34</td>
</tr>
<tr>
<td>Type 3</td>
<td>29.56</td>
<td>8.33</td>
</tr>
<tr>
<td>Type 4</td>
<td>6.09</td>
<td>-</td>
</tr>
<tr>
<td>Type 5</td>
<td>14.78</td>
<td>47.92</td>
</tr>
<tr>
<td>Type 6</td>
<td>3.48</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Figure 1. Chemical composition of Os-rich alloys at Ingaringda (a) and Burlakovsky (b) in coordinates Ir – Os.

It should be noted that short transport distances are indicated by the preservation of crystal shape of Os-rich grains and this is more pronounced at Burlakovsky (Table 1).

4.2 Chemistry of Os-rich alloys

The majority of Os-rich grains at Ingaringda and Burlakovsky, both single crystals (e.g., euhedral, subhedral, etc.) and aggregates of Os-rich crystals, are Os-rich alloys (osmium, according to the classification by Harris & Cabri 1991) with considerable inter-nugget variation of Ir and Ru (Figure 1, Table 2). To avoid confusion with osmium and iridium as elements, we refer to the Os-rich grains as osmium (Os content >80 at. %), iridium osmium (Os, Ir) and osmian iridium (Ir, Os). Average chemical composition of Os-rich alloys presented in Table 2 implies that type 1, 2, 5 and 6 are osmium, whereas type 3 and 4 belong to iridium osmium. Osmium is commonly intergrown with Ru-Os sulphides and olivine, whereas iridian osmium frequently forms intergrowths with
chromite and rarely with osmian iridium.

Equilibrium phase relationships of Os-rich alloys at Guli, based on the binary system Os-Ir (Massalski 1993), and exsolution lamellae of uncommon polycomponent Ru-Os-Ir-Pt alloy in Pt-Fe alloy (Malitch & Badanina 1998) are indicative of high temperatures, which could be only reached under mantle conditions.

<table>
<thead>
<tr>
<th>Type</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingaringda (n=115)</td>
<td>86</td>
<td>11</td>
<td>3</td>
<td>91</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Burlakovsky (n=48)</td>
<td>82</td>
<td>13</td>
<td>5</td>
<td>82</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>Type 1</td>
<td>71</td>
<td>23</td>
<td>6</td>
<td>70</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>Type 2</td>
<td>71</td>
<td>23</td>
<td>6</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>Type 3</td>
<td>71</td>
<td>23</td>
<td>6</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>Type 4</td>
<td>71</td>
<td>23</td>
<td>6</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>Type 5</td>
<td>71</td>
<td>23</td>
<td>6</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
<tr>
<td>Type 6</td>
<td>71</td>
<td>23</td>
<td>6</td>
<td>84</td>
<td>11</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2. The mean chemical composition (at. %) of Os-rich alloys from distinct morphological types

<table>
<thead>
<tr>
<th>Type</th>
<th>(^{187}\text{Os}/^{188}\text{Os})</th>
<th>T, Ma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingaringda (LA MC-ICP-MS, n=86)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-1 (n=3)</td>
<td>0.12446 (17)</td>
<td>588</td>
</tr>
<tr>
<td>I-2 (n=39)</td>
<td>0.12449 (17)</td>
<td>585</td>
</tr>
<tr>
<td>I-3 (n=28)</td>
<td>0.12475 (53)</td>
<td>548</td>
</tr>
<tr>
<td>I-4 (n=3)</td>
<td>0.12468 (15)</td>
<td>558</td>
</tr>
<tr>
<td>I-5 (n=10)</td>
<td>0.12455 (33)</td>
<td>576</td>
</tr>
<tr>
<td>I-6 (n=2)</td>
<td>0.12443 (10)</td>
<td>593</td>
</tr>
<tr>
<td>All types (n=86)</td>
<td>0.12459 (32)</td>
<td>570</td>
</tr>
<tr>
<td>Burlakovsky (LA MC-ICP-MS, n=35)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-2 (n=11)</td>
<td>0.12455 (23)</td>
<td>576</td>
</tr>
<tr>
<td>B-5 (n=22)</td>
<td>0.12451 (12)</td>
<td>582</td>
</tr>
<tr>
<td>B-6 (n=2)</td>
<td>0.12507 (9)</td>
<td>503</td>
</tr>
<tr>
<td>All types (n=35)</td>
<td>0.12455 (20)</td>
<td>576</td>
</tr>
</tbody>
</table>

Note. Numbers in parentheses are 2σ uncertainty in the last decimal places of \(^{187}\text{Os}/^{188}\text{Os}\) ratios using machine error; model ages were calculated with values estimated by Chen et al. (1998) and a \(^{187}\text{Re}\) decay constant of \(\lambda = 1.666 \times 10^{-11}\) year\(^{-1}\) (Smolar et al. 1996)

4.3 Osmium isotope systematics

The average \(^{187}\text{Os}/^{188}\text{Os}\) values and calculated model ages for Os-rich alloys (osmium and iridium osmium) from Ingaringda and Burlakovsky are presented in Table 3.

At Ingaringda average \(^{187}\text{Os}/^{188}\text{Os}\) values of Os-rich alloys (Table 3) vary from 0.12443 ± 0.00010 (type I-6) to 0.12475 ± 0.00053 (type I-3), whereas at Burlakovsky those range from 0.12451 ± 0.00012 (type B-5) to 0.12507 ± 0.00009 (type B-6). It is noteworthy that the Os isotope composition of Os-rich alloys from type 3 and 4 (i.e., I-3 and I-4) slightly differs from that of other types (Table 3). This variability supported my mineralogical evidence can be attributed to difference in rock sources. Indeed, iridium osmium was previously documented in chromitite, whereas osmium has been observed in dunite only (Malitch, 1999). Since chromitite at Guli show podiform features, it is not surprising that model age estimates for iridium osmium of type 3 and 4 are slightly younger than mean model ages of osmium from type 1, 2, 5 and 6. Isotopic fractionation, however, among majority of investigated Os-rich alloys is insignificant (Table 3). Consequently, Os-rich alloys from distinct localities at Guli (e.g. Ingaringda and Burlakovsky) yield similar model \(^{187}\text{Os}/^{188}\text{Os}\) ages (570 and 576 Ma, respectively).

The early formation of Os-rich minerals at high temperatures implies that the Os isotope composition of Os-rich alloys should reflect that of the source region. Therefore, the low \(^{187}\text{Os}/^{188}\text{Os}\) values obtained and the constant Os isotope ratios of Os-rich alloys from distinct types clearly indicate a common chondritic or subchondritic mantle source for the PGE. We, thus, conclude that the PGE were derived from the mantle without any significant crustal contribution of Os, and that the \(^{187}\text{Os}/^{188}\text{Os}\) values have not been changed by subsequent processes (e.g. transport, sedimentation and weathering during placer formation).

The \(^{187}\text{Os}/^{188}\text{Os}\) values for the Os-rich alloys studied are close to those from a former NTIMS study (Malitch, 2004a), which showed mean value of 0.12463 ± 0.00034 (the expanding uncertainty corresponds to the 95%-confidence interval). The similar range of \(^{187}\text{Os}/^{188}\text{Os}\) values of Os-rich alloys, exemplified by both LA MC-ICP-MS and N-TIMS (Figure 2), is consistent with that for PGM from Kondyor, and likely indicates a highly productive single-stage PGM formation in clinopyroxenite-dunite complexes. Os-isotope model ages of distinct PGM at Guli indicate that this event took place in the late Proterozoic (late Riphean), which corresponds to a stage of active tectonism in the development of the Siberian Craton.
5 ACKNOWLEDGEMENTS

The financial support through research projects 98/6-H and 7F-TAO/2005 is gratefully acknowledged. We are indebted to M.M. Goncharov, O.V. Petrov, S.S. Shevchenko, O.N. Simonov and E. Pernicka for scientific discussions and logistic support during the field work. This study forms part of IGCP Project 479.

REFERENCES


Chromium and Platinum-Group Elements (PGE) mineralizations in Tethyan ophiolites of Turkey: Examples from Kahramanmaras, Ortaca and Kop complexes

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ABSTRACT: Three podiform-type deposits, namely Kahramanmaras, Ortaca and Kop, have been investigated for their chromite composition, Platinum-group elements geochemistry and mineralogy. The investigated chromitites are associated with the mantle sequence of ophiolites representing remnants of Tethys Oceanic crust. Based on the composition of chromite, the analyzed chromites can be classified as refractory and metallurgical. As typical for mantle-hosted ophiolitic chromitite, the PGE contents are low (less than 541 ppb) with an enrichment in Os-Ir-Ru. The platinum group minerals (PGM) form small grains (generally less than 10µm in size) and most of them are Os-Ir-Ru phases, rarely accompanied by Pt and Pd minerals. These observations indicate that the investigated Turkish chromitites represent only a future potential target for PGE recovery.

KEYWORDS: Turkish ophiolites, chromitites, Platinum-group elements, Platinum-group minerals

1 INTRODUCTION

About 2000 large-scale economically important deposits of podiform-type chromitite are widespread from west to east in Turkey. Most of them occur in the mantle sequence of ophiolites considered to represent remnants of Tethys Oceanic crust. The Turkish ophiolites belong to the major orogenic belt that extends from the Balkans through Greece along Turkey into Iran and Pakistan. They display tectonically complex structure and field relationships with other geological units and formations. The Turkish ophiolitic complexes are Cretaceous in age and, in agreement with the last literature data (Parlak et al. 2004; Uysal et al. 2005, 2006) formed in a supra-subduction zone (SSZ) geodynamic environment. Recently, podiform-type chromitites have attracted the attention of economic geologists, not only for chromium recovery, but also for their platinum-group elements (PGE) potential. Despite of this economic interest and the great number of chromitite occurrences known, little data is available on the chromite composition and PGE mineralogy and geochemistry of the Turkish chromitites (Uysal et al. 2005, 2006). In this work we present and compare the results of a mineralogical and geochemical study of three different mantle-hosted chromitite occurrences, namely Kahramanmaras, Ortaca and Kop, located in southeast, southwest and northeast, respectively, of Turkey (Figure 1).

2 GEOLOGICAL BACKGROUND

The Kahramanmaras complex belongs to the so-called Southern Peri-Arabic ophiolite belt. It comprises a mantle tectonite at the base and an oceanic crustal section composed of ultramafic and mafic cumulates, showing cumulate structure such as igneous lamination and rhythmic
layering. The ophiolitic rocks were intruded by syn-collisional granitoids. In the mantle sequence, several economically important chromite deposits are present. The ophiolite of Ortaca crops out in the Western Tauric ophiolite belt. It consists of a serpentinised mantle peridotite, in which the following three units have been recognized: clinopyroxene-bearing harzburgite, harzburgite and dunite. These rocks are cut by a great number of dolerite dykes, and thin pyroxenite veins are abundant particularly in the dunite. Small chromite deposits, mined in the past, are associated with the dunite. The complex of Kop, is part of the Eastern Pontide ophiolite belt. It is composed of a mantle tectonite made up of abundant harzburgite and minor dunite and lherzolite. Chromite deposits, variable in size, occur in both dunite and harzburgite.

3 DESCRIPTION AND COMPOSITION OF THE INVESTIGATED CHROMITITES

The investigated chromitites display a great variety of textures: massive, nodular, schlieren-type and disseminated. They occur in an envelope of dunite and their country rocks are harzburgites with different degrees of serpentinization. Despite the serpentinization, chromite is generally fresh, alteration being limited to development of ferrian-chromite along grain boundaries and cracks. Therefore, the primary composition of chromite has been preserved in the core of the spinel grains. All the chromites analysed by electron microprobe are characterized by a variable concentration of Cr$_2$O$_3$ wt% varying from 39.62 to 60.01, 48.9 to 61.24 and from 48.53 to 61.93 in the Kahramanmaras, Ortaca and Kop chromitites respectively. The maximum contents, as wt% of other elements are: Al$_2$O$_3$ 18.93, MgO 14.63 and total FeO 19.88. TiO$_2$ wt% content is very low, generally being less than 0.24 in Kahramanmaras and Ortaca, and less than 0.4 in Kop chromitites.

4 PLATINUM-GROUP ELEMENTS (PGE) GEOCHEMISTRY

All six PGE have been analyzed in selected samples from Kahramanmaras and Kop, whereas in the Ortaca chromitites Os was not analyzed. PGE concentrations are low, ranging from 28 to 541 ppb. Chondrite-normalized distribution patterns are presented in Figure 2, and...
compared with mantle hosted chromitites world-wide.

The general trend of the investigated chromitites resembles most mantle-hosted ophiolitic chromitites, displaying an enrichment of Ru+Os+Ir over Rh+Pt+Pd. However, in some samples from Kahramanmaras and Ortaca a weak Pt and Pd enrichment has been observed.

5 PLATINUM-GROUP ELEMENTS (PGE) MINERALOGY

All the investigated chromitites contain Platinum-group minerals (PGM). They are listed in Table 1.

<table>
<thead>
<tr>
<th>PGM</th>
<th>Kahramanmaras</th>
<th>Ortaca</th>
<th>Kop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laurite</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Erlichmanite</td>
<td></td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Iridium</td>
<td>R</td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Osmium</td>
<td>R</td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td></td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Irarsite</td>
<td></td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Hollingworthite</td>
<td>R</td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Un. Pt-PGM</td>
<td></td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Un. Pd-PGM</td>
<td></td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Un. Rh-PGM</td>
<td></td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>Un. Os-PGM</td>
<td></td>
<td>R</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. The PGM in the investigated chromitites (A = abundant, R = rare, Un. = unidentified).

The PGM form small grains, generally less than 10 microns in size (Figure 3), and occur enclosed in fresh and altered chromite crystals and along fissures and in the silicate matrix.

The PGM form single phase grains or they are associated with base-metals sulphides, silicates and other PGM. Laurite is ubiquitous, being present as the most abundant PGM in all the chromitites, as is typical for ophiolitic chromitites. In the Kahramanmaras chromitites, laurite is accompanied by iridium (containing 10.89 wt% of Pt), irarsite, hollingworthite, and an unidentified Pt-Rh-Ir-Cu sulphide. In the Ortaca chromitites erlichmanite, iridium and osmium were found. The Kop chromitites contain osmium, platinum, hollingworthite and the following unidentified PGM: Rh-Ir sulphide, (Os,Ru,Ir)(Ni,Fe)₂ and Pd-Sb-Te. In the ternary diagram of Figure 4, the composition of minerals of the laurite-erlichmanite series of the Kahramanmaras, Ortaca and Kop chromitites has been plotted as atomic %. Laurite from Kahramanmaras and Kop shows enrichment in Ir, whereas laurite from Ortaca displays a high Os content reaching, in some cases, the composition of erlichmanite.

Figure 3. Electron microscope images showing laurite in fresh (A) and altered (B) chromite. Scale bar = 5 µm.

Figure 4. Composition of the analyzed minerals of the laurite-erlichmanite series in the investigated chromitites, as atomic %.

4 CONCLUDING REMARKS

The present study has demonstrated that chromite composition, PGE geochemistry and
mineralogy of the chromitites from Kahramanmaras, Ortaca and Kop display similarity with those hosted in the mantle sequence of SSZ ophiolites world-wide, thus confirming that they formed in such a geodynamic environment.

On the basis of the composition of the chromite in all the investigated localities, refractory and metallurgical chromitites are present.

The most abundant PGM discovered are Ru-Os-Ir phases (laurite, erlichmanite, Os-Ir-Ru alloys and irarsite). Rarely, Rh, Pt and Pd bearing PGM have been encountered in the Kahramanmaras and Kop chromitites.

Due to the small size of PGM, low PGE content (maximum total PGE = 541 ppb), and the predominance of Ru-Os-Ir minerals over Rh-Pt-Pd phases, the investigated Turkish chromitites represent only a future potential target for PGE recovery.

ACKNOWLEDGEMENTS

Financial help to I.U. by Karadeniz Technical University (Socrates/Erasmus) and German Academic Exchange Service is acknowledged. A. Haydar Aygün is thanked for his assistance during the field trip.

REFERENCES


PGE in ultramafic rocks of the hidden ophiolite complex near Svitavy, Bohemian Massif

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ABSTRACT: Anomalous concentrations of platinum-group elements (PGE) Pd – up to 281 ppb, Pt – up to 110 ppb, Ir – up to 7.4 ppb, Ru – up to 19.8 ppb, Rh – up to 8.4 ppb and Au (up to 18.5 ppb) have been detected in low Ni-Cu (Cr) mineralized pyroxenite and serpentinite recovered from the HSV-1 structural borehole at Svitavy. Based on geological and geotectonic position and geochemical data these rocks hidden under Cretaceous sediments represent most likely continuation of the Letovice ophiolite complex. Maximum Ni, Cu and Cr values reach 0.67, 0.11 and 0.35 wt.%, respectively and abundant spinels (Cr-spinel, magnesiocromite, chromite) and magnetite with minor sulphides (millerite and chalcopyrite) were identified as major ore bearing minerals in the most richest PGE sample. No discrete PGE phases were identified.

KEYWORDS: PGE, ultramafic rocks, Svitavy, Bohemian Massif

1 GEOLOGY

According to Malkovský (1979) and Mísař (1984) the mafic and ultramafic rocks of the Svitavy anomaly complex that are hidden under the platform Upper Cretaceous sediments and known only from drill holes can be considered as the continuation of the Letovice ophiolite (Fig. 1). The whole basement complex underwent similarly as the Letovice ophiolite a polyphase deformation under the conditions of an amphibolite facies (T = 400-600°C, p = 200-500 MPa, Kopecký 1992). This ophiolite complex is believed to be formed in an oceanic basin separating the Brunovistulian-Moravian block to the east and the Moldanubian block to the west, thus younger than 600 Ma (i.e. the Cadomian formation of the Brunovistalicum) (Dudek 1980, Mísař et al. 1984, Jelinek et al. 1984, Höck et al. 1997).

2 MATERIAL AND METHODS

Samples of low Ni-Cu (Cr) mineralized and barren rocks (pyroxenite and serpentinite) from the structural HSV-1 borehole (800m deep) were kindly provided by Dr. E. Jelinek from the Faculty of Science, Charles University. The borehole HSV-1 encountered a package of mafic and ultramafic rocks (serpentinites with variously preserved relics of olivine and pyroxene). Layers of pyroxenites with Ni-Cu (Cr) mineralization were described from a depth of 294.0-297.4m, 316.8-319.0m, 373.0-385.0m and 443.4-445.0m (Kopecký 1992). The samples were powdered and analyzed for selected major elements (wet chemistry), trace and REE elements (ICP-MS) in the laboratories of the Faculty of Science, Charles University in Prague. Preconcentration of Pt, Pd, Rh, Ru and Ir into Ni-button was done in the laboratories of the Czech Geological Survey and subsequent determination of PGE by ICP-MS in the labs of the Analytika Ltd. in Prague).

3 RESULTS AND DISCUSSION

3.1 Geochemistry of host rock

Distribution of major oxides and trace elements in major mineralized and barren rocks from Svitavy is given in Table 1. The geochemistry of trace elements was studied by Kopecký (1992) who reported up to 0.4 wt.% Ni, 0.1 wt.% Cu and 0.98 wt.% Cr in mineralized pyroxenite. Our data confirm similar level of Ni and Cu enrichment (Table 1).
The concentration of PGE in ophiolite cumulates is highly variable. The most consistently mineralized facies are chromite-rich dunites in which Os, Ir, Ru and Pt may be concentrated with total PGE often reaching the ppm range (Crocket 2002). Pyroxenites and gabbros may concentrate Rh, Pt and Pd, at least locally. In the Troodos complex, Prichard & Lord (1990) found little concentration of PGE in gabbros with the exception of one in nine localities sampled. In the anomalous locality, 

**Table 1. Chemical composition of low Ni-Cu (Cr) mineralized and barren rocks from the HSV-1 borehole at Svitavy (major oxides in wt.%, selected trace elements in ppm, PGE and Au in ppb).** Pyx – pyroxenite, spt (pyx)–serpentinite with pyroxenite layers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H-1</th>
<th>H-2</th>
<th>H-3</th>
<th>H-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock</td>
<td>spt (pyx)</td>
<td>spt (pyx)</td>
<td>spt (pyx)</td>
<td>pyx</td>
</tr>
<tr>
<td>Depth(m)</td>
<td>296</td>
<td>297</td>
<td>297.4</td>
<td>318.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>40.92</td>
<td>39.98</td>
<td>37.92</td>
<td>43.73</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.13</td>
<td>0.09</td>
<td>0.01</td>
<td>0.08</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.88</td>
<td>2.23</td>
<td>2.29</td>
<td>2.4</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6.64</td>
<td>5.82</td>
<td>6.82</td>
<td>3.75</td>
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<tr>
<td>FeO</td>
<td>3.25</td>
<td>2.45</td>
<td>1.97</td>
<td>2.3</td>
</tr>
<tr>
<td>MnO</td>
<td>0.07</td>
<td>0.09</td>
<td>0.1</td>
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gabbros near a contact with ultramafic rocks averaged 75 ppb total Pt and Pd over 35 m with the PGE enrichment occurring in sulphide-bearing samples. Significantly higher Pd-dominated PGE enrichment (averaged total Pd+Pt = 251 ppb, Pd/Pt = ~2) was newly found in Ni-Cu (Cr) mineralized rocks at Svitavy (Table 1). Primitive mantle normalized PGE patterns for our mineralized and barren samples are shown on Fig. 2. These patterns show strong PGE fractionation similar to pyroxenites from Thetford ophiolite complex.

The mineralized serpentinite samples from Svitavy show different REE patterns with significant MREE depletion. The mineralized serpentinite with pyroxenite layers (H-1) shows apparent LREE enrichment compared to other rocks (Fig. 3) particularly to LREE depleted barren pyroxenite sample (H-4). Such kind of difference can be product of various processes (e.g., partial melting and refertilization).

### 3.2 Mineralogy

In serpentinites from the HSV-1 borehole, Kopecký (1992) reported the following ore minerals: pyrrhotite, chalcopyrite, pyrite, sphalerite, pentlandite, millerite and frequent spinel (Cr-spinel, magnesiochromite) and magnetite.
ten replace and/or are developed on younger fractures in spinels (Fig. 4).

None of platinum group minerals (PGM) were detected. We suggest that Pd and Pt (Ir) could be present either in the form of submicroscopic inclusions in sulphides and/or bound to spinels (especially Ru and Rh as suggested based on crystallochemical considerations by Barnes & Maier 1999).

4 CONCLUSIONS

Preliminary results of geochemical and mineralogical investigations indicate that low Ni-Cu (Cr) ultramafic rocks are anomalously enriched in PGE ($\sum$PGE = up to 0.4 ppm) with frequent spinels and minor Ni and Cu sulphides. We suggest that sub-Cretaceous mafic and ultramafic complex at Svitavy is a prosperous target for Ni-Cu (PGE) mineralization. If it were really a part of the Letovice ophiolite complex it would be interesting to evaluate Ni-Cu-PGE potential of the whole complex.

ACKNOWLEDGEMENTS

This project was funded within the CGS grant no. 3254 to I. Kněsl and grant KJB300130612 from the Grant Agency of the Academy of Sciences, Czech Republic to L. Ackerman.

REFERENCES


Kopecký L (1992) Perspectives of Ni-Cu (Pt), Cr mineralizations of the subcretaceous basic and ultramafic complex near Svitavy. *Věst česk geol úst* 67(4): 245-257.


ABSTRACT: Isoferroplatinum of two generations (early high-temperature and late) dominantly represent the platinum group mineralogy of the Kondyor zonal alkali-ultrabasic massif. The minor PGM are the Os–Ir–Rh–Pt solid solutions (including native Pt, Os, Ir and Ru) of the magmatic stage as well as the post-magmatic minerals: tetraferroplatinum, tulameenite, hongshiite, minerals of the erlichmanite-laurite and irarsite-hollingworthite series, sperrylite, and others. The latter minerals form rims around isoferroplatinum and inclusions at its edge. Gold is closely associated with bismuthides, antimonides, and tellurides of Pt and Pd and occurs as a pure metal or alloys with Ag (up to aurum silver), copper-platinum and copper-palladium, ranging in composition from Au₃Cu to AuCu₃.

KEYWORDS: PGE, gold, Kondyor alkaline ultrabasic massif, eastern Russia

INTRODUCTION

This paper briefly presents results of our long-term study of accessory platinum group elements (PGE) from the Kondyor alkaline-ultrabasic massif. These results were described in greater detail in our monograph (Nekrasov et al., 1994).

The Kondyor ring alkali-ultrabasic massif is located in the eastern Aldan Shield, 250km northwest of the Okhotsk Sea coast in Russia. The massif is composed of dunites forming a core about 6km in diameter, surrounded by olivine clinopyroxenites grading to olivine-free magnetite clinopyroxenites and gabbros towards the periphery of the massif. The ultrabasites and gabbros are cut by monzodiorite and granodiorite intrusions and by numerous thin syenite dikes.

1 PGE MINERALOGY

Accessory PGM from ultrabasites and related placers are dominated by isoferroplatinum, in which inclusions of Os–Ir–Ru and Os–Ir–Pt solid solutions are common. The less common PGM are tetraferroplatinum, tulameenite, hongshiite, sulphides, sulphoarsenides, arsenides, bismuthides, antimonides, tellurides, stannides, Pd germanide, and hydroxides, occurring at rims around isoferroplatinum grains.

There are two distinct generations of isoferroplatinum in the Kondyor massif: 1) an early (cumulative) phase related to dunites with chromite (up to 64 wt.% Cr₂O₃) impregnations and Mg-rich olivine (6-9 % Fa); 2) a later phase filling interstices in lenses and veins of chromitites (up to 54 wt.% Cr₂O₃) or in phlogopite-magnetite pyroxenite forming vein and dike-like bodies (up to 40m in thickness) in dunites. Isoferroplatinum of the second generation with 7.5-11.5 wt.% Fe, similar to that of the earlier phase, shows depletion in other platinum-group elements. Isoferroplatinum of the chromitite lenses and veins in dunites of the upper Kondyor intrusion contains 0.3-1.0 wt.% Os, less than 0.6 wt.% Ir (increasing up to 1.9 in the lower horizons), and up to 0.4 wt.% Pd and Rh, while isoferroplatinum of magnetite pyroxenite contains 0.3-0.9 wt.% Os, less than 0.6 wt.% Ir, and up to 0.6 wt.% Pd and Rh. In contrast, Pt–Fe alloys crystallized at the early stage are enriched in other PGE and characterized by Fe content distinctly decreasing with depth.

The maximum Fe content in the Pt–Fe solid solutions (up to 11.5 wt.%) is found at the up-
permost part of Kondyor massif. Meanwhile, the Fe content of the isoferroniplatinum, separated from chromite impregnations of the deepest dunite body, is as low as 8-9 wt.%. Other PGE impurities in Pt–Fe alloys show similar relations to the depth of crystallization. At the least eroded areas of dunites, isoferroniplatinum contains 0.8-3.8 wt.% Ir, up to 2.9 wt.% Os, up to 1.5 wt.% Pd, and 0.5-1.8 wt.% Rh, whereas it contains 2.5-5.3 wt.% Ir, 0.7-0.9 wt.% Os, 0.2-1.0 wt.% Pd, and 0.7-1.1 wt.% Rh at the most eroded zone of dunites.

Osmium is the most common end member of the Os–Ir–Ru and Os–Ir–Pt solid solutions, while the platinum, iridium, and ruthenium are very rare. Platinum commonly forms isolated inclusions (10-15 µm) at edges of the isoferroniplatinum and tetraferroplatinum grains. There also are rare inclusions of iridium (up to 30 µm) and ruthenium (30x170 µm) in the isoferroniplatinum grains. Total content of Ir and Os in ruthenium does not exceed 1 wt.%. Osmium is represented by three morphological varieties. One of them forms rare, predominantly laminar, sometimes rounded and worm-like inclusions in cumulative isoferroniplatinum enriched in other PGE. This osmium contains up to 6 wt.% Pt and 17 wt.% Ir. The second variety forming lamellar and rounded grains shows obviously lower content of Pt and Ir (3 and 11 wt.%) and zonal distribution of Ir in relatively large grains (with maximum Ir in the centre). It also forms inclusions in isoferroniplatinum of the second generation. The third variety is represented by isolated lamellar aggregates of relatively coarse-grained osmium with minor impurities of Pt and Ir (up to 2 wt.%), hosted by isoferroniplatinum of the second generation.

Ir-Os solid solutions with wide variation of ruthenium are rare. There also were findings of osmium-bearing ruthenium, osmium-bearing platinum and osmiumiridium.

In addition we have found in the Kondyor massif the solid solutions of Os–Ru–Ir, Ru–Ir–Os, and Os–Ir–Pt compositions, near-binary Ru-Os (with only 6 at.% Ir), and Pt–Ir–Ru–Os solid solutions (with up to 10 at.% Pt) and osmium (with up to 6 at.% Pt) predominant. Inclusions of Ir–Os, Ru–Ir–Os and Pt–Os–Ir are exceptionally developed in the highest-temperature Pt–Fe alloys.

Vast diversity of mineral forms characterizes the post-magmatic PGE mineralization.

Solid solutions on the platinum basis are rare, represented by tetraferroplatinum, tulameenite and hongshite. They commonly form rims on isoferroniplatinum, replacing it completely in some cases. Tetraferroplatinum exhibits the most stable composition with persistent Cu (up to 3 %) and Ni (up to 1.5 %) impurities. Tulameenite contains variable Fe (8.5-13 %) and Cu (8.8-12.8 %) with constant Pt contents. Some irregularly distributed impurities of Ni (up to 3.5 %) and Ir (up to 2.5 %) enriched in the grain rims are found in tulameenite in association with bornite. The chemical composition of hongshite appears to be most variable. Sn-Sb-varieties of tulameenite represented by both end and intermediate members of the Pt(Fe,Cu)–Pd(Cu,Fe) series were reported. We have also found a tin-bearing hongshite with 69.3 % Pt, 2.8 % Pd, 9.7 % Cu, 7.2 % Sn, and 9.5 % Fe.

The PGE sulphides and sulphoarsenides are much more abundant at the post-magmatic mineralization. Among them, the laurettierlichmanite and irarsite-hollingworthite series minerals are most common, while the malanite-cuprorodsite-cuproridsite and especially inaglyte-konderite series minerals are rarer.

The PGE monosulphides are represented by cooperite and pentlandite-xingzhongite series minerals. Cooperite form rims around isoferroniplatinum grains or veinlets in tulameenite.

We also determined monosulphides of pentlandite-xingzhongite series in many isoferroniplatinum grains from the placer. They occur in thin rims (up to 10 µm and more) or isometric and lens-like inclusions at the edges of isoferroniplatinum grains. They also form intergrowths with magnetite, pentlandite and pyrrhotite in dikes of magnetite-phlogopite pyroxenite cutting dunites. The pentlandite-xingzhongite sulphide has up to 26 wt.% Ir.

Two of the rest phases analyzed may be classified as xingzhongite-like minerals with high Fe and Ni contents. One of them is essentially rich in Ir (19.40 wt.%) and Rh (16.20 wt.%), while the second contain more Rh (up to 28.2 wt.%) than Ir (7.2 wt.%). The forth phase has high nickel (27.30 wt.%) and moderate rhodium (12.60 wt.% ) contents.

Complex sulphides, represented largely by PGE thiospinel of malanite-cuprorodsite-cuproridsite composition and rarely by Cu- and Pb-bearing inaglyte-konderite minerals, form isometric inclusions and veinlets in isoferroniplatinum and thin corrosive rims around it. Their individual rounded grains up to 0.3 mm
in size and polyminal intergrowths with iridosmine, erlichmanite, laurite, and sometimes sperrylite, bismutharsenide, irarsite, and hollingworthite are much rarer. They occur predominantly in dunites with lenses and veinlets of Cu, Fe, Ni, and Co sulphides.

Maximum Pt, Ir, and Rh contents in thiospinel are 38, 49 and 21 wt.% respectively. Most of the thiospinels correspond to malanite with increased concentration of Rh and Ir. Others are cuproiridite, its rhodium variety, iridian cuprorhodsite and a platinum-rich variety. Fe (up to 3.4 wt.%) is a constant impurity in these minerals.

Inaglyites oversaturated with rhodium predominate among Cu- and Pb-bearing sulphides. One of them is konderite and other two represent a new mineral – Pt variety of inaglyite and konderite enriched in Cu,PbPt₈Si₆ (up to 46%). Like the latter this sulphide has a microhardness of 412-435 kg/mm² and contains some Fe, while Ni is absent.

We have also found one complex sulphide in the placer grains. It contained palladium and gold (52.47 wt.% Pd, 11.53 wt.% Au, 4.94 wt.% Ag, 15.64 wt.% Bi, 8.46 wt.% Pb, 0.69 wt.% Ni, 7.34 wt.% S). Together with palladium germanide, it forms heterogeneous reaction rims of variable composition around hongshiite.

Disulphides of the erlichmanite-laurite series are characterized by both end members and less commonly by grains of intermediate variety. These minerals contain 0.2-2.1 wt.% Pt, 0.5-5.1 wt.% Rh, 0.2-2.9 wt.% Ir, 0.5-2.7 wt.% Pd and 0.4-2.2 wt.% As.

Irarsite-hollingworthite sulpharsenides form polymineral aggregates. Like the disulphides, they are represented by both end members and intermediate varieties, this is not typical for PGE occurrences in Alpine-type podiform ultrabasics.

Sperrylite is the dominant PGE arsenide and occurs in the form of fine (50-250µm) inclusions in isoferronplatinum and joint grains with tulameenite. Single octahedral crystals up to 1.5 mm in size are much rarer. The association of sperrylite with antimonpalladinite, irarsite, and cooperite was also noted. Composition of sperrylite corresponds to stoichiometric PtAs₂ with negligible sulphur impurity.

Complex palladium and platinum arsenides are characterized by considerable compositional variations. However, the (Pd+Pt+Ag)/(As+Bi+Sb) ratio in most minerals is close to 3/1, corresponding to a formula (Pd,Pt)₃(Bi,Sb,Te,As). Most common among them are antimony- and bismuth-arsenides.

Bismuthides, antimonobismuthides, and antimonides of palladium, represented by minerals of sobolevskite (PdBi)-sudburyite (PdSb) series, are rare. Fine (10-25µm) inclusions of sobolevskite close to PdBi stoichiometry are common in copper-bearing gold and isoferronplatinum. Many bismuthide grains are zoned. The central part is composed of PdBi, while margins are rich in palladium. We found both as separated grains and in tetraauricupride. Several grains of sudburyite up to 25 µm in size were found in joint grains with sobolevskite and the Pd₃(Bi,Sb) phase enclosed in gold. Needle-shaped inclusions of native antimony are sometimes present in gold as well. Antimonides, arsenide-antimonides, sulphoantimonides, and phases of more complex composition with PGE were also found as intergrowths with the sobolevskite-sudburyite bismuthides.

Minerals of the sobolevskite-kotulskite series have limited distribution. Due to the complete isomorphism between Te and Bi, inclusions of two or three phases can occur. These phases differ from each other in composition. In some of them, the minor elements are Pb (up to 2 wt.%) and Pt (up to 2.7 wt.%). The kotulskite-sudburyite series includes a bismuth-free phase with more then 15 wt.% Sb, that may be considered as a new mineral species.

Bi–Te palladinite is distributed wider than the sobolevskite-kotulskite minerals. It occurs as fine inclusions (10-15µm) in bornite occurring as sulphide lenses in dunites with low-grade gold. This mineral is characterized by zoning with variations of Pd as wide as 2-3 wt.% and other elements - 0.5-1.5 wt.%. Some Bi–Te palladinite compounds decompose into two to three phases, one of which is Pt-oxide and other two are identified as BiTe and native bismuth. The BiTe compound occurs also as individual flake-like aggregates up to 0.5µm in size. In aggregates with high-grade Au (fineness 880-920), BiTe cemented gold segregations.

Insiziwaite (PtBi) found in isoferronplatinum and geversite Pt(Sb,Bi)₂ are not common in the Kondyor massif. Palladium bismuth plumbide forms single grains but is also found in copper-bearing gold as inclusions 5-15µm in size. This supposedly new mineral phase contains 57.52 wt.% Pd, 34.74 wt.% Pb, 7.02 wt.% Bi, 1.2 wt.% Pt. Rare inclusions of zvyagintsevite are found in tetra-auricupride.
Platinum and palladium stannides are spread more widely in the form of fine (15-60 µm) inclusions in tetra-auricupride, tulameenite, and isoferroplatinum. Their chemical composition allows us to subdivide them into three groups. The first has a negligible Sb impurity (to 1 wt.%) and lacks Cu. Sum of Pt and Pd is up to 82 wt.%, Sn about 17 wt.%, corresponding to rustenburgite formula \((\text{Pt}, \text{Pd})_3\text{Sn}\). The second group includes copper-rich (to 14 wt.%) alloys of \((\text{Pt}, \text{Pd})_2\text{Sn} \cdots \text{Cu}, \text{Fe}\) system. Their impurities are Ni (up to 0.4 wt.%) and Bi (up to 1.3 wt.%). The compounds of this group are characterized by notable variations of Sn (9-17.2 wt.%), relatively constant Pt (63-73.4 wt.%), and presence of Fe (to 5.8 wt.%). These phases are associated with sobolevskite and palladium-bearing gold. High-palladium solid solutions represent the third group of stannides.

Palladium germanide, a new and not yet named mineral, was found together with a new palladium- and gold-bearing sulphide, forming a narrow (5-17 µm) rim around a palladium hongshiite grain. Although some rhythmic zoning was observed in the germanide structure, all eight analyses of its grain show similar results, averaging to 75.62 wt.% Pd, 1.12 wt.% Ag, and 23.89 wt.% Ge.

2 GOLD MINERALOGY

Accessory gold regularly occurs in the rocks of the Kondyor massif and in derived stream sediments. It is represented by gold-copper, gold-silver, gold-palladium and gold-platinum solid solutions. Most common is copper-bearing gold in serpentinized dunites within included bornite-chalcopyrite lenses and veinlets.

The copper-bearing gold, which in some cases overgrows the isoferroplatinum grains shows a characteristic feature of decay exsolution lamellar texture of several morphological types. In the Au-Cu phase, the content of Au, Cu, and Ag ranges as follows (wt.%): 75-86.5, 24.4-9.5, and 0.01-0.05 (rarely up to 3.3), respectively. Some isoferroplatinum grains are found to be surrounded with a layer of Au-Cu compound with some PGE antimonides, sulphoarsenides, tellurides and bismuthides.

Gold-silver solid solutions are less common. High-grade gold forms unusual, probably hypogene fine-grained coating on cubic crystals of isoferroplatinum. Individual grains of gold with a high-grade margin and a low-grade core are rarer in the placer. The third type of gold-silver alloys has a high-grade core and low-grade rim and is related to monzonite and granodiorite intrusions at the massif periphery.

Palladium (or palladium-copper)-bearing gold is found in dikes of magnetite-phlogopite clinopyroxenite at the southeastern massif and in the derived alluvium. This gold is represented by silvery white plates and contains up to 10.3 wt.% Pd and 25% Cu. Palladium (platinum-copper)-bearing gold is found only in one site of the placer deposit in form of light-yellow plates up to 5 mm long. The maximum Pt content reaches 10.3 wt.%, and Cu content reaches 24.4 wt.% A genetic relation of platinum-copper-bearing gold with dunites and sulphide lenses occurring in the latter is clearly established.

3 CONCLUSION

Precious metal mineralization of the Kondyor alkali-ultrabasic massif is extremely diverse, resembling that of gabbro-pyroxenite-dunite intrusions in the Urals and in Alaska. Under high-temperature conditions during formation of chromian dunites of the central massif, accessory isoferroplatinum with minor PGM and Ir–Os–Ru–Pt solid solution was crystallized. Somewhat later, isoferroplatinum filled interstices inside the massive chromite lenses and veins in dunites and as inclusions in dykes of magnetite-phlogopite pyroxenite. Crystallization of PGM chalcogenides shows restricted distribution, but is highly diverse in composition, and took place at a post-magmatic stage under the influence of residual volatiles containing Pb, Cu, Sn, Au, Ag, S, As, Bi, Sb, Te and Ge in addition to Pt and Pd.

ACKNOWLEDGEMENT

The work was partly supported by the Russian Foundation of Basic Research, Grant 06-05-96-106.

REFERENCE

Investigation of Platinum-group minerals (PGM) from Pindos and Vourinos chromitites (Greece) using new technology

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ABSTRACT: Low-grade Platinum group elements (PGE) within podiform chromitites from the Vourinos and Pindos ophiolite complexes have been investigated using the hydroseparation new technology, with the aim to determine the nature of the associated Platinum group minerals (PGM). The obtained results reveal that this new methodology is a very useful tool to concentrate a representative proportion of PGM, even in low PGE grade samples. In particular, our results show that PGM from concentrate are different (i.e., grain size, type of PGM) from those reported from in situ investigation and several PGM phases previously unrecorded in the investigated chromitites have been recognized herein. However, the traditional in situ investigation is also recommended to obtain textural information on the PGM.

KEYWORDS: Platinum-group minerals, podiform chromitites, hydroseparation, Pindos-Vourinos, Greece.

1 INTRODUCTION

In the last few decades, podiform-type chromitites hosted in the mantle sequence of ophiolite complexes, have been grouped among the deposits that represent a future potential source for Platinum-group elements (PGE) recovery. The PGE are carried in a number of specific minerals (PGM) associated with the chromite. The PGM assemblage, in these type of chromitite, is characterized by the presence of abundant Ru, Os, Ir minerals and very rare Rh, Pt and Pd phases. The PGM are scarce, form small crystals (generally less than 10 µm) and are randomly distributed. Hence, it is not easy to find them, and it is also difficult to obtain their chemical composition and structural data. However, the development of modern mineralogical analytical technique now allows us to investigate also small and rare phases, such as the PGM. Study of these minerals commonly relies on in situ investigation, based on study of thin and polished sections by optical and electronic microscopy and microprobe analyses. A novel patented technique called “hydroseparation” has recently been developed in Russia to produce representative heavy-mineral concentrates composed of very tiny particles (Rudashevsky et al. 2002, Cabri et al. 2005). This innovative technology was applied to study selected samples of podiform chromit-
ites from the Vourinos and Pindos ophiolitic complexes (Greece) to better define the nature of the associated PGM.

2 PROVENANCE OF THE INVESTIGATED SAMPLES

The Vourinos and Pindos complexes (Figure 1) belong to the Tethyan ophiolite belt that, extending from Spain to Himalayas, is one of the longest ophiolite belts in the world. According to last geodynamic interpretation, these complexes are of Middle-Upper Jurassic in age and formed in a supra-subduction zone (Rassios & Smith 2000).

The Vourinos ophiolite is located in northwestern Greece (Figure 1) and it contains more than 700 occurrences of podiform chromitite, including some of the previously largest producing chromium mines in the country, are found. Most of them are hosted in the mantle tectonite unit. The chromitite samples investigated were collected from Voidolakkos and Xerolivado areas. The ophiolite complex of Pindos is located in the western part of northern Greece (Figure 1). Small chromitite bodies are hosted in the Dramala tectonite unit, that it is composed of large, variably depleted harzburgite-dunite masses (Economou-Eliopoulos & Vacondios 1995, Economou-Eliopoulos et al. 1999). The chromitite samples object of this investigation were collected in the localities Pefki and Milia. The total PGE concentrations in the Vourinos and Pindos chromitites are relatively low (< 400 ppb).

3 METHODOLOGY

After a pre-concentration step that includes rock crushing, gradual milling and final removing and sieving of the fine fraction on about 1 kg of chromitite, the PGM were concentrated using the hydroseparation technique (Rudashevsky et al. 2002, Cabri et al., 2005, Kapsiotis et al. 2006) carried out at NATI Research JSC, St. Petersburg, Russia. This innovative technique relies on the separation of particles by density in a carefully controlled water flow. The hydroseparator apparatus consists of two main components: 1) a water flow regulator and 2) a glass separation tube. The regulator controls the water flow, pulse intensity and pulse rate, which are adjusted to yield the maximum separation of the desired particles. The separation tube is positioned vertically with its lower end connected to the water outlet of the regulator. Sample material is introduced as a particle suspension at the upper end of the tube. Clustering of grains was avoided by using an antiflocculant. The hydroseparator uses a pulsating water flow to simulate the swash action of waves on natural beach placers. Therefore, heavy-mineral concentrates were produced by the settling of particles in an upward fluid flow. After its separation, the heavy-mineral concentrate is washed from the tube by the water flow on to a filter paper for drying. Finally, each concentrate was mounted in epoxy blocks, polished investigated by electronic microscope and analyzed by electronic microscope. Selected chromitite samples were also investigated in situ, using the traditional method to located PGM using optical microscope on polished section and then to study the discovered PGM by electronic microscope and microprobe.

3 THE PLATINUM GROUP MINERALS

3.1 Vourinos

According to the previous in situ study on the Vourinos chromitites (Augé 1985, Garuti & Zaccarini 1997), the PGM assemblage is dominated by the presence of Ru-Os-Ir phases, mainly laurite, Ru-Os-Ir alloys and Ru-Os-Fe oxides, accompanied by very rare Rh-Pt-Pd bearing minerals. These PGM occurred as single or polyphasic grains forming small crystals (generally less than 10 µm in size). Most of them are included in fresh chromite crystals or, more rarely, are found in the silicate matrix.

The Voidolakkos concentrate sample contains 74 PGM. They comprise unidentified Ru minerals (35.1%), followed by irarsite (18.9%), Os-Ir-Ru alloys (17.6%), laurite (12.2%), Ir(Rh,Ru,Ni,Fe) (9.5%), erlichmanite (5.4%), and Ru-rich base metal sulphides (BMS) (1.4%). One grain of the rare mineral chengdeite has been also identified. The size of the 52.7% of PGM is less than 10 µm, whereas the 29.7% are bigger than 20 µm. The investigation of Xerolivado concentrate sample yielded 45 grains of PGM. The PGM assemblage is dominated by laurite (38.3%), followed by iridium (31.9%), unidentified Ru (12.76%), Ir-Ru-Rh-Pt-arsenides (10.64%), erlichmanite (2.13%) and PGE-sulphides (4.26%). Most of the PGM (80.84%) are smaller than 20 µm. The remaining is greater than 20 µm. The PGM found in the Vourinos concentrates and their sizes are
reported in Figure 2.

3.1 Pindos

Tarkian et al. (1996) reported the first PGM occurrence in the Pindos chromitites. They studied, using the in situ investigation, samples of chromitite from Korydallos area. They reported that PGM assemblage is dominated by Os-rich laurite, sperrylite and an unidentified phase, with the following composition Pt(Ni,Fe)₃.

Our investigation on concentrates from Pefki revealed the presence of specific phases of all six PGE, and 65 PGM have been found. They are listed in decreasing order of abundance in the following: unidentified Ru minerals (31.3%), ruarsite (28.4%), laurite (17.9%), irarsite (8.9%), Os-Ir-Ru alloys (4.5%), Rh-Pt-Pd PGM (4.5%). Furthermore, 4 unidentified PGM, some grains of electrum (Au, Ag) and native silver have been also identified. The 41.8% of PGM have a size between 5 and 15 µm, whereas 21% of the grains is less than 5 µm, and 37.3% more than 15 µm.

The Milia sample contains 51 PGM including, in decreasing order of abundance, laurite (51%), Os-Ir-Ru alloys (31.3%), irarsite (5.9%) erlichmanite (3.9%), unidentified Ru PGM (3.9%), ruarsite (2%) and Ru-BM sulphides (2%).

Most of the PGM (68.7%) have a size between 5 and 15 µm, whereas 12 grains (23.5%) are greater than 15 µm, and only 7.8% are less than 5 µm. The PGM found in the Pindos concentrates and their sizes are reported in Fig 3.

4 SUMMARY AND CONCLUSIONS

The present study on chromitites from Vourinos and Pindos ophiolites indicates that the innovative hydroseparation technique is a very useful tool to concentrate a representative proportion of PGM, even in low PGE grade samples. Our results show that PGM from concentrate are different (i.e., grain size, type of PGM) from those reported from in situ investigation. Several PGM phases, such as ruarsite, irarsite, hollingworthite, PGE-alloys, paolovite, braggite, erlichmanite, chengdeite and other unidentified Ru-Rh-Pt-Pd minerals, previously unrecorded in the investigated chromitites have been recognized herein. However, one of the most relevant problems with hydroseparation is that all the textural information is lost when the samples are crushed. Therefore, the application of both the methodologies, i.e., in situ and hydroseparation, is strongly recommended to obtain a complete characterization of the PGE mineralogy.

ACKNOWLEDGEMENTS

Research was partially supported by the University of Patras, Karatheodoris Project, B097.

REFERENCES


Figure 2. A = Diagrams showing the percentage of PGM (139 grains) in the Vourinos concentrates, B = Size distribution of PGM in the Vourinos concentrates.

Figure 3. A = Diagrams showing the percentage of PGM (139 grains) in the Pindos concentrates, B = Size distribution of PGM in the Vourinos concentrates.
Platinum-Group Minerals (PGM) from lode and placers deposits from the Uktus concentrically-zoned intrusive complex (Central Urals, Russia)

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ABSTRACT: Platinum group elements (PGE) are rare and strategic metals with high market prices. Their worldwide production derives mainly from magmatic ores, although Alaska and Russia produced quantities of platinum from placers deposits. A description and comparison of Platinum-group minerals PGM occurring in lode (dunite-chromitites) and placers deposits of the concentrically zoned complex of Uktus (Central Urals) is provided. PGM from lode and placer deposits are mineralogically similar consisting mainly of Pt-Fe-Cu and Ru-Os-Ir alloys with minor other PGM. The main difference resides in the PGM size, generally less than 20 and more than 500 microns in lode minerals and nuggets respectively. Most of the PGM from both lode and nuggets were affected by alteration processes. The PGM from Uktus lode deposits represent only a future target for PGE recovery, whereas those from the placers have some economic importance even now.

KEYWORDS: Platinum-group elements, Platinum-group minerals, concentrically-zoned complex, Uktus, Urals.

1 INTRODUCTION

Platinum group elements (PGE = Os, Ir, Ru, Rh, Pt and Pd) are considered strategic metals because of: 1) their scarcity in the earth’s crust, 2) up to 99% of the world production mainly comes from few mining districts located in South Africa and Russia, that alone, supply 90% of Pt and the 85% of Pd respectively and 3) their growing use in advanced technological applications, such as auto catalysts, medicals and electronics. As consequence, the demand for these rare metals has increased. The worldwide production for PGE derives mainly from magmatic ores, i.e. large igneous intrusions, such as the Bushveld layered complex (South Africa) and flood basalts-associated mafic intrusion of Noril’sk in Siberia (Cawthorn 1999). Production from placer deposits is minor, although areas in Alaska and Russia produced significant quantities of platinum in the past (Cabri et al. 1996). Most of PGE are carried in specific phases, the so-called Platinum-group minerals (PGM), although small amounts of PGE may occur in solid solution in other minerals, such as base-metal sulphides, arsenides and sulpharsenides. Since the end of the nineteenth century it was realized that dunites and related chromitites from concentrically-zoned intrusive complexes, also known as Uralian-Alaskan type complexes, were the major contributors of platinum in large placer deposits occurring in the so-called “Platinum-Belt” of the Urals (Figure 1, Betekhtin 1961; Razin 1976; Cabri & Genkin 1991 and references therein). In this contribution we provide, for the first time, a detailed description and comparison of Platinum group minerals (PGM) occurring in lode and placers deposits of the concentrically-zoned complex of Uktus, located in Central Urals, at the periphery of Ekaterinburg. According to Cabri & Genkin (1991) the Uktus complex is the place where, for the first time in 1819, was discovered a nugget of platinum associated with a gold placers, in the Urals. Despite of this historical discovery, platinum placers deposits in the Uktus complex have been never investigated and mined. Some genetic and economic aspects of the Uktus PGE mineralizations are also briefly discussed.
The Uktus complex is located south-west of Ekaterinburg, and covers an area of about 50 km² (Figures 1 and 2). Dunite, clinopyroxenite, wherlite, olivine and amphibole gabbro, arranged in a concentrically-zoned structure are major constituents of the Uktus complex (Figure 2). The Uralian-Alaskan-type affinity of the Uktus complex was established since the early twenties, based only on petrographic and structural similarities with Uralian-Alaskan-type complexes sensu stricto of the Urals, although it has been confirmed with petrologic data only recently (Pushkarev 2000 and references therein). Chromitites occur exclusively in the dunites of the Uktus complex. They consist of tiny aggregates of a few millimeters, or form larger podiform veins and schlieren about 0.5-5 cm thick and 15-30 cm long. More extended lenses and layers up to some meters in size are very rare, and they are found only in the southern dunite body. Fourteen samples of chromitite were investigated in this study, taken from surface outcrops and boreholes in the southern and northern dunite bodies.

Previous work on the Uktus chromitites (Garuti et al. 2002, 2003) revealed that they are characterized by a large variation of the chromite composition: \( \frac{\text{Cr}}{\text{Cr+Al}} = 0.46-0.77 \), \( \frac{\text{Fe}^{2+}}{\text{Fe}^{2+}+\text{Mg}} = 0.28-0.66 \), and \( \frac{\text{Fe}^{3+}}{\text{Fe}^{3+}+\text{Fe}^{2+}} = 0.23-0.59 \). The textural features in the Uktus chromitites (Garuti et al. 2002, 2003) indicate that they crystallized concomitantly with their dunite host, possibly by
accumulation of chromite grains, followed by slow cooling, annealing and sintering. Chromite is generally fresh, and alteration is limited to formation of ferrian chromite along cracks and crystal boundaries. Fracturing of chromite occurred at some late stage, as testified by the secondary nature of the silicate filling of cracks and fissures, mainly consisting of chlorite and serpentine accompanied by minor talc and carbonates. Total PGE concentration in chromitites varies from 0.5 to 1.5 ppm (Garuti et al. 2002, 2003). The investigated nuggets were collected from the alluvial-delluvial deposits in two small valleys with temporary water flows (Figure 2). The volume of the washed samples varies from 30 to 80 dm³, and few tens of PGM nuggets have been found.

3 METHODOLOGY AND RESULTS

PGM in chromitites samples were investigated in situ, scanning polished sections using reflected-light and electron microscopes. Then, the PGM found in the chromitites and those of the nuggets where quantitatively analysed using an ARL-SEMQ electron microprobe, operated in the WDS mode. A list of the discovered PGM is reported in table 1.

Except for one composite PGM grain that is about 1 mm in size, all the other PGM found in the chromitites are less than 20 microns in size. On the contrary, the size of the PGM nuggets is, in most cases, more than 500 microns. The PGM associated with chromitites mainly occur as polyphasic grains composed of different PGM and silicates, enclosed in fresh chromite crystal or along cracks filled with altered silicates. The analyzed nuggets consist mostly of single phases crystals, although some polyphasic nuggets composed of different PGM have been also found. The most abundant PGM in chromitites and in the nuggets are Pt-Fe-Cu-Ni and Os-Ir-Ru alloys, accompanied by minor other PGM (Table 1). Garuti et al. (2002, 2003), on the basis of textural relations, paragenesis and composition, divided the PGM in the Uktus chromitites in two main groups: primary and secondary. Primary PGM are interpreted as early liquidus phases entrapped during crystallization of the host phase at high temperatures. On the contrary, the secondary PGM represent phases altered and modified after their magmatic formation, at lower temperatures. Composition of the analyzed PGE alloys found associated with chromitite and from the nuggets have been plotted, as atomic proportion, in the Ru-Os-Ir and Pt-Fe-Cu+Ni ternary diagrams of figure 3.

Table 1. PGM in the Uktus massif.

<table>
<thead>
<tr>
<th>PGM</th>
<th>Chromitites</th>
<th>Placers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laurite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Erlichmanite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Kashinite</td>
<td>X</td>
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<td>Cuprorhodsite</td>
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<tr>
<td>Malanite</td>
<td>X</td>
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</tr>
<tr>
<td>Cooperite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Osmium</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Iridium</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Pt-Fe alloys</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Tulameenite</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Irarsite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Tolovkite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Potarite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Geversite</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Unidentified</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

4 DISCUSSION AND CONCLUSIONS

Genkin (1997) proposed that the high-grade Pt ore deposits related with dunite in the complex of Nizhny Tagil (Figure 1) show textural and mineralogical evidence to have been formed by re-mobilization at relatively low temperature of a low-grade Pt “proto-ore” of magmatic origin. Similar alteration processes have been also recognized in the Uktus chromitites (Garuti et al. 2002, 2003). The mineralogical similarity that characterized the PGM from lode and placers deposits of the Uktus complex suggests that these alteration process started in situ by the action of hydrothermal fluids. These new-formed PGM were subsequently liberated from their country rocks, and possibly re-altered in the placers environment. From a practical point of view, it is well known that one of the most relevant difficulty to recovery PGE resides in the minute grain size of the PGM (generally less than 15 microns). Therefore, owing to the small size of their PGM, the Uktus lode deposits can be considered only a future potential target. On the contrary, the bigger size of the PGM nuggets, the fact that the Uktus PGE placers have never been mined, and the recent exponential increas-
ing for the PGE demand, make placers deposits related with the Uktus complex potentially very important for the economic recovery of these rare metals, at least at small scale.

Figure 3. Composition of the PGE alloys (At%) in the Uktus complex. Gray field = miscibility gap according to Harris & Cabri (1991).

ACKNOWLEDGEMENTS

This investigation was partially funded by the Russian grant to E. P. (RFBR ¹ 06-05-64795-à).

REFERENCES


Platinum group elements of Russian Far East: implementation of the GIS prototype

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ABSTRACT: Some efforts have been undertaken to establish the geographic information system “Platinum Group Elements of the Russian Far East”. This information resource includes systematized data describing and related to the PGE deposits of the region. This information has a sufficient spatial component, so that the system integrates traditional technologies of information resource management with those of geographic data management and analysis.

KEYWORDS: PGE, metallogeny, geodynamics, GIS, eastern Russia

1 INTRODUCTION

Geographic data describing position of different objects in space, their shape and relations with surrounding environment become more and more important. That is not surprising, as the world experience shows about 85% of information, used for decision-making, to have a certain geographic aspect, so the GIS (tools for geographic data analysis) are considered to be systems of strategic decision-making.

Success of scientific research, business management, local or regional development greatly depends on how perfect the informational resource is, in particular, how comprehensive, accessible, well-structured, and provided with analytical tools its data are.

All these aspects were considered when we established the present GIS prototype. They will also be taken into account in a future development of the GIS management of Russian Far East PGE resources.

2 GOALS

At the first step of the current work the following tasks were accomplished:

a) Accumulation and systematization of complex information related to metallogenic research, prognosis and evaluation of lode and placer PGE mineralization in the region;

b) Creation of the local resource integrating all associated information in a digital form;

c) Selection of software environment and interface customization that provide management, geoprocessing and mapping tools

3 NATURE AND COMPLETENESS OF DATA

3.1 Information sources

Basic information sources are as follows:

- Published maps and atlases, as well as sketches showing spatial distribution of PGE mineralization.
- Thematic catalogues, tabular data from different cadastres, reference and guide books, working materials and field data.
- Descriptive data on PGE occurrences from different publications for over 20 years.
- Not georeferenced types of images (photos, schemes, etc).
- Free digital data, such as GTOPO30 and SRTM3, published by US Geological Survey, NASA, and other organizations.
- Commercial digital data, such as Digital Chart of the World (USGS) and others.

3.2 Digitally derived data

A series of thematic digital layers was produced as a result of primary data geoprocessing.

In this way, the territory was zoned accord-
ing to PGE object types (geological, geochemical, mineralogical, and commercial). Such zoning was necessary to organize special searches and to classify the areas by richness in mineral deposits, prospects and occurrences of different nature.

Geodynamic and metallogenic zoning of the region was made on the basis of terrane analysis of orogenic belts. This approach has been successfully tested by previous geological works at the same territory (Nokleberg et al., 1994; Khanchuk & Ivanov, 1999; and others).

Geodynamic zoning of the region in this project was carried out using 1:2,500,000 geological-geochemical (Khanchuk et al., 1999) maps made with consideration of new conceptual principles of plate tectonics.

Reconstruction of the Mz-Kz geodynamic settings was established for the region as well.

4 GEOGRAPHIC DATABASE (GDB)

In the project presented the personal geodatabase storage format by Environmental Systems Research Institute, Inc. (ESRI) was used as basis, with the exclusion of raster data of large volume and digital elevation models (DEM), that are stored as external files in Imagine format (*.img).

The coordinate system used in our geodatabase is geographic (lat/lon, WGS84).

Our GDB uses the vector model presenting data as objects with their own characteristics, behavior and relations. Possibilities to work with objects of different type were built into the system. These objects are considered to be simple (pictures and graphs such as schematic geological cross-sections, text files and tables from geological reports and so on), geographic (with coordinates), net (spatially related to other objects), topologically linked, annotations, and other more specialized ones. This model allows us to establish relations between the objects and rules to support their integrity.

Geographic objects can have unlimited number of attributes, which may be organized as separate tables, the links between which are defined with the help of the original identifier and/or additional fields of the table of attributes of geographic object types. The last variant is reasonable in case of a limited number of attribute characteristics and high density of data in the table rows. Attribute characteristics allow us to organize the search and selection of objects, quantitative analysis of their features, easy and fast creation of electronic maps, and links to the outer data, like those included into other databases.

5 DATA STRUCTURE

Information is thematically structured in our GDB into the following blocks:

5.1 The core geographic data
- Index grids - 1M and 200K topographic map sheets
- 30 arc seconds DEM (GTOPO30)
- 3 arc seconds DEM (SRTM3, up to 60°N)
- 1M base map:
  - administrative division (objects of Russian Federation);
  - hydrography;
  - roads, railroads;
  - populated places areas.
- Annotations for cartographic presentation of GDB materials in 1M, 2.5M and 5M scales.

5.2 Geology
- Digital model of regional geological structure. Its units are established in accordance with geochronological and genetic (for Quaternary deposits) subdivisions of the legend:
  - Polygon shapes of geological units;
  - Boundaries of geological unit polygons.
- Indexes (signs) of geological units.
- Faults (digital description of nature and geometry of fracture zones and zones of correlation disruption).
- Digital model describing the sea floor lithology.

5.3 Geodynamics
- Terranes.
- Orogenic belts.
- Overlaying and sutural rocks:
  - volcano-plutonic belts;
  - plutonic belts and fields;
  - massifs of autonomous anorthosite.
- Faults.

5.4 Metallogeny
- Metallogenic belts and zones.
- Lode and placer districts.
- Lode deposits
- Placer deposits

6 SOFTWARE ENVIRONMENT / TOOLS

ArcGIS 8.2 Desktop products are used as a
working environment of the end users. They can be used for managing and editing geographic and tabular data, as well as making maps and performing spatial analysis.

Maps of 1M, 2.5M and 5M scales were composed for cartographic presentation of GDB materials. The user’s interface of ArcGIS Desktop-products was customized with Map Book toolset (available from ESRI’s web site). It allows creation and output of map books, multi page documents based on a dataset, and index grid representing the pages. These toolset helps to produce a complete and organized hard copy of geographic data.

We also realized a possibility to “publish” the maps for cooperative work inside the institution and for exchange of maps with different persons. These “published” maps can be viewed, explored and printed in ArcGIS ArcReader. These software is available free.

Every map may have its own characteristics, including its graphical presentation and interface personalized for a final user.

7 CONCLUSIONS

The strategic goal of this work was creation of large-scale GIS for management of the regional PGE mineral basis. It proved to be efficient to: a) create information resource integrating all the data related to metallogenic analysis of the matter; b) apply the corresponding set of instruments of information management and analysis.

The created information resource allowed fulfilling a complex of tasks associated with geodynamic, geotectonic and metallogenic zoning of the region, focusing on its PGE mineralization. It allowed a set of computer modeling tasks to start.

The personal Geodatabase core functionality is similar to that of a large multi-user geodatabases be stored and managed using industrial-strength DBMS technology. This approach will allow easy development of large multi-user geodatabases and implementation of enterprise-like workflow process in future.

This project will be continued in future. Thus, accumulation of additional information, development of data management, and widening of its functions will constitute the second stage of our work. We also plan to link this GIS project with other projects devoted to systematization of the data on geology and metallogeny of the Far East, such as the similar recently developed project “Gold of the Russian Far East”.

ACKNOWLEDGEMENT

The work was partly supported by the Russian Foundation of Basic Research, Grant 06-05-96-106.

REFERENCES


On the origin of the PGE-enrichment in chromitites associated with ophiolite complexes: the case of Skyros island, Greece

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ABSTRACT: Small massive and schlieren-type chromite bodies hosted in the Skyros serpentinitized peridotites are dominated by high-Al variety in both PGE-poor and PGE-enriched (up to 3 ppm ΣPGE) chromitites, although both types are found in the entire island. Detailed investigation, by SEM/EDS, showed that apart from laurite (RuS₂) occurring as small inclusions within unaltered chromite grains, Ru-Ir-Os-minerals were identified within silicate matrix interstitially between chromite grains. Both Ru-Ir-Os alloys and sulphides exhibit significant Fe, Ni, Cr, Sb and As contents and a wide compositional variation. They are accompanied by serpentine, chlorite and Cr-garnet. The relatively high IPGE enrichment in chromitites may be related to post-magmatic processes during an extended period of deformation, including the ductile asthenospheric mantle flow and crustal brittle deformation. Metasomatic fluids have substantially modified the composition of primary laurite, generating Ru-Ir-Os-Fe-Cr-Co-Ni-bearing minerals.

KEYWORDS: PGE, PGM, chromite, PGE-enrichment, ophiolites, Skyros, Greece

1 INTRODUCTION

Platinum-group elements (PGE) abundances in large chromite deposits of Greece are generally low (few hundreds of ppb). A PGE-enrichment either in all PGE, only in Os, Ir and Ru (IPGE or refractory), or in Pt and/or Pd (PPGE), are a common feature of relatively small chromite occurrences.

This enrichment seems to be local and independent of the major element composition of chromite (Economou-Eliopoulos, 1996; Zhou & Robinson, 1997; Economou-Eliopoulos et al., 1999; Tsoupas & Economou-Eliopoulos, 2005). Agiorgitis et al., (1978) and Economou-Eliopoulos (1996) investigated the PGE contents in chromitites from the Skyros ophiolitic massifs. Tarkian et al. (1992) gave compositions of the PGE-minerals (PGM), the accompanying base metal-bearing minerals and silicate minerals.

In the present contribution SEM/electron microprobe analyses of individual mineral phases are presented, documenting the compositional variation of chromite, PGM and accompanying silicates, and their evolutionary stages.

2 CHARACTERISTICS OF THE SKYROS OPHIOLITES

The ultramafic massifs of the Skyros Island belong to the Eohellenic Pre-Cretaceous nape. A tectonic melange and ophiolitic rocks compose the Skyros dismembered ophiolitic massifs, which over thrust on to the Pelagonian massif (Katsikatsos, et al., 1986). Serpentinitized harzburgites, and to a lesser extent lherzolites and dunites are the predominant petrologic types. Broad mantle shear zones, are characterized by the presence of fish-shaped serpentinite bodies, commonly containing juxtaposed blocks with distinct compositional and microstructural characteristics. Small (a few thousand tons) massive and schlieren-type chromite bodies are hosted within serpentinitized dunites (Economou-Eliopoulos, 1996).

3 METHODS OF INVESTIGATION

Polished sections prepared from the chromite occurrences of the Skyros area were examined by reflected light microscopy and scanning electron microscope. Quantitative analyses.
were carried out at the University of Athens, Department of Geology, using a JEOL JSM 5600 scanning electron microscope, equipped with automated OXFORD ISIS 300 energy dispersive analysis system. Analytical conditions were 20 kV accelerating voltage, 0.5 nA beam current, <2 µm beam diameter and 50 second count times.

4 CHEMICAL COMPOSITION OF CHROMITE ORES AND PGE MINERALOGY

4.1 Chromite and silicates

The compositions of chromitites from the entire Skyros island area fall within both high-Cr and -Al types (Economou-Eliopoulos, 1996). Detailed investigation of numerous polished thin-sections from the area of Achladones (Skyros) showed a dominance of the high-Al variety in both PGE-poor and PGE-enriched chromitites. Although the composition of chromite is commonly homogeneous, dark gray and light colored phases can be distinguished (Fig. 1a,c) close to highly brecciated zones. A salient feature of PGE-enriched samples is the alteration of chromite (the average Cr/(Cr+Al) ratio of unaltered chromite is 0.56 and Mg/(Mg+Fe2+) is 64) to ferrian chromite (the Cr/(Cr+Al) ratio ranging from 69 to 0.76 and Mg/(Mg+Fe2+) from 57 to 51) even in the same polished section (Fig. 1c).

All silicate minerals occurring in interstices between chromite grains have been entirely altered to Fe-poor serpentine and chlorite. Cr-andradite (13-14 wt% Cr2O3 and 14 – 16 wt% FeO) as veinlets and interstitial secondary minerals are common (Fig 1a,b).

4.2 PGE contents and Ru-Ir-Os-minerals

Whole ore PGE analyses of massive chromitites in previous studies indicated that there is a local PGE-enrichment, mostly in refractory PGE in certain ophiolites of Greece (Table 1). Laurite (RuS2) has been identified as small inclusions within unaltered chromite grains in the Skyros (Achladones) chromitites (Tarkian et al., 1992; Table 2). Ru-Ir-Os- minerals were, however, identified within silicate matrix as interstitial secondary minerals (Fig. 1c, d, e). Both Ru-Ir-Os alloys and sulphides exhibit significant Fe, Ni and Cr contents and a wide compositional variation (Table 2; Fig. 1d,e). In addition sulphides contain Pt, Sb and As. Heazlewoodite (Ni 3S2) occurs commonly within fractures and the serpentine-chlorite matrix.

5 DISCUSSION

It has been accepted that inclusions of laurite in unaltered chromite are early magmatic phases formed by direct crystallization from basaltic magmas (Auge, 1985; Brenan & Andrews, 2001; Peregodova & Ohnenstetter, 2002; Mungall, 2005). Also, the presence of Os-, Ir, Ru- and Rh-bearing PGM within chromitites from some ophiolite complexes have been attributed in both in situ alteration or/and re-mobilization and re-deposition of PGE during post-magmatic processes, such as retrograde hydrothermal metamorphism (Tarkian & Prichard, 1987; Garuti & Zaccarini, 1997; Ahmed & Arai, 2003).

The mineralogical characteristics and textual relationships between PGM and hosting chromitites from the Skyros ophiolites are similar to those from Veria in terms of: (a) the IPGE enrichment, although it is much higher in the Veria chromitites (up to 25 ppm), (b) the association of the IPGE-enrichment with shearing zones, (c) the presence of laurite as inclusions within chromite and Ir-group phases in in-

| Table 1. Representative whole ore analyses of chromitites from Skyros (Achladones area) and Veria concentrations in ppb |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Location       | Os             | Ir             | Ru             | Rh             | Pt             | Pd             |
| Skyros         | 13-140         | 30-480         | 150-1200       | 7-160          | 20-280         | 20-40          |
| Veria          | 13-7400        | 26-6020        | 15-9700        | 11-310         | 2-760          | 3-750          |

Data from Economou-Eliopoulos & Eliopoulos (1999); Tsoupas & Economou-Eliopoulos (2007)

| Table 2. Representative microprobe analyses of PGM (Figure 1) from PGE-rich chromitites of the Skyros (Achladones) island |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Laurite*        | Fig. 1a,1      | Fig. 1a,2      | Fig. 1a,3      | Fig. 1a,4      | Fig. 1a,5      | Fig. 1a,6      |
| Os              | 14.1           | 5.88           | 7.96           | 15.49          | 13.05          | 44.8           |
| Ir              | 7.8            | 6.31           | 5.66           | 18.51          | 27.21          | 7.2            |
| Ru              | 43.4           | 53.35          | 48.48          | 38.23          | 30.59          | 37.8           |
| Pt              | n.d.           | 2.74           | 4.37           | 3.61           | 4.59           | n.d.           |
| Ni              | n.d.           | 0.68           | 1.17           | 1.21           | 1.03           | 6.7            |
| Fe              | n.d.           | 0.95           | 0.73           | 0.67           | 0.51           | 1.5            |
| Cr              | n.d.           | 0.38           | 0.34           | 0.34           | 0.44           | 0.9            |
| Sb              | n.d.           | 0.52           | 0.63           | 1.14           | n.d.           | n.d.           |
| As              | n.d.           | 2.11           | 2.76           | 5.81           | 10.01          | n.d.           |
| S               | 34.8           | 26.71          | 27.15          | 14.78          | 11.85          | n.d.           |

|                   | Fig. 1a,7      | Fig. 1a,8      | Fig. 1a,9      | Fig. 1a,10     | Fig. 1a,11     | Fig. 1a,12     |
| Os                | 100.1          | 99.11          | 99.14          | 99.28          | 100.42         | 98.9           |
| Pt                | 100.5          | 98.1           |                |                |                |                |

Symbols: n.d. = below detection limit; * = data from Tarkian et al. (1991).
Figure 1. Back-scattered electron images of strongly fragmented chromite (chr) associated with garnet (grt) and serpentine (srp) (Fig. 1a,b), IPGM in a matrix of serpentine associated with chromite/Fe-chromite (Fe-chr) (Fig. 1c,d,e) and alloys along cracks of chromite and Fe-chromite (Fig. 1f) from Skyros island. Heazlewoodite (hz) is common (Fig. 1b).
terstitial to strongly fragmented chromite grains, (d) the significant Ni, Cr, Fe As and Sb contents in both Ru,Ir,Os-sulphides and alloys, and their wide compositional variation, (e) the association of IPGM with Cr-garnet and low-Fe serpentine.

Thus, besides the typical laurite grains found as inclusions within chromite and the Pt and Pd- enrichment in chromitite attributed to magmatic processes (Prichard et al., 1996; Economou-Eliopoulos, 1996) the mineralogical and texture characteristics of relatively high IPGE enrichment in chromitites may be related to post-magmatic processes. They may cover an extended period of deformation, including the ductile asthenospheric mantle flow and culminated in shallow crustal brittle deformation. Metasomatic fluids have substantially modified the composition of primary PGM, mostly laurite, generating Fe-Cr-Co-Ni-bearing Os-Ir-Ru -minerals (Tsoupas & Economou-Eliopoulos, 2005, 2007). Furthermore, it seems likely that the most targeted locations for the chromitite-IPGM association are small chromite occurrences found along shear zones within ophiolite complexes.

ACKNOWLEDGEMENTS

The University of Athens is greatly acknowledged for the financial support of this work.

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Proceedings of the Ninth Biennial SGA Meeting, Dublin 2007 1633