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Zhang, L., Wang, C., Peng, Z., Tong, X. and Nan, J.
SY02, Magmatic sulphide and oxide ore deposits in maic and ultramaic rocks, a symposium in memoriam of the work and life of Prof. Hazel Prichard

Convenors:
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Michel Houlé
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Abstract. Any major physical system can be represented on a plot of length scale vs time scale. Different types of process have distinctive slopes on such diagrams, related to intrinsic properties of the system that resist transfer of components, specifically viscosity, in the case of fluid systems, or diffusivity in chemical systems. The fastest process at a given scale wins out in any competition for chemical or thermal components. These principles are applied to some of the critical processes in magmatic ore formation: derivation of sulfide from country rock, mechanisms of transport of sulfide liquid in magmas, and the behaviour of sulfide liquids after deposition.

1 Introduction

Mineral systems are the product of multi-scale interactions of physical and chemical processes. A goal of exploration geoscientists is to reverse-engineer these systems in order to recognise and detect the critical signals of these processes. Underpinning the science is a very simple principle: in attributing a particular effect to a proximal cause, both must be operating at similar length and time scales. Thinking of mineral systems in this way allows us to arrive at some useful conclusions. We illustrate this principle first in general terms then by specific reference to magmatic Ni-Cu-PGE sulfide mineral systems.

Any major physical system can be represented on a plot of length scale vs time scale (Fig 1). Sets of processes that make up major Earth system process – atmospheric circulation, ocean dynamics, tectonic cycles and mineral transformations – plot along linear arrays on this diagram. The slope of each array is related to the resistance to change within the system, which is controlled by viscosity, in the case of fluid systems, or diffusivity in chemical systems (these are analogous in the sense that viscosity is a measure of the diffusivity of momentum). From fast to slow, atmospheric dynamics are limited by the viscosity of air, ocean dynamics by the viscosity of water, tectonics by the viscosity of the mantle, and mineral reactions by chemical diffusivities.

2 Magmatic processes and ore formation

We apply this principle to magmatic processes in Fig. 2, identifying a range of processes that operate from the scale of LIP-forming mantle plumes to grain-scale processes within the magma or country rock. Processes can be divided broadly into three groups controlled by four different properties: chemical and thermal diffusivity, and magma and crust/mantle viscosity.

Figure 1 (below). Time scale - length scale plot for major types of Earth process
By applying the scale dependence principle, and adding a second principle saying that the fastest process at a given scale wins out in any competition for chemical or thermal components, we can draw some conclusions about the role of various mechanisms in ore formation.

2.1 Incorporation and transport of wall-rock sulfur

Magmatic Ni sulfide systems require a source of S from country rocks, and a number of mechanisms have been proposed, including volatile transport from pyrite breakdown in thermal aureoles, diffusion of liberated S through country rock, and direct incorporation of sulfide-bearing xenoliths through stoping or wall rock spallation, followed by melting of the xenolith. Following the scaling principle, it is clear that direct melting of xenoliths is by far the fastest process (Robertson et al. 2015a), although it overlaps in length-time space with the process of thermomechanical erosion of immediate footwall rocks beneath lava flows (Kauahikaua et al. 1998). Xenolith melting falls on the overlap between the magma viscosity and thermal diffusivity control domains, and consequently is a slower process than the flow of the assimilating magma, which falls entirely within the magma viscosity domain. Hence, it is likely that sulfide xenoliths are liable to be transported some distance from their site of incorporation before they have time to melt and release all of their sulfides as molten sulfide liquid.

A consequence of this is that much of the mass transfer of assimilated sulfide in magmas may be in the form of partially molten and disaggregated xenoliths (Robertson et al. 2015b). This may account for the very common close association between sulfide accumulations and xenoliths in many mafic-intrusion-hosted deposits (Barnes et al. 2017a).

2.2 Reaction rates and sulfide liquid equilibration

Subsequent enrichment of the sulfide liquid depends on processes of chemical diffusion in the magma, one of the slower classes of process (Mungall 2002). The critical controls here are the diffusivities of chalcophile elements in silicate magma, and the thickness and stability of compositional boundary layers developed around suspended droplets, in relation to the rates of transport and accumulation of sulfide liquid to form ore-grade accumulations. Robertson et al (2017) estimated equilibration times for sulfide droplets undergoing Stokes settling in a basaltic magma of the order of 100 days for mm sized droplets. Assuming typical magma flow rates of the order of 1 ms⁻¹ (Fig 2) droplets could be transported many km over this time scale. The implication is that unless flow is turbulent, with resulting rapid breakdown of chemical boundary layers, sulfide droplets or sulfide-silicate aggregates would need to be transported on a scale of km from their source in order to attain high R factors. Turbulent flow is unlikely for mafic magmas. A further implication is that sulfide droplets could be transported considerable distances in sulfide-undersaturated magmas.

Lesher 2017), rather than purely as suspended droplets (Robertson et al. 2015b). This may account for the very common close association between sulfide accumulations and xenoliths in many mafic-intrusion-hosted deposits (Barnes et al. 2017a).
2.3 Sulfide melt-infiltration fronts and migration of sulfide liquids through permeable rocks

A number of lines of evidence, summarised by Barnes et al (2017b), indicate that the sulfide liquids can percolate considerable distances through partially (or even completely) solidified cumulates as a result of gravity-driven displacement of less dense silicate liquid. This process underpins the formation of some if not all matrix ores and interspinifex ores and at least some sulfide matrix ores such as those at Voisey’s Bay (Barnes et al. 2017a). In the case of interspinifex ores (Barnes et al. 2016), sulfide liquid can penetrate over dm scales through originally solid komatiite on the time-scale of solidification of a ~10 m thick komatiite flow, of the order of a year. Considering the sulfide-matrix breccias at Voisey’s Bay, we estimate that sulfide liquid migrates through the pore space in a coarse silicate xenolith “sludge” at a rate of metres over weeks over length scales of tens of m. In the case of the pinch-out ores at Kambalda, sulfide liquids have evidently melted their way into footwall basalts on length scales of ~ 10 m, also on the time scale of solidification of individual ~10s of m thick flows (Staude et al. 2016). It is therefore entirely plausible that hot molten sulfide bodies could melt their way into non-refractory country rocks such as argillites at a scale of tens of metres on the thousand to hundred thousand year time scale expected for the solidification of typical ore-hosting small intrusions, particularly if these intrusions are kept hot over long periods of time by continuous magma flux. The presence of semi-massive sulfide ore bodies tens of metres away from host intrusions should not automatically be taken as the consequence of tectonic remobilisation; in many cases it may very well be a consequence of magmatic infiltration of sulfide melt into country rock, like the metaphorical hot knife through butter.

3. Conclusions

The time and length scale estimates presented here are in many cases back-of-envelope calculations with very large order-of-magnitude uncertainties. However, it is clear that even at such rough levels of estimation, it is possible to draw some fundamental and in some cases counter-intuitive conclusions about ore forming processes, and to challenge some long-established pieces of received wisdom. The next step is to place some more rigorous and quantitative constraints on some of the arguments above. Much of the work has already been done in the literature of volcanology, intrusion emplacement and terrestrial mass and heat flow. Our next challenge as economic geologists is to move from the comfort zone of geochemical modelling into rigorous understanding of the physics of ore forming processes. Computational fluid dynamic codes run on the current generation of supercomputers have enormous potential to generate the next step change in our understanding of the intriguing processes that form some of the world’s most valuable metal accumulations.

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Fe-Ti-P deposits associated with massif-type anorthosites

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Abstract. Proterozoic massif-type anorthosite are known to host potential resources for Fe-Ti-P ores. Three major ore deposits are presently mined for ilmenite and Ti-magnetite: Allard Lake, Tellnes and Damiao. Additional occurrences have been documented with some of them currently explored. This review discusses the controlling factors on ore grades, mineralogy, and major & trace element distribution. We present petrogenetic models of currently mined deposits and the characteristics of minor ore bodies from anorthosite provinces worldwide (Grenville, North China Craton, East European Craton, Rogaland, Laramie). A mineralogical classification of Fe-Ti-P ores is proposed: (1) Gabbro-noritic ilmenite ore ± apatite ± magnetite; (2) Ti-magnetite-dominated ore; (3) Nelsonite (Fe-Ti oxides + apatite); (4) Rutile-ilmenite ore. Potential ore-forming processes explaining the formation of huge concentrations of ilmenite, ±magnetite, ±apatite are reviewed.

1 Massif-type anorthosites

Massif-type anorthosites are thought to crystallize in two stages (Ashwal 1993). The first involves the accumulation of plagioclase at the top of deep-seated magma chambers, followed by the intrusion of buoyant plagioclase mushes into mid-crustal levels. The ascent of the plagioclase crystal mush from the upper part of the deep magma chamber results from gravitational instability due to its low density relative to the crust. The polybaric crystallization of anorthosites is largely deduced from the occurrence of high-alumina orthopyroxene megacrysts containing plagioclase exsolutions. The alumina content of orthopyroxene commonly displays a continuous range from 2 to 8 wt % Al2O3, supporting continuous polybaric crystallization during diapiric rise of the anorthositic mush, from 11-13 kbar down to 5-3 kbar (Charlier et al. 2010a).

Massif-type anorthosite plutons and associated mangerite, charnockite and (rapakivi) granite (AMCG suite) occur in various terranes but are restricted to the Proterozoic (Fig. 1). The most important Fe-Ti ores are associated with andesine anorthosite, but significant resources of Ti-magnetite also occur in labradorite anorthosites.

2 Major deposits

2.1 Lac Tio, Quebec

The Lac Tio (or Allard Lake) hemo-ilmenite ore body is situated on the north shore of the Saint Lawrence estuary (Quebec). The deposit outcrops in the 1.06 Ga Lac Allard anorthosite, which is part of the Grenville province in North America (e.g. Morisset et al. 2009). The ore body is the world’s largest known hard-rock ilmenite deposit, with current reserves estimated at ca. 138 Mt at grades exceeding 60 wt.% hemo-ilmenite. The TiO2 content of the ore is variable but is mainly between 32 and 38 wt.% TiO2 (Fig. 2).

The main ore body is a funnel-shaped intrusion
measuring 1.03 x 1.10 km and 100-300 m thick. Two smaller bodies are separated from the main deposit by faults and anorthosite. The ore is an ilmenite-rich norite (or ilmenitite) made up of hemo-ilmenite (Hem22.6-29.4, 66.2 wt.% on average), andesine plagioclase (An45-50), aluminous spinel and locally orthopyroxene. Compared to other deposits, ilmenite in Lac Tio is significantly richer in hematite and has a moderate MgO content (2.5-3.0 wt.%).

The ilmenite-rich body has usually been considered to have formed as an enormous drop of immiscible Fe-Ti-enriched liquid separated from the magma remaining after the crystallization of the andesine anorthosite (e.g. Lister 1966). However, whole-rock compositions are controlled by the proportions of ilmenite and plagioclase ± orthopyroxene, which supports a cumulate origin for the deposit (Charlier et al. 2010b). Cr concentrations in ilmenite reveal normal and reverse fractionation trends, suggesting multiple episodes of magma emplacement and alternating periods of fractional crystallization and magma mixing. This mixing produced hybrid magmas located in the stability field of ilmenite, resulting in periodic crystallization of ilmenite alone. The unsystematic differentiation trends in the Lac Tio deposit, arising from a succession of magma pulses, hybridization, and the fractionation of hemo-ilmenite alone or together with plagioclase, suggest that the deposit formed within a magma conduit (Charlier et al. 2010b). This dynamic emplacement mechanism associated with continuous gravity-driven accumulation of Fe-Ti oxides, and possibly plagioclase buoyancy in a fractionating ferrobasalt, explains the huge concentration of hemo-ilmenite.

2.2 Tellnes, SW Norway

The Tellnes ore body is an ilmenite-rich norite averaging slightly more than 18% TiO2. It was discovered in 1954 during an aeromagnetic survey, and has been mined since 1960 by TITANIA A/S as an open-pit (Krause et al. 1985). Reserves are estimated at 57 Mt TiO2, representing 14% of the world reserves of ilmenite and 12% of the total world reserves of titanium minerals (ilmenite + rutile). By-products are magnetite and Ni-Cu sulphide concentrates. The Tellnes ore body is intruded into the Ana-Sira anorthosite, which is part of the Rogaland anorthosite province in SW Norway. It has a sickle-shaped outcrop oriented WNW-ESE to NNW-SSE with a maximum width and length of 400 m and 2700 m, respectively. Its 3D shape is that of a gently plunging elongated trough. The intrusive character of the ore body is evident from sharp contacts with the host anorthosite, numerous apophyses and anorthosite xenoliths. The TiO2 content of the ore is usually 16-20 wt.% (Fig. 2), with concentrations generally highest in the centre of the ore body and decreasing towards the margins (Charlier et al. 2006). The MgO content of ilmenite (1.4-4.4 wt%) is systematically lower in samples from the margins of the ore body. This has been interpreted to be due to extensive postcumulus re-equilibration with trapped liquid and ferromagnesian silicates, and is correlated with distance to the host anorthosite (Charlier et al. 2007). The hematite content varies slightly between Hem10 and Hem14 and is systematically higher in samples from the margins of the ore body.

The deposit displays significant variation in the compositions and proportions of minerals. The lower part of the ore body mainly contains plagioclase and ilmenite. Upsection, orthopyroxene and olivine appear. Marginal zones are characterized by high plagioclase and apatite contents and lower proportions of ilmenite. Variations in ilmenite composition with stratigraphic height indicate that fractional crystallization was the major differentiation process in the Tellnes ilmenite deposit. The calculated cotectic proportions of ilmenite in plagioclase-ilmenite cumulates is 17.5%, significantly lower than the proportion of cumulus ilmenite in the bulk deposit (ca. 50%; Charlier et al. 2007). This implies sorting of ilmenite and its preferential accumulation at the bottom of the chamber, which has been interpreted to have had a sill shape that is now deformed into an elongated trough (Charlier et al. 2006).

2.3 Damiao, China

The Damiao deposit is hosted in the ca. 1.74 Ga Damiao andesine anorthosite complex, located in the northern part of the North China Craton (Zhao et al. 2009). The deposit

![Figure 2: Histograms of the TiO2 content (wt.%) of whole rocks from Lac Tio (data from Charlier et al. 2009), Tellnes (data from Charlier et al. 2006) and Damiao deposits (data from Chen et al. 2013).]
has been mined in open pits and underground for several decades at an annual production of 2 Mt ore with economic concentrations of Fe, Ti, P and V. It is subdivided into many discordant ore bodies (more than 90) occurring as irregular lenses, veins or pods crosscutting the anorthosite (e.g. Chen et al. 2013). The ore has an average grade of about 36 wt.% Fe₂O₃tot, 7.0 wt.% TiO₂, 0.3 wt.% V₂O₅, and 2.0 wt.% P₂O₅ (Sun et al. 2009). Various types of ore rocks are identified (Li et al. 2014): massive Fe ore with Ti-magnetite and ilmenite (Fe-Ti ore); massive P ore containing more than 50% apatite (nelsonitic ore); massive Fe-P ore with apatite, Ti-magnetite and ilmenite (oxide-apatite gabbronorite ore); and disseminated Fe and Fe-P ore representing more than 60% of the total reserve. The ore is dominated by Ti-magnetite and the whole-rock TiO₂ content of the Damiao deposit is comparatively low, mainly between 6 and 12 wt.% (Fig. 2). However, the composition of the ilmenite is of much higher fraction with low Cr and Mg (Chen et al. 2013). Ilmenite contains less than 0.5 wt.% MgO, and has a low hematite fraction (< 7 mol%). Immiscibility, promoted by oxidizing crystallization conditions and high phosphorous concentration in the magma, and formation of a nelsonitic melt (Fe-Ti-P-rich ferrobasalt) have been proposed as a major ore-forming process (Chen et al. 2013). The crystallization products of this melt, enriched in Ti-mag, ilm ± apatite, would have been accumulated in residual melt pockets of the host anorthosite.

3 Ore-forming processes

Besides the three major mines, many occurrences have been described in the literature (Table 1). These ores have been partly mined or represent potential prospect. For all these Fe-Ti-P ores, a range of ore-forming processes have been suggested.

3.1 Fractional crystallization, crystal sorting and plagioclase buoyancy

In the Tellnes deposit, the Grader intrusion (Charlier et al. 2008) and the Lac Tio mine, plagioclase and ilmenite are the first liquidus phases. In more differentiated cumulates, ilmenite and plagioclase may be accompanied by olivine, orthopyroxene, clinopyroxene, magnetite and apatite. Calculations of the cotectic proportions of ilmenite in ferrobasaltic liquids yield values of ca. 20 wt%. This proportion of ilmenite in a cumulate corresponds to ca. 8 wt% TiO₂ in the rock, which is not sufficient to form a titanium ore. Melts associated with anorthosite also have high concentrations of FeOtot, which exert a strong influence on the density of the melt. Several studies have discussed the “plagioclase-magma density paradox” (e.g. Scoates 2000), i.e. that intermediate-composition plagioclase (An₄₀₋₆₀) is less dense than the melt with which it is in equilibrium. In melts saturated with plagioclase + Fe-Ti oxides, the different densities of these minerals can result in flotation of plagioclase but sinking of the dense Fe-Ti oxides (ρilm = 4.7, pmag = 5.2). This cumulate sorting produces Fe-Ti oxide abundance greater than the cotetic proportions would suggest.

3.2 Immiscibility

Immiscibility between two silicate melts (ferrobasalt-rhyolite) has been recognized experimentally and in natural systems as a potential differentiation mechanism in evolved basaltic magmas (e.g. Philpotts 1982; Charlier and Grove 2012). Philpotts (1967) proposed that immiscibility is responsible for the origin of certain Fe-Ti oxide and apatite rocks. However, data presented by Philpotts (1967) for the immiscibility of an Fe-Ti-P-rich melt were obtained at the unrealistically high temperature of 1420°C. Duchesne (1999) proposed instead that nelsonites represent cumulates. The absence or low abundance of ferromagnesian silicates could result from earlier saturation of ilmenite and apatite compared to ferromagnesian silicates.

Another hypothesis is that nelsonites represent cumulates crystallized from iron-rich immiscible melts (Namur et al. 2012). In this scenario, the Fe-rich melt segregates from the Si-rich melt. The ore-rock does not correspond to the immiscible liquid. Instead, the ore is a cumulate crystallized from the Fe-rich melt. The Si-rich melt will produce cumulate rocks with the same cumulus assemblage but different phase proportions.

Table 1: Major Proterozoic anorthosite provinces containing Fe-Ti-P ores

<table>
<thead>
<tr>
<th>Anorthosite province</th>
<th>Country</th>
<th>Areal Extent</th>
<th>Age (Ma)</th>
<th>Main ore deposits</th>
<th>Dominant ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Korosten</td>
<td>Ukraine</td>
<td>2185</td>
<td>1789±2</td>
<td>Fedorivka</td>
<td>IIminite-magnetite</td>
</tr>
<tr>
<td>Damiao</td>
<td>China</td>
<td>80</td>
<td>1740±20</td>
<td>Damiao, Maying, Heishan</td>
<td>Magnetite-Ilmenite</td>
</tr>
<tr>
<td>Mazury</td>
<td>Poland</td>
<td>8000</td>
<td>1559±39</td>
<td>Suwalki</td>
<td>Magnetite-Ilmenite</td>
</tr>
<tr>
<td>Laramie</td>
<td>Wyoming, USA</td>
<td>800</td>
<td>1434±3</td>
<td>Iron Mountain, Sybille, Strong Creek</td>
<td>IIminite-magnetite</td>
</tr>
<tr>
<td>Kunene</td>
<td>Angola-Namibia</td>
<td>18000</td>
<td>1385±25</td>
<td>Oryeheke</td>
<td>IIminite</td>
</tr>
<tr>
<td>Riviere Pentecôte</td>
<td>Quebec, Canada</td>
<td>600</td>
<td>1354±3</td>
<td>Riviere Pentecôte</td>
<td>IIminite-magnetite</td>
</tr>
<tr>
<td>De La Blache</td>
<td>Quebec, Canada</td>
<td>1500</td>
<td>1327±16</td>
<td>Hervieux, Schmoo, Lac Dissimieu</td>
<td>IIminite-magnetite</td>
</tr>
<tr>
<td>Lac St Jean</td>
<td>Quebec, Canada</td>
<td>20000</td>
<td>1156±2</td>
<td>Saint Charles, Buttercup, Lac à Paul (apatite)</td>
<td>Magnetite-Ilmenite</td>
</tr>
<tr>
<td>Morin</td>
<td>Quebec, Canada</td>
<td>2500</td>
<td>1155±3</td>
<td>Degrobois, Ivory, Saint-Hippolyte</td>
<td>IIminite-magnetite</td>
</tr>
<tr>
<td>Adirondacks</td>
<td>New York, USA</td>
<td>3000</td>
<td>1154±6</td>
<td>Sanford Lake</td>
<td>Magnetite-Ilmenite</td>
</tr>
<tr>
<td>Havre St Pierre</td>
<td>Quebec, Canada</td>
<td>5500</td>
<td>1060±3</td>
<td>Grader, Allard Lake, Dig Island, Everett</td>
<td>Ilmenite-Rutile</td>
</tr>
<tr>
<td>Saint-Urbain</td>
<td>Quebec, Canada</td>
<td>450</td>
<td>1053±3</td>
<td>Coulombe, Bignel, Dupont, General Electric</td>
<td>Ilmenite</td>
</tr>
<tr>
<td>Oaxaca</td>
<td>Mexico</td>
<td>400</td>
<td>1012±12</td>
<td>Ptuma Hidalgo</td>
<td>Ilmenite</td>
</tr>
<tr>
<td>Valin (Labrieville, Mattawa)</td>
<td>Quebec, Canada</td>
<td>1265</td>
<td>1010±5</td>
<td>Minepoix, La Hache, Lac Brule</td>
<td>Magnetite-Ilmenite</td>
</tr>
<tr>
<td>Rogaland</td>
<td>Norway</td>
<td>580</td>
<td>931±2</td>
<td>Tellines, Storgangen, Hesnes, Bjerkrein-Sokndal</td>
<td>Ilmenite</td>
</tr>
</tbody>
</table>

SY02 – Magmatic sulfide and oxide ore deposits in mafic and ultramafic rocks
A symposium in memoriam of the work and life of Prof. Hazel Prichard
3.3 Magma mixing

The Cr concentration in ilmenite from the Lac Tio deposit displays normal and reverse fractionation trends upsection. Charlier et al. (2010b) interpreted these compositional characteristics as evidence for multiple pulses of magma emplacement and alternating periods of fractional crystallization and magma mixing. Mixing of magmas would have produced hybrid magmas located in the stability field of ilmenite, resulting in crystallization of ilmenite alone after each mixing event. It is highly probable that the natural plagioclase-ilmenite cotectic is curved and that mixing of two magmas lying on the cotectic can produce a hybrid located in the stability field of ilmenite, which will therefore crystallize only ilmenite until the liquid joins the cotectic. This ilmenite would accumulate due to a high density contrast with the liquid.

3.4 Filter-press compaction

Anorthosite plutons are emplaced as diapirs and crystallize during the ascent of the plagioclase mush. This dynamic emplacement provides the conditions necessary to produce stress-driven melt segregation in partially molten rocks. The result is the formation of pure anorthosite that is segregated from the residual melt (enriched in Fe-Ti-P). The residual melt can be collected in the margins of massif anorthosites, where mafic intrusions are commonly observed.

3.5 Solid-state remobilization

It is not rare to observe veins or seams of pure hemo-ilmenite in massif-type anorthosites. Their emplacement as a melt is highly questionable because the melting point of hemo-ilmenite (at least 1365°C, depending on the amount of dissolved hematite in the solid solution) is hotter than typical magmatic temperature. In Fe-Ti-rich cumulate rocks, ilmenite and magnetite are always interstitial to the silicate minerals, even when they crystallize on the liquidus after plagioclase and before pyroxenes. In these rocks, ilmenite tends to concentrate in low-stress zones such as pressure shadows. It is thus observed that ilmenite can easily recrystallize and migrate by diffusion creep in subsolidus conditions. Such a migration process may also occur on a larger scale during high-T deformation linked to anorthosite emplacement, giving rise to massive veins of ilmenite.

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Litho- and chemostratigraphy of the 42 Moz Flatreef PGE deposit, northern Bushveld Complex

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Abstract. The Flatreef is a world-class PGE deposit recently discovered by Ivanhoe Mines in the northern lobe of the Bushveld Complex, down-dip of existing mining and exploration operations. Current resources stand at 42 Moz PGE’s (346 Mt with 3.8g/t 4E, 0.32% Ni and 0.16% Cu) which, in the case of Pt, is equivalent to > 4 years global annual production, making it one of the largest PGE deposits globally. The grade and thickness of the mineralised interval is highly unusual, with some drill core intersections having over 4ppm over 90m. Here, we document the down-dip and along-strike litho- and chemostratigraphy of the Flatreef, based on a diamond drill core database totalling > 720km.

1 Introduction

Since the discovery of the Merensky Reef and the Platreef in the 1920s, debate has continued about the potential stratigraphic correlation between the two types of reef. This is an important question for the exploration industry as a good stratigraphic understanding is critical in generating greenfields and brownfield targets. The early workers (Wagner 1929; van der Merwe 1976) argued that the Platreef is a strongly contaminated stratigraphic equivalent of the Merensky Reef. This view has remained controversial. In the present paper we aim to contribute to this important question by documenting the litho- and chemostratigraphy of the recently discovered Flatreef that constitutes a down-dip extension of the Platreef. Based on the inspection and analysis of more than 720km of diamond drill core, we argue that the Flatreef sequence shows strong similarities to, and thus can be correlated with, the Upper Critical Zone (UCZ).

2 Regional geology of the Northern Lobe

In the northern lobe of the Bushveld Complex the Rustenburg Layered Suite (RLS) is regionally transgressive relative to the floor rocks. In the south, the RLS overlies the Magaliesberg quartzite, whereas towards the north, the RLS progressively transgresses through the entire Transvaal Supergroup until, from the farm Drenthe northwards, it overlies the Archean basement. Simultaneously, the igneous sequence undergoes significant changes; in the south the RLS forms a compact 1.2km thick sequence consisting of Lower Zone, putative Lower Critical Zone (LCZ), UCZ, Main Zone (MZ) and Upper Zone (UZ). Layers correlated with the Merensky Reef and UG2 chromitite were intersected by deep bore holes (Hulbert 1983) and appear to transform into Platreef-style zones at shallow levels (Maier et al., 2008). To the north of the Planknek fault, the correlation of the Platreef with the UCZ remains less accepted. Proponents of the model include White (1994), Kinnaird et al (2005) and Mitchell and Scoon (2015) whereas other authors favour distinct staging chambers (McDonald and Holwell, 2011). This uncertainty arises partly from the fact that deep drill core exposure has been lacking until relatively recently.

3 Geology of the farm Turfspruit and discovery of the Flatreef

Turfspruit is located some 15km to the north of Mokopane. The basal part of the RLS (LZ) intruded shallow-marine to shelf-clastic sediments of the Duitschland Formation, stratigraphically situated at the base of the Pretoria Group. The Duitschland Formation attains a maximum thickness of approximately 1,000m to 1,200m and is divided into two parts by a clear sequence boundary. Below the sequence boundary, the formation is characterised by a basal conglomerate and diamicite unit, whereas the upper portion consists of carbonate shale and interbedded carbonates, formed in an initial deep-water environment (Bekker, 2001).

Exploration by Ivanhoe Mines in the late 1990s initially focussed on delineation of mineralization that could support open-pit mining. In 2007, Ivanhoe Mines commenced a deep drilling program to investigate the continuity and grade in an area targeted as having underground mining potential. This led to the discovery of thick mineralised units (up to 4.5ppm over 90m) and the recognition that at a depth of around 500m, the dip of the Platreef is approximately 1,000m to 1,200m and is divided into two parts by a clear sequence boundary. Below the sequence boundary, the formation is characterised by a basal conglomerate and diamicite unit, whereas the upper portion consists of carbonate shale and interbedded carbonates, formed in an initial deep-water environment (Bekker, 2001).

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4 Lithostratigraphy of the Flatreef

At the base of the exposed sequence are up to 700m-wide sills of LZ (Yudovskaya et al. 2013) and 100-200m-wide sills of putative LCZ emplaced (locally with chilled margins) into pelitic, dolomitic, and locally quartzitic and evaporitic rocks belonging to the Duitschland Formation. Next is an approximately 100 -300m sequence of sulfide...
mineralised (1-5% sulfide) layered mafic-ultramafic rocks containing occasional sedimentary xenoliths that we interpret to represent the Upper Critical Zone (UCZ). At the base are Cr-rich pyroxenites locally containing an up to 1m wide chromitite seam interpreted to represent the UG2 chromitite (2-6ppm Pt+Pd) (Figure 1). This is overlain by pyroxenite and then layered noritic-anorthositic rocks. Next is a sequence consisting of strongly mineralised orthopyroxenite and harzburgite overlain by unmineralised pyroxenite and then noritic-anorthositic cycles interpreted as the equivalent of the Merensky Cyclic Unit (MCU). This is in turn overlain by mineralised pyroxenite overlain by noritic cycles assigned to the Bastard Cyclic Unit (BCU).

**Figure 1:** Drill core intervals of Flatreef units. (a) Bastard Reef, (b) Merensky Reef, (c) UG2 chromitite

The base of the Main Zone is defined by a mottled anorthosite, correlated with the Giant Mottled Anorthosite of the Western Bushveld Complex. It is overlain by >1000m of Main Zone consisting of relatively massive gabbro-norite. Compared to the Western Bushveld Complex, the entire Flatreef UCZ is strongly enriched in sulfide and PGE. It also shows higher CaO, K₂O, Rb and Zr, and lower Al₂O₃ indicating pervasive contamination with calcsilicatite and hornfels, notably in the rocks below the Merensky Reef, and infiltration and intrusion by granitic melts. Lateral continuity of layers between drill cores is locally less persistent than in the WBC, likely resulting from the pinching-out of feldspathic intervals whereas ultramafic units are locally considerably thickened. The considerable lateral variation in the thickness of layers and units, and the generally greater thickness of the mineralisation, are interpreted to result from a combination of regional-scale potholing, lateral facies variation, and sediment assimilation. In the shallow, up-dip portions of the project area, the entire Flatreef package becomes increasingly contaminated to the extent that individual units are becoming somewhat more difficult to correlate between drill cores. However, within these shallow areas it is still possible to correlate higher grade mineralized zones with the UG2, Merensky and Bastard reefs. This package essentially represents the Platreef as exposed in outcrop and shallow bore holes across much of the northern limb. The new data thus suggest that the Flatreef is the correlative of the UCZ, and that the Platreef is an up-dip extension of the UCZ.

5 Representative drill core intersections

Drill core UTM232 (Figure 2a) is located in the centre of the Flatreef and intersects well-developed Bastard and Merensky cyclic units overlain by the Giant Mottled Anorthosite and underlain by contaminated pyroxenites and norites. Remnants of the UG2 chromitite occur sporadically in places. The Bastard Reef is approximately 5m wide and has 3ppm PGE. Mineralisation associated with the Merensky Reef is about 24m wide at a grade of about 3.8 ppm. Higher grades of >5ppm occur over about 5m. Notably PGE contents and Pt/Pd decrease with depth, analogous to most other intersection on the project area.

Drill core TMT006 (Figure 2b) was also collared in the central portion of the property. This hole intersected the most richly mineralised interval in the entire property, with about 4.5ppm PGE over 90m (Ivanhoe Mines media release October 2013). The Bastard unit overlies pyroxenite of the Merensky Unit (i.e. the latter is “beheaded”, possibly through potholing). The Bastard Reef is about 4m wide grading about 3ppm PGE. The Merensky Unit consists predominantly of pyroxenite and is about 40m thick. The well mineralised interval is however about 90m wide, running at an average grade of 4.5ppm PGE, with peak grades of 6-12ppm over about 30m. This reflects the percolation of PGE-rich sulphides into the strongly contaminated footwall of the Merensky Reef. PGE grade and Pt/Pd decrease with depth. The sequence has similar major and trace element contents as most other Merensky intersections, with about 30% MgO, 2500ppm Cr, 1-5% sulfide, 10-15ppm Zr, and 2-4 ppm La.

6 Lateral correlation of units

Leapfrog profiles across the property (Error! Reference source not found.) clearly indicate that the Flatreef represents an area where the mineralised sequence both flattens and becomes markedly thicker. The profile also illustrate that the LZ and the LCZ represent sills,
intruded below a regionally extensive raft of metamorphosed shale and dolomite. Also note that the distance between the top of the UCZ and certain marker horizons in the Main Zone (i.e. the Tennis Ball Marker) increases above the Flatreef. Of further note is the up-dip extension of the Flatreef where a major magmatic slump has developed, with an interlayer of MZ within the UCZ.

7 Conclusions

The data presented here indicates that the Flatreef shows laterally correlatable cyclic units featuring basal chromitite and pyroxenite overlain by norite and anorthosite, analogous to the WBC. The mineralised interval can be correlated across the property. However, interaction with the dolomitic-pelitic floor has locally led to a strong alteration overprint. Furthermore, a combination of potholing and irregular floor topography has led to significant thickness variations along strike and dip. The data indicates that the Flatreef is a down dip extension of the Platreef and that both can be correlated with the UCZ of the western and eastern Bushveld Complex.

Acknowledgements

Permission to present and financial support from Ivanhoe Mines Ltd is acknowledged.

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Ivanhoe Mines reports unprecedented 90-metre intersection of 4.51 grams of platinum, palladium, rhodium and gold per tonne, plus 0.37% nickel and 0.20% copper, at its Flatreef exploration and development project on South Africa’s Bushveld Complex (Media Release, 16 October 2013).


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Petrogenetic constrains on Ni-Cu-PGE deposits from the south Rae Craton and Chesterfield Block in the Canadian Shield

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Abstract. In the western Churchill Province, the southern portions of the Rae craton and Chesterfield block are host to the lesser known ca. 2.6 Ga Nickel King and Axis Lake and the >2.6 Ga Ferguson Lake Ni-Cu±PGE deposits. The Nickel King and Axis Lake deposits are hosted by metanoritic intrusions, whereas the Ferguson Lake ore is contained in a metagabbro. The metanorites have LREE enrichments over HREE (La/Yb=8.1-17.3), and negative Nb and Zr anomalies, indicative of an arc-derived magma. The low Zr/Y (1.4-3.0) and Th/Yb (0.2-0.7) values, and minor LREE to HREE enrichments (La/Yb=1.6-4.8) of the Ferguson Lake host-rocks are comparable to those of the neighboring back-arc basin derived tholeiitic basalts of the 2.7 Ga MacQuoid belt. We suggest the Ferguson Lake intrusion was formed under an analogous geodynamic environment.

These preliminary data indicate the mafic units that host Archean Ni-Cu-PGE deposits in the southern Rae craton and Chesterfield block may represent different sections of protracted (2.6 and ~2.7 Ga) convergent margin magmatism (arc/back-arc) during initial formation and assembly of the Rae craton. The important implication is that widespread Neoarchean basaltic rocks with arc/back-arc-like signatures in the southern Rae craton and Chesterfield block may be important targets for Ni-Cu-PGE.

1 Introduction

Magmatic Ni-Cu-PGE deposits occur in mafic to ultramafic rocks mainly situated along extensional margins (e.g., continental rifting, Noril’sk district: Yakubchuk and Nikishin 2004). These ore-systems were formed from the Archean to the Phanerozoic (Naldrett 2010), where most of the Ni sulfide mineralization was generated in association with intra-plate magmatic activity or early rifting of the continental crust (e.g., Naldrett 2004). Other less common examples of Ni-Cu-PGE mineralization and occurrences are found in the subduction-related Alaskan/Ural-type intrusions (e.g., 2.7 Ga Quetico: Canada; Pettigrew and Hattori 2016) and in back-arc basin tholeiitic rocks (e.g., 2.7 Ga Belledere-Angliers belt Quebec, Canada: Barnes et al., 1993).

The Canadian Shield has long been known to host a number of world class Precambrian Ni-Cu-PGE deposits (e.g., Raglan, Quebec), and as such, it is considered a prime target for mineral exploration of this type of ore.

The western Churchill Province (wCP) in the Canadian Shield includes the Rae and Hearne cratons (Hoffman 1988), and the intercalated Chesterfield block (Berman et al. 2007). The Chesterfield block and Rae craton have multiple greenstone belt-hosted (e.g., Yathkyed, MacQuoid and Rankin) Au and base metal mineral occurrences (e.g., Meliadine gold district: Lawley et al. 2016; Meadowbank gold deposit: Armitage et al. 1996), including the past-producing Rankin Inlet Ni-Cu-PGE deposit (e.g., Bannatyne 1958).

The most significant Ni-Cu±PGE occurrences of the southern Rae craton (Nickel King and Axis Lake deposits) and southwestern Chesterfield block (Ferguson Lake deposit) are hosted in a series of less studied and ill-constrained Neoarchean metanoritic and metagabbroic intrusions. In this study we provide results of whole rock major and trace element geochemistry and present preliminary interpretations on the petrogenesis and tectonic setting of the Nickel King, Axis and Ferguson Lake deposits. Additionally, the clinopyroxene chemistry of Nickel King is used as a petrogenetic indicator.

2 Geological setting

2.1 Rae craton and Chesterfield block

The Rae craton contains variably deformed Mesozoic to Neoarchean (ca. 3.2–2.6 Ga) tholeiitic to calc-alkaline metaplugitic and metasupracrustal rocks (e.g., Pehrsson et al. 2013) ultramafic through felsic in composition. The southern Rae craton consists of a variety of, upper amphibolite- to granulite-grade metasedimentary, metavolcanic, banded iron formation and metamultrusive rocks (e.g., Hamner 1997; Martel et al. 2008).

The Chesterfield block includes the Yathkyed, Angikuni, and MacQuoid greenstone belts, collectively
interpreted as being deposited in a back arc-tectonic setting (e.g., Sandeman et al. 2006). The geochemical composition of these volcanic rocks varies from tholeiitic to calc-alkaline basalt and calc-alkaline andesite to rhyolite (Sandeman et al. 2006). As a whole, these units are interpreted to comprise multi-deformed sheets of juxtaposed arc, back arc, and fore arc rocks, that were intruded by 2.69–2.67 Ga tonalite and ca. 2.61 Ga monzogranite- to granodiorite-dominated plutonic complexes (e.g., Davis et al. 2004; 2006).

The Chesterfield block and the Hearne craton are separated by the Snowbird Tectonic Zone (STZ; Pehrsson et al. 2013), which is a northeast-trending structure defined by a >2800 km long zone of steep gravity gradients extending from Hudson Bay into the Alberta subsurface (Goodacre et al. 1987).

### 2.2 Geology of the Nickel King, Axis and Ferguson Lake deposits

The ca. 2.6 Ga Ni-Cu Nickel King deposit is located west of the STZ, in the southeastern portion of the Northwest Territories (NWT). It consists of two arcuate and stacked, south-dipping, undeformed to weakly strained metamorphic intrusions, with variable thicknesses (10 to 100m) that are hosted by a paragneiss unit. The intrusions are metamorphosed up to granulate facies and comprise an orthopyroxene-plagioclase-clinopyroxene-biotite-pargasite assemblage. The sulfide mineralization consists of pyrrhotite, pentlandite and chalcopyrite that occur as disseminated to semi-massive concentrations and in millimeter to centimeter thick veins. The total inferred resource of the Nickel King deposit is 33.1 Mt grading at 0.36% Ni, 0.09% Cu and 0.017% Co (Strongbow, 2010).

The ca. 2.6 Ga Axis Lake deposit is located in northern Saskatchewan, within lower crustal, high-grade granulite facies rocks of the STZ, also referred as the East Athabasca mylonite triangle (e.g., Hamner 1994). The Ni-Cu mineralization is found in a highly strained meta-norite to -anorthosite (~2 x 10 km; Knox and Lamming 2014). The meta-norite is comprised of orthopyroxene-plagioclase-clinopyroxene-garnet-biotite ±biotite±quartz and it is hosted by a paragneissic unit (Knox and Lamming 2014). The ore is constrained to an east-striking, 6-10m wide by 1 km long band that dips steeply to the south and is parallel to the dominant regional fabric. The sulfide-rich band consists of semi-massive, millimeter to centimeter thick veins and disseminated pyrrhotite, pyrite, and chalcopyrite. The resource estimate for the Axis Lake deposit is 3.4 million tons grading 0.66% Ni and 0.66% Cu (non NI43-101 compliant; Pure Nickel, 2017).

The >2.6 Ga (inferred age, Martel et al. 2004) Ferguson Lake deposit is located west of the STZ in the Chesterfield block (Nunavut), and lies between the Yathkyed and McQuoid greenstone belts. The deposit is hosted by a multiphase (or differentiated) overturned metagabbroic intrusion (10-600 m thick; Martel et al. 2004). The metamorphosed products (up to amphibolite facies) of the metagabbro are amphibole (± biotite) schists, hornblende–plagioclase gneisses and hornblende diorite (Martel et al. 2004). Within the latter unit, a hornblende layer (74 m thick) contains the sulfide mineralization (Martel et al. 2004). Compositionally, the hornblende diorite and hornblende are mineralogically equivalent (hornblende–plagioclase–quartz ±garnet ±biotite assemblage), except for locally greater amounts of quartz in the former lithology.

The sulfide ore occurs in laterally discontinuous and irregular east-west oriented pods and lenses up to 21 m thick and with lengths ranging from tens to hundreds of meters (Campos-Alvarez et al. 2012) containing massive, disseminated and vein sulfide Ni-Cu-Co-PGE mineralization. The deposit has non NI43-101 compliant inferred resources of 19.4 million tonnes grading 0.68% Ni, 1.13% Cu, and 0.08% Co, 0.28 ppm Pt, and 1.75 ppm Pd (Nicholson 2007).

### 3 Analytical methods

Major and trace element analyses were carried out on drill core material of the metamorites from the Nickel King (n=4 samples) and Axis Lake (n=5 samples) and hornblende and hornblende dioresite from the Ferguson Lake (n=6 samples) deposits. The analytical work was done by Activation Laboratories, Canada. The major elements were determined by X-ray fluorescence (XRF) on a Panalytical Axios-Advanced wavelength-dispersive XRF. The trace element concentrations were acquired using ICP-MS and ICP-OES methods. A sodium peroxide fused blank was run in triplicate for every 22 samples, duplicates were run every 10 samples, and the instrument was recalibrated every 44 samples. The analytical precision of the ICP-MS and ICP-OES is ±100% at detection limit, ±20% at10× detection limit, and 5% at 100× detection limit. For XRF the analytical precision is 5% (or better).

### 4 Geochemistry

The covariances of major, most trace, and REE elements in least altered rocks of all deposits are consistent with fractional crystallization or accumulation processes. As such, we suggest that despite their metamorphic overprints, the geochemical signature of the primary source is preserved.

The Nickel King (SiO₂=51-54 wt.%; MgO=15-23 wt.%; TiO₂=0.2 wt.% and Axis Lake (SiO₂=47-52 wt.%; MgO=4-22 wt.%; TiO₂=0.1-0.5 wt.) and Axis Lake (SiO₂=47-52 wt.%; MgO=0.1-0.5 wt.%; TiO₂=0.1 wt.%) metanorites and the Ferguson Lake hornblende and hornblende diorite (SiO₂=43-51 wt.%; MgO=0.1-0.5 wt.%; TiO₂=0.1-1.0 wt.%) have subalkaline basaltic compositions when plotted in major and trace element discriminant diagrams such as that of Winchester and Floyd (1977). The well-defined positive covariation of SiO₂ against TiO₂ of the Ferguson Lake rocks further indicates a tholeiitic affinity.

In general, all suites are enriched in incompatible trace elements, up to 10× relative to those of primitive mantle (PM; figs. 1A,B). The samples from Nickel King and Axis Lake deposits have parallel normalized multi-element trends (for each suite; fig. 1A), are enriched in LREE elements relative to HREE (La/Yb = 8.1-17.3).
have low Zr/Y (2.1-3.5) and variable Th/Yb (0.5-1.6 and 0.1-0.4, respectively) values, and well-defined negative Nb (La/Nb=7.3-20.0) and Zr anomalies. However, diorite (SiO₂=43-51 wt.%; MgO=6-11 wt.%; TiO₂=0.5-1.0 wt.%) have subalkaline basaltic compositions when plotted in major and trace element discriminant diagrams such as that of Winchester and Floyd (1977). The well-defined positive covariation of SiO₂ against TiO₂ of the Ferguson Lake rocks further indicates a tholeiitic affinity.

In general, all suites are enriched in incompatible trace elements, up to 10X relative to those of primitive mantle (PM; figs. 1A,B). The samples from Nickel King and Axis Lake deposits have parallel normalized multi-element trends (for each suite; fig. 1A), are enriched in LREE elements relative to HREE (La/Yb=8.1-17.3), have low Zr/Y (2.1-3.5) and variable Th/Yb (0.5-1.6 and 0.1-0.4, respectively) values, and well-defined negative Nb (La/Nb=7.3-20.0) and Zr anomalies. However, distinct from the Axis Lake samples, the Nickel King samples have more tightly grouped normalized trace element patterns and consistent negative Ti anomalies (fig. 1A).

In contrast, the Ferguson Lake samples have flat to weakly LREE-enriched profiles (La/Yb=1.6-4.8; La/Nb=1.1-1.6), also with low Zr/Y(1.4-3.0) and Th/Yb (0.2-0.7) values. The presence of negative Zr, Nb and Ti anomalies is less common relative to those of the Nickel King and Axis Lake metanorites.

5 Petrogenesis

The Nickel King and Axis Lake metanorites preserve geochemical characteristics usually attributed to a hydrous magma component in subduction-related environments, e.g., low TiO₂ contents (<1 wt.%), enrichment of LREE (La and Ce) over HREE (high La/Yb), and negative Nb, Zr and Ti (Nickel King) anomalies (fig. 1A). Similar arc-like features, though, can be achieved by combined crustal assimilation-fractional crystallization of continental basalts (e.g., Xia 2014).

In the absence of other petrogenetic indicators (e.g., Nd isotopes) and solely based on the geochemical data, it can be difficult to assess the role of crustal contamination. Nonetheless, compared to typical crustally contaminated rift-related basalts, the Nickel King and Axis Lake metanorites have lower amounts of incompatible-elements, parallel PM normalized incompatible-element profiles (fig. 1A), and lower Zr/Y values. In addition, the covariation of Th/Yb and Nb/Yb shown in figure 2 is consistent with a subduction-related mantle source. Thus, the preliminary geochemical evidence indicates that the 2.6 Ga Axis Lake and Nickel King metanorites were emplaced in an arc-setting.

Figure 2. Mantle sources of the Nickel King, Axis Lake and Ferguson Lake deposits. Diagram modified after Pearce et al. (2008). Abbreviations, MA, Mariana arc (Elliot et al. 1997; Pearce et al. 2005); OIB, Ocean island basalt; EMORB, enriched MORB; N-MORB, normal MORB.

6 Conclusions

The geochemistry of the basaltic units hosting Ni-Cu-PGE deposits in the south Rae craton and Chesterfield block are not consistent with typical continental extension, as is the case for other younger Paleoproterozoic deposits in the Canadian Shield. Their
genesis, instead, may represent different sections of protracted (Axis Lake and Nickel King at ca. 2.6 Ga; Ferguson Lake, at >2.6 Ga) convergent margin magmatism (arc/back-arc). Therefore, Neoarchean basaltic rocks with arc/back arc-like signatures may have economic significance for mineral exploration of Ni-Cu-PGE deposits in the western Churchill Province.

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PGE distribution in Fe-Ni-Cu sulfides from the Potosí mine (Eastern Cuban Ophiolites)

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Abstract. Unusual sulfide-rich chromitites of the Potosí mine are hosted in the MoHo Transition Zone (MTZ) of the Moa-Baracoa ophiolite. Bulk-rock compositions of samples of these sulfide-rich chromitites are characterized by flat chondrite-normalized PGE patterns due to enriched Pt and Pd. A positive correlation between PGE content and increasing abundance of sulfides (mainly Co-free pentlandite, pyrrhotite, cubanite and chalcopyrite) is observed. However, LA-ICP-MS analyses on different sulfides exhibit low PGE contents, which cannot explain the general PGE abundance in the sulfide-rich ore. All analyses of sulfides are strongly depleted in Pt. Interestingly, many pentlandite grains host visible nano- to micrometric crystals of sperrylite. Textural observations together with new analytical data reported in this contribution suggest that sperrylite has crystallized from a Pt–arsenide-saturated melt, prior or contemporaneous with the crystallization of the sulfide melt from which the base metal sulfides were crystallized.

1 Introduction

Massive Fe-Ni-Cu sulfides associated with chromite are unusual features of podiform chromitites located within ophiolitic mantle sections. On a worldwide scale such associations have been described from the Eretria area (Greece) (Economou and Naldrett 1984) as well as from the Limassol Forest (Cyprus) (Foose et al. 1985; Thalhammer et al. 1986). In both cases sulfides have been interpreted as precipitates from hydrothermal fluids related to serpentinization. On the other hand, disseminated magmatic sulfides with generally high platinum-group elements (PGE) contents have been observed in chromite-rich dunites from mantle tectonites of the Shetland Ophiolite complex (Prichard and Lord 1993).

More recently, sulfide-rich (up to 50 vol.% sulfides) chromitites from the Potosí mine (Eastern Cuba) with platinum-group elements (PGE) contents up to 1.1 ppm were reported from Proenza et al. (2001). These chromitites reveal flat chondrite-normalized PGE patterns, which are explained by relatively high contents of Pt and Pd. Such features are usually not observed in podiform chromitites (González Jiménez et al. 2014 and references therein). Preliminary investigation of PGE mineralogy revealed rarely occurring, rounded to subhedral crystals of sperrylite (<10 μm in size) found either disseminated in the sulfides or associated with chlorite and titanite in contact with sulfide grains (Proenza et al. 2004).

Here we apply a multi-disciplinary approach including heavy mineral separation via hydroseparation, field-emission scanning electron microscopy (FE-SEM), and trace-element analysis in sulfides with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) with the aim to understand the formation of the sulfide-rich chromite ore at Potosí mine. The mineralogy of the main PGE hosts is emphasised and integrated with a detailed mineralogical and textural characterization of the minerals present in the Potosí mine.

2 The Potosí mine

The Potosí mine is located in the Mayarí-Baracoa ophiolitic belt (Eastern Cuba) (Fig. 1). The deposit was discovered in 1889 and during its long exploitation history approximately 450,000 t of refractory-grade chromite ore was extracted (Muñoz and Campo 1992; Proenza et al. 2001). However, production stopped in the 1970s due to technology issues, hence leaving large known reserves (>100,000 t) of chromite ore in the deposit.

Figure 1. Geographic map of Cuba highlighting the Mayarí-Baracoa ophiolitic belt which hosts the Potosí mine.

In the Potosí mine, the chromite ore mineralization occurs within the MTZ which is characterized by the interlayering of ultramafic and gabbroic rocks. Chromitites display dunite envelopes of variable thickness and are hosted by harzburgites. Pegmatitic gabbro dikes cross-cut the chromitites as well as the host dunites and harzburgites (Fig. 2).
The mineralized area has a lateral extension of about 220 m and is 8 to 25 m wide. Chromitites are found in lenses with extremely variable size and irregular shapes, from tabular to lenticular. These bodies are oriented N 40º E to N 74º E and dip between 32º and 45º to the NW, corresponding to the foliation of the peridotites (Thayer 1942).

Figure 2. Schematic stratigraphic section of the Moa-Baracoa Ophiolitic Massif; the position of studied sulfide-rich chromitites at the Potosí mine is highlighted.

The original mineralogy at the Potosí mine has been modified by two magmatic intrusive events. The first event formed olivine-norite pegmatitic dikes, whereas the second led to the crystallization of pegmatitic gabbro dikes (Proenza et al. 2001). Three types of ores can be distinguished: (1) sulfide-poor chromitites (similar to the other chromitites found throughout the Moa-Baracoa Ophiolitic massif); (2) sulfide-rich chromitites in the contact between the chromitites and the olivine-norite pegmatitic dikes (chromitite samples in this contribution); and (3) breccia-textured chromitites which are spatially associated with the pegmatitic gabbro.

3 Methods

Whole-rock PGE contents were obtained at Genalysis Ltd., Maddington, Western Australia, by ICP-MS after nickel sulfide fire assay collection, following the method described by Chan and Finch (2001). Detection limits are 1 ppb for Rh, and 2 ppb for Os, Ir, Ru, Pt and Pd. One sulfide-rich chromitite sample (m=350 g) was processed by means of hydroseparation techniques (www.hslab-barcelona.com) and subsequently investigated via Quanta 200 FEI XTE 325/D8395, and a field-emission scanning-electron microscope (FE-SEM) JEOL JSM-7100 at the Centres Científics i Tecnòlogics, University of Barcelona, Spain. Quantitative EMP analyses were obtained with a JEOL JXA-8230 electron microprobe (EMP) in the wavelength-dispersive spectroscopy (WDS) mode, operating with an accelerating voltage of 20 kV, a beam current of 10 nA and a beam diameter of 1 μm.

The in-situ trace-element methodology follows that of Alard et al. (2000; 2002) and Saunders et al. (2015; 2016). All analyses were done on polished sections by an Agilent 7700cx ICP-MS coupled with a Photon Machines Excite 193 nm excimer laser ablation system (LA-ICP-MS) in the Geochemical Analysis Unit (GAU) at CCFS/GEMOC, Macquarie University, Sydney. Laser-ablation analyses of sulfides were carried out at spot sizes ranging from 50-65 μm. A quenched NiS bead (PGE-A: Alard et al. 2000; 2002), doped with selected chalcophile and siderophile elements was used as an external calibration for all elements with the exception of Sb. Sulfur, determined by EMP, was used as an internal standard for all LA-ICP-MS analyses of sulfides to quantify the trace-element abundances.

4 Mineralogy

Figures 3a and b show typical mineralogical features of sulfide-rich chromitites from the Potosí mine. They display a magmatic assemblage which mainly consists of chromite, Mg-rich ilmenite, Co-free pentlandite, pyrrhotite, cubanite, chalcopyrite, orthopyroxene, olivine, apatite, baddeleyite, zirconolite and zircon. However, this mineral assemblage has been affected by post-magmatic, hydrothermal events which formed Fe-rich chlorite (chamosite), rutile, titanite and vallereite. PGM were found in the contact zone between pentlandite and chromite. The main PGM in the Potosí mine is sperrylite (PtAs₂) which occurs as (i) idiomorphic nanoparticles as well as micrometric grains included in pentlandite, and (ii) as elongated grains in fractures filled by Fe-Cu sulfides (Fig. 3c). In addition, euhedral laurites (RuS₂) included in chromite are observed.
5 PGE distribution in sulfides

LA-ICP-MS analyses revealed relatively low total PGE contents in pyrrhotite (~3 ppm) and pentlandite (~6 ppm). However, PGE contents in cubanite reached values up to 156 ppm. Chondrite-normalized PGE patterns show similar PGE distributions which are characterized by a general depletion in Ir and extreme depletion in Pt, being the most depleted PGE in all analysed sulfides (Fig. 4). Two notable differences in the PGE distribution show significant Ir and Rh enrichment in chalcopyrite and cubanite, respectively (Fig. 4).

Figure 3. a Reflected-light image of interstitial pentlandite (pn) with chromite (chr); b Back-scattered electrons (BSE) image of various sulfides from the Potosí mine (vlr = vallerite; cbn = cubanite); c euhedral sperrylite.

Figure 4. Chondrite-normalized PGE patterns of cubanite, pyrrhotite, pentlandite and chalcopyrite from the Potosí mine; for comparison the field for typical residual monosulfide solid solution (mss) as well as the average composition of the primitive mantle (PM) are indicated which were taken from Piña et al. (2015) using data from Alard et al. (2000) and Lorand and Alard (2001). Normalizing values are those of McDonough and Sun (1995).

6 Discussion

Previous work has shown that the sulfide-rich chromite ores from the Potosí mine formed by fractionation of an immiscible sulfide melt which segregated from a volatile-rich silicate melt (Proenza et al. 2001). The sulfide melt was the principal collector of Rh, Pt and Pd (+other incompatible elements), which is supported by the clear correlation of relative enrichment of these incompatible elements with the abundance of sulfides in chromite ores. LA-ICP-MS analyses show that sulfides are relatively depleted in PGE, which suggest that not all the PGE were collected by the sulfide liquid parental to the base-metal sulfides.

Interestingly, many grains of sperrylite were found associated with the base-metal sulfides depleted in PGE, particularly Pt. Sperrylite is a very rare mineral in chromitites associated with ophiolite complexes, and where present it is usually interpreted to have been precipitated by post-magmatic hydrothermal solutions (Prichard and Tarkian 1988). In the Potosí mine sperrylite occurs as idiomorphic nanoparticles and micrometric crystals included in magmatic pentlandite, which clearly suggest a primary magmatic origin. Indeed, the strong negative Pt anomaly observed in analysed base metal sulfides from the Potosí mine can be related with the segregation of a Pt-rich arsenide melt previously or contemporaneously with the immiscible segregation of a base-metal PGE-poor sulfide liquid. In fact, minute peaks
of Pt-As phases were detected during ablation runs in our samples.

Our results provide confirmation in nature of the experimental studies by Helmy et al. (2013) who observed that a Pt–arsenide-saturated melt can crystallize in equilibrium with a sulfide melt, leaving behind sulfides strongly depleted in this element. Further examination with imaging techniques of our samples should provide additional constraints for this work.

7 Concluding remarks

To the best of the authors’ knowledge the Potosí mine in Eastern Cuba represents the only known occurrence in the world where sulfide-rich, podiform chromitites included in mantle peridotites reveal a sperrylite-dominated PGM assemblage.

Whereas sulfide-rich ores are significantly enriched in Pt, LA-ICP-MS analyses of this contribution show an extreme depletion of Pt in pentlandite, cubanite and pyrrhotite.

Our data point to a formation of sperrylite as nanoparticles from a Pt–arsenide-saturated melt, previous to the crystallization of a sulfide melt as observed in experimental work by Helmy et al. (2013).

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Magmatic sulphide mineralisation of the Munali nickel deposit: evidence for immiscible sulphide-carbonate-phosphate-silicate melts?

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Abstract. The Munali deposit is a brecciated mafic-ultramafic hosted massive sulphide nickel deposit located within the Zambezi belt of southern Zambia. The mafic-ultramafic units are heavily brecciated forming part of the Munali Igneous Complex, emplaced around the margins of an unmineralised Central Gabbro Unit. Seven styles of sulphide mineralisation have been identified, principally as massive sulphide infilling the matrix to the magmatic breccia. Sulphide mineralogy is similar across all styles comprised of pyrrhotite >> pentlandite > chalcopyrite > pyrite +/- magnetite. Interstitial sulphide is present in the brecciated ultramafic-mafic units representing sulphide crystallisation prior to the brecciation and associated massive sulphide infill. Cross-cutting sulphide-carbonate-magnetite injections suggest a later stage mineralisation style. Abundant apatite and carbonate is associated with some of the mineralisation styles and unusual emulsion and droplet textures of sulphide-silicate-carbonate-phosphate provide evidence of three, or even four, way liquid immiscibility, supporting suggestions that mantle melts of carbonatitic affinity may have played a role in the development of Munali.

1 Introduction

The Munali deposit is an enigmatic magmatic nickel sulphide megabreccia deposit hosted by a multi-stage mafic-ultramafic intrusion with an unusual apatite-carbonate-magnetite-sulphide ore assemblage. Located 75 km south of Lusaka in southern Zambia within the Zambezi belt, Munali was emplaced during the Neoproterozoic in a period of extensional tectonic activity related to the break-up of the Congo and Kalahari cratons. The Munali Igneous Complex (MIC) was intruded into metasediments, forming part of the Zambian Supracrustal Sequence (ZSS), deposited during rifting and formation of the Zambezi Ocean. Munali is comprised of four deposits/prospects: Enterprise (site of the Munali Ni mine), Voyager, Intrepid and Defiant which form part of the MIC. The igneous complex is steeply dipping and exhibits typical characteristics of a magmatic-conduit system located along a trans-lithospheric fault zone.

Mineralisation in all four deposits/prospects is hosted by mafic-ultramafic units, which are extensively brecciated with a sulphide infill matrix. These mafic-ultramafic rocks are intruded around the margins of an unmineralised, elongated to the NW, Central Gabbro Unit (CGU) emplaced within marbles of the ZSS. Locally, the ZSS is comprised of metamorphosed Neoproterozoic carbonate and siliclastic sediments which consist of biotite-kyanite schists to the east and carbonate-rich metasediments to the west, which include biotite-andalusite schists. The sulphide-mineralised Marginal Ultramafic-mafic Breccia Unit (MUBU) comprise poikilitic gabbros and a range of atypical ultramafic rocks (olivines, phoscorites and pegmatic wehrlites), with characteristically no chromite. The MUBU, located as a rim around the CGU, is thickest along the south-western margin and subsequently richer in sulphide mineralisation in comparison to the north-eastern margin. The three largest prospects, Enterprise, Voyager and Intrepid, are located along this south-eastern margin and is the main focus of this study.

2 Mineralisation

Seven styles of magmatic sulphide mineralisation have been identified texturally and mineralogically by field-mapping, petrological and geochemical analysis. The research builds upon five previous styles identified by Holwell et al. (2017), which has been refined within this study.

Mineralogy across all styles comprises pyrrhotite >> pentlandite > chalcopyrite > pyrite +/- magnetite, however, the geochemistry, associated mineralogy abundance and textural association differ between the styles.

There are three main stages of sulfide mineralisation. The earliest is disseminated, interstitial sulphides hosted within the mafic and ultramafic clasts of the MUBU, followed by multiple main stage breccia fills, and finally, late-stage sulphide-rich carbonate injections.

2.1 Interstitial sulphides in mafic units of the MUBU

Sulphide is present, although rare, within the poikilitic gabbro of the MUBU, comprised of interstitial pyrrhotite, pentlandite and chalcopyrite blebs. This represents a sulphide stage prior to the main brecciation event and massive sulphide infill and is abundant towards the hanging-wall contact of the orebody. Uranium-Pb zircon dating of the mafic and ultramafic units (Holwell et al. 2017) suggest that timing of the mafic emplacement pre-dates the ultramafic units of the MUBU by ~4.5 Ma. Therefore the sulphides present within the mafic units represent the youngest mineralisation style.
2.2 Interstitial sulphides in ultramafic units of the MUBU

Sulphide is more abundant within the ultramafic units of the MUBU, present as blebs and interstitial aggregates of pyrrhotite, pentlandite, chalcopyrite, variable magnetite, minor pyrite and apatite. This style of mineralisation represents sulphide crystallisation prior to the brecciation and massive sulphide injections, but, like some of the latter, is also associated with cogenetic olivine, magnetite and apatite.

2.3 Massive sulphide breccia fill

The majority of the orebody at Munali consists of massive sulphide which appears to have infilled brecciated mafic and ultramafic units of the MUBU. These brecciated igneous units are present as sub-rounded to angular clasts on a scale of 1 mm to >5 m and show variations in clast lithology and abundance throughout the orebody. The massive sulphide mineralisation is predominant and thickest, with the least amount of clasts present, towards the footwall contact of the MUBU. Sulphide mineralisation in this zone, where clasts are limited, exhibit primary sulphide assemblages and loop textures, with pentlandite forming along the grains of pyrrhotite with rare chalcopyrite and sporadic pyrite. Variable amounts of magnetite, apatite and carbonate are associated with the massive sulphide breccia. This difference in clast lithology within the sulphide infill, likely represents separate phases and timing of sulphide liquid injections.

2.4 Sulphide with apatite, carbonate, magnetite and olivine glass

Some breccia-fill massive sulphides have a distinct textural and mineralogical association with apatite, carbonate and magnetite. Sub-angular to rounded chloro-apatite is abundant and present within the massive sulphide assemblage (pyrrhotite >> pentlandite) on a scale of 5 μm to >30 cm. Magnetite is nearly always present in close association to the apatite. Carbonate as calcite is also present and occurs interstitially to rounded sulphides blebs (Fig. 1a). A highly unusual and perhaps unique feature of this style at Munali is the presence of a glass of olivine composition (Fo60) that coats and invades cracks in sulphide blebs. Where present with carbonate, it coats the sulphide, with carbonate filling the interstitial spaces.

Figure 1a shows a common texture at Munali, but one that is highly unusual for magmatic sulphides ores. Massive to semi-massive sulphide is present as a mass of blebs, with some interstitial material (mostly carbonate) producing an emulsion-like texture. Subhedral to spherical apatite grains are observed within the pyrrhotite-pentlandite sulphide associated with olivine glass and carbonate (Fig. 1b). Magnetite is present within the silicate glass and also as a rim on the edge of spherical apatite. Figure 1c shows a remarkable texture of pyrrhotite present along the edge of the spherical apatite grain, forming a semi-spherical droplet texture into the olivine glass (Fig. 1c). The apatite is separated from the main sulphide assemblage by this olivine glass which appears to preferentially wet the edge of the apatite. Similarly, the calcite within this style, shows a similar texture to that of apatite, forming as sub-rounded grains, rimmed by magnetite surrounded by olivine glass.

Figure 1. a XRF elemental map showing sulphide associated with apatite. Carbonate is shown in green, sub-angular to rounded apatite in blue and Po-Pn sulphide in red. Silicates are uncoloured. SU - serpentinised ultramafic clast. b Thin section (transmitted and reflected light) image showing spherical calcite (ca) and a spherical apatite (ap) grain wetted by silicate olivine glass (olg) surrounded by pyrrhotite (po) and pentlandite (pn) sulphide. Magnetite (mag) and sulphide droplets present along edge of apatite. c Backscattered electron photomicrograph showing pyrrhotite droplet with magnetite on edge of apatite at olivine glass interface.
The texture shown in Figure 1c bears a significant resemblance to sulphide droplets along the edges of gas bubbles in silicate glass forming a compound drop in experiments shown by Mungall et al. (2015). Clearly the silicate glass appears to be wetting the apatite, but also sulphide globules appear to be wetting the apatite as well. The rounded droplets of apatite (wetted by glass), and carbonate, in sulphide suggests that the sulphide, silicate and phosphate/carbonate were possibly present as immiscible liquids at the time of formation.

2.5 Sulphide with interstitial silicate glass

Massive sulphide is observed in association with silicate (olivine) glass. The sulphides display a sub-rounded to rounded blebbly shape with interstitial silicate glass showing what appears to be an emulsion texture (Figs. 2 and 3).

![Figure 2](image1.png)

**Figure 2.** Core sample showing sulphide (po-pn) emulsion texture with olivine glass (olg). Magnetite (mag) is present as a rim between sulphides and ultramafic. Late carbonate veins (ca) cross-cut sulphide and olivine glass.

![Figure 3](image2.png)

**Figure 3.** XRF elemental map showing sub-rounded to rounded sulphide grains; pyrrhotite in blue, pentlandite in pink and copper rich sulphide (chalcopyrite) in green. Sulphide is associated with interstitial silicate glass shown in black.

However, the glass is seen to penetrate cracks in the sulphide and is clearly injected into the solid sulphide. This texture is similar to the apatite rich style, but due to the absence of apatite, is classed separately, however it is possible that this style is part of a continuum to the apatite-silicate-sulphide style.

2.6 Sulphide with talc-carbonate altered ultramafic rocks

Intensely talc-carbonate altered ultramafic clasts are observed associated with massive sulphide. Mineralisation is comprised of pyrrhotite and pentlandite as well as pyrite and chalcopyrite having a higher abundance compared to the other styles. These altered units exhibit shearing and ductile deformation textures which appear to cross-cut and post-date the main brecciation mineralisation and may represent a late stage sulphide remobilisation.

2.7 Carbonate-sulphide-magnetite injections

Sulphide mineralisation is present associated with magnetite rich carbonate injections. Dolomite, rather than calcite (see apatite-associated style) is the main carbonate, being primary in nature and host to sulphide inclusions (Fig. 4).

![Figure 4](image3.png)

**Figure 4.** Thin section (transmitted and reflected light) image of fractionated sulphide inclusion with pyrrhotite (po), pentlandite (pn), chalcopyrite (cpy) and magnetite (mag) in dolomite (dol) with plagioclase (pl).

The sulphide inclusions are predominately fractionated blebs comprising pyrrhotite, pentlandite, chalcopyrite and minor pyrite. Plagioclase is also commonly associated with the dolomite as well as rare apatite grains. These carbonate injections crosscut many mineralisation styles and features of the ore-body and therefore emplaced post-brecciation and represent a later event in the paragenesis of Munali, interpreted as the last stage of mineralisation (Holwell et al. 2017).

2.8 Platinum-group minerals

Platinum-group minerals (PGM) observed at Munali comprise Pd and some Pt phases. Semi-quantative analysis indicates that the primary PGM minerals dominantly form as Pd and Pt tellurides. These tellurides are present as well formed single-phase blebs and include merenskyite (PdTe₂), kotulskite (PdTe) and moncheite (PtTe₂). The PGM are texturally associated with the primary sulphide assemblage; pyrrhotite, pentlandite and chalcopyrite, either...
as inclusions within the sulphide or at silicate-sulphide boundaries. Secondary Pt and Pd atimonides have been identified associated with pyrite in the carbonate-magnetite-sulphide injections and differ from the primary PGM, with a multi-phase mineralogy and more deformed appearance.

3 Implications for immiscible sulphide-carbonate-phosphate-silicate melts

Sulphide across all mineralisation styles comprise pyrrhotite, pentlandite with variable amounts of chalcopyrite, pyrite and magnetite. This is typical of magmatic sulphide deposits, but the deposit is unusual in exhibiting a strong carbonate signature and association of phoscorites and abundant apatite with sulphide. Holwell et al. (2017) proposed that this association of carbonate and sulphide, including the presence of phoscoritic ultramafic rocks may be from a carbonatitic influence. Mineralisation present in the carbonate-magnetite injections show fractionated sulphide within primary looking magmatic dolomitic carbonate, with lesser calcite, plagioclase and apatite, and may be representative of a later stage carbonate melt in the Munali paragenesis.

The most significant finding of this study is the identification of highly unusual textures of sulphide-apatite-calcite and olivine glass that appear to show emulsion like textures suggestive of immiscibility, not just of sulphide and silicate, but also compelling evidence of phosphate and carbonate immiscibility too. Furthermore, the silicate component is a highly unusual glass of olivine composition. However, olivine should have a much higher melting point than sulphide, but the textural evidence clearly shows infiltration of silicate melt into cracks in solid sulphide. As such, we interpret that the silicate component must have a depressed eutectic, possibly from the presence of abundant carbonate (analogous to limestone being used as a flux in blast furnaces).

Emulsion textures observed between sulphide and silicate with apatite and carbonate (e.g., Fig. 1), with rounded carbonate and apatite ‘droplets’ in sulphide indicates the presence of immiscible carbonate and phosphate with sulphide and silicate as well. Sulphide, as droplets, and olivine glass appear to wet the surface of apatite and provides additional evidence indicative of the presence of immiscible magmatic sulphide-silicate-carbonate-phosphate liquids. This may have implications for the transport mechanism of the sulphides.

A similar textural and mineralogical association is observed in peridotite xenoliths in Loch Roag, Scotland (Hughes et al. 2016). These mantle xenoliths show inclusions of rounded Ca-carbonate and apatite preserved within base metal sulphides, with the authors supporting a three-way immiscible liquid (carbonate-phosphate-sulphide) and potential links to a carbonatite melt. This immiscibility texture at Loch Roag, shows preservation of the interaction of CO$_3$-PO$_4$-S liquids within the mantle. The liquid immiscibility and very similar associations observed at Munali, may provide evidence of the interaction of similar deep seated mantle melts, but preserved at upper crustal levels. The presence of the immiscible and droplet textures and the glassy nature of olivine at Munali, therefore suggests mobility of immiscible liquids and rapid transport of melts from the upper mantle to sites along crustal fault systems. Such rapid transport from the mantle to the crust, would have required significant energy, which may be the cause for the brecciated nature of the orebody at Munali.

As such, Munali represents a magmatic sulphide deposit, emplaced in an intraplate rifting setting close to the margin of a craton, but one that provides evidence of carbonatitic as well as mafic magmas utilising the same pathways.

4 Summary

The Munali nickel sulphide deposit shows seven styles of mineralisation within three main stages. Disseminated and interstitial sulphides hosted within mafic-ultramafic clasts of the MUBU represent the earliest stage of mineralisation. This is followed by the main style, massive to semi-massive sulphides infilling the MUBU breccia, and is lastly followed by late stage sulphide-rich carbonate injections which cross-cut the earliest sulphide stages.

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New U-Pb geochronology and structural-stratigraphic interpretation for the Raglan Belt, northern Quebec

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Abstract. The Raglan area of the Cape Smith Belt, northern Quebec, hosts one of the most significant Proterozoic komatiite-associated Ni-Cu-(PGE) districts in the world. Although the geological setting is reasonably well understood, questions remained as to the exact timing of mineralization, the role of numerous differentiated mafic-ultramafic sills in the ore-bearing sequence, and to what extent thrusting has played a role in shaping this sequence. Here we discuss significant progress towards resolving these questions, with new high-precision U-Pb ages for key sills in conjunction with new critical field observations. Precise and accurate (i.e. concordant) U-Pb ages are now available for half a dozen sills, all converging on a narrow c. 1882-1884 Ma time interval, including for the “Footwall Gabbro” sill at Katinniq and a hanging-wall sill above some of the main ore lenses in the adjacent “5-8 Zone” area. The Cross Lake sill, with an apparently conflicting age of c. 1918 Ma, has also been redated to c. 1882 Ma. All data suggest a sharp onset of komatiitic volcanism and mineralization at c. 1883 Ma, an age that is identical to that for the Thompson district. Thrust imbrication is less significant than previously envisaged and the critical Povungnituk to Chukotat Group contact is stratigraphic, pinned by both thermal erosion channels and identical sills above and below. Spatial correlation of the numerous sills with the komatiite flows, on a regional scale, suggests they were part of an overall (proximal?) feeder system.

1 Cape Smith Belt: Introduction

At Raglan, a generally north-dipping sequence of volcanic and sedimentary rocks, overlying basement of the northern Superior craton, has long been viewed as a fold-thrust belt severely imbricated by multiple major thrusting events. For the para-autochthonous belt this model was based on a stratigraphic template in which significant sedimentary units were thought to be restricted to the base of the Povungnituk Group (e.g., St-Onge and Lucas 1993; see Fig. 1a). In broad outline, from south to north, the (tectono-) stratigraphy consists of autochthonous to para-autochthonous lower Povungnituk sedimentary rocks, a thick pile of c. 2000 Ma Povungnituk basaltic lavas, more panels of sedimentary rocks, numerous mafic-ultramafic sills, Mg-rich and more primitive Chukotat volcanic rocks, additional sedimentary panels, and a complex of overlying and possibly allochthonous tectono-stratigraphic units, including the c. 2000 Ma Watts Group (e.g., St-Onge et al. 1992; Lucas and St-Onge 1992; St-Onge and Lucas 1993).

With a simplified three-fold stratigraphic template in mind (lower Povungnituk sedimentary sequence, Povungnituk lavas, Chukotat lavas and related intrusives), many thrust were interpreted based primarily on the reappearance of clastic sedimentary rocks in the otherwise volcanic dominated pile. If these tectono-stratigraphically higher panels of clastic sedimentary rocks indeed represent structural repeats of lower Povungnituk sedimentary rocks, from the base of the stratigraphic section, then such thrusts are required. However, as shown in Figure 1b, our alternative interpretation is that many of the higher sedimentary intercalations are in fact unique stratigraphic units, each with their own character—i.e. they are not structural repeats. Indeed, it is now evident that many of these sedimentary panels are unique stratigraphic units intercalated within and overlying the Povungnituk Group lavas, and also within the Chukotat Group. No major thrusts are required, and although early thrusts may not be accompanied by major shear zones, outcrop is far from perfect, we found no obvious field evidence for many of the thrusts. In simple terms, there are far fewer thrusts and there is more coherent stratigraphy.

Nevertheless, the Raglan belt is obviously deformed and the entire “Raglan horizon” (essentially the mineralized contact between the upper Povungnituk Group, top of the Nuvilik Formation, and the overlying Chukotat Group) is structurally repeated by a major south verging syncline-anticline pair, the overturned limb of which evolved into a thrust fault (for details, see Bleeker 2013; see Lucas and St-Onge 1992, their Figure 5)—the only clearly resolvable thrust in the area based on stratigraphic and structural field observations. This structure repeats the mineralized Raglan horizon to the north of main mineralized belt, with the main belt currently supporting half a dozen producing Ni-Cu-(PGE) sulphide deposits. Smaller scale parasitic fold structures, on the scale of individual deposits, also occur and locally resulted in overturned or south facing stratigraphy of both ore and host rocks, such as at the Kikialik deposit (again, see Bleeker 2013 for details).

Well north of the Raglan belt, we interpret the broad, basement-cored Kovik Antiform as an extensional core complex, rather than being related to on-going shortening and high-amplitude contractional folding (cf. Hoffman, 1985). Deformed sheets of leucogranite on the contact of this antiform can test this interpretation and may date the formation of this core complex (Bleeker and Ames 2017).
The interpretation of multiple distinct stratigraphic units, rather than repeated thrust panels, specifically applies to thin units of quartz-rich sedimentary rocks within the continental Povungnituk basalts (Fig. 1b). More importantly, the mostly deep water, turbiditic, greywackes and mudstones of the Nuvilik Formation represent a distinct formation at the stratigraphic top of the Povungnituk Group, not a repeat of its basal sedimentary section. These progressively deeper water turbiditic sediments post-dated the main pulse of Povungnituk basaltic volcanism, perhaps representing the thermal subsidence phase following the waning of Povungnituk magmatism and an associated rifting phase. The Nuvilik Formation is neither bounded by a major thrust at its base, nor at its top.

Higher in the (tectono-) stratigraphy, distinct lenses of
clastic sedimentary rocks, including sandstone and polymict conglomerate with mafic volcanic as well as granitoid clasts (Fig. 2), may represent syn-orogenic clastic rocks infolded into the Chukotat Group, not older basal sediments brought up by yet another major thrust. This interpretation is easily tested with detrital zircon data.

Figure 2. Polymict conglomerate of probable syn-orogenic origin, with a variety of granitoid and mafic volcanic clasts. Conglomerates such as these are intercalated in the Chukotat Group lavas north of the Raglan belt. If indeed of syn-orogenic origin, only minor, late-orogenic thrust imbrication or infolding is required. If on the other hand this conglomerate represents lower Povungnituk sedimentary rocks (cf. St-Onge and Lucas 1993), major early thrust imbrication would be indicated. Detrital zircons may provide an easy test between these radically different hypotheses.

3 New high-precision U-Pb geochronology

We have precisely dated several gabbro sills within the critical part of the stratigraphy. Differentiated gabbro sills intruding into the Nuvilik Formation were thought to be perhaps as old as c. 1918 Ma (e.g., the Cross lake sill, see Parrish 1989). Careful evaluation and reinterpretation of the variably discordant baddeleyite and zircon data already suggested that these gabbro sills may be c. 1883-1884 Ma (Bleeker 2014). New U-Pb dating of chemically abraded single zircons confirms this interpretation and provides precise concordant data at c. 1882 Ma (see also Kamo et al., this volume), with all newer ages on the various sills now converging to a short time interval at 1882-1884 Ma (see also Randall 2005; Mungall 2007).

A new U-Pb zircon age on the main “Footwall Gabbro” sill below the Katinniq ore body, again based on chemically abraded concordant zircons, shows this sill to be also c. 1883 Ma. Some of the main Ni-sulphide ore lenses at Raglan (e.g., Katinniq ore body) occur in thermomechanically eroded lava channels that drilled down into this footwall gabbro sill (Fig. 3; see Lesher 2007, and references therein). The precise age of this footwall gabbro sill thus provides a maximum age for the onset of the komatiite lava channels at the base of the Chukotat Group, and the onset of ore formation.

A gabbro sill intruding the lower Chukotat lavas, above some of the main sulphide ore lenses, is also c. 1882-1883 Ma, further bracketing the onset of komatiitic volcanism and peak ore formation to a ~1 Myr interval at c. 1883 Ma.

Figure 3. Image collage of diamond drill hole (DDH) 718-3333, “5-8 Zone”, Raglan belt. Intersection shows the basal contact of the massive sulphide lens on the underlying “footwall gabbro” sill. Diameter of core is ~4.8 cm in all images (NQ). a) Overview image of ~1 m of core through basal sulphide contact. Note massive sulphide straight on medium-grained gabbro. b) Close-up of this contact. Only weak shearing is observed in the sulphides, while the chilled margin of the gabbro sill is lacking—conclusive evidence for a primary thermal erosion contact. c) Image of net-textures sulphides with larger sulphide blebs ~1 m above the massive sulphide zone.

4 Conclusions

Much of the Ni-Cu-(PGE) sulphide ore endowment of the Raglan belt occurs at or near the basal contact of the Chukotat Group lavas (see red curve, Fig. 1b), and some of the larger ore lenses occur demonstrably in thermal erosion channels that have drilled down into just marginally older footwall gabbro sills. This has been demonstrated in many areas along the belt (Lesher, 2007). The onset of komatiitic volcanism is now precisely bracketed to 1882-1884 Ma, and most of the ore is associated with peak komatiitic effusion rates early in this interval.

Large komatiite flows will necessarily channelize, while flowing over a substrate of slightly older flows and
(or) sulphidic footwall sediments of the Nuvilik Formation (see Lesher et al. 1984; Williams et al. 1998). Channelization and the consequent eroding into, and contamination with, sulphidic sediments is much less predictable for sill systems—hence the strong concentration (>90%) of ore endowment with the most Mg-rich komatiite flows along the base of the Chukotat Group. The evidence for thermal erosion, and the similarity in sills below and above, weld the basal Chukotat lavas, and thus the whole group, stratigraphically to the underlying Nuvilik Formation. The key Povungnituk to Chukotat Group contact is therefore a stratigraphic contact, not a regional thrust.

Sulphide-bearing mudstones of the uppermost Nuvilik Formation, the stratigraphic substrate (ambient seaﬂoor) over which the Chukotat komatiite flows were emplaced, acted as a proximal sulphide source for the Raglan Ni-Cu-(PGE) sulphide ore bodies, as has long been surmised empirically, and from S isotopic data (Lesher 2007). The numerous mafic-ultramafic differentiated sills, now dated to the same event, and spatially correlated with the komatiite flows on a regional scale, must be part of the feeder system. Dynamic parts of this feeder system could host economic mineralization, but the base of the lava pile is more prospective and predictable.

Most of the published and unpublished U-Pb data on units associated with the Raglan horizon, from the northern Labrador Trough to the western Cape Smith Belt, suggest a short-lived, LIP scale magmatic event at about 1883 Ma (see also Ernst and Bleeker 2010). As far as we can currently resolve (~1-2 Myr), this age is identical to that of komatiitic magmatism along the western margin of the Superior craton (Thompson, Manitoba; e.g., Scoates et al. 2017), and to the age of large intra-cratonic dykes that intruded the craton (Molson swarm, Heaman et al. 2009; Pickle Crow dyke, Bleeker and Kamo, unpubl. data). The overall scale and volume of this magmatic event, its short-lived nature of ~1-2 Ma, and the involvement of high-T magmas compare well to modern LIP events.

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On the controls of low- and high-Cu/Pd mineralization in the Eastern Gabbro, Canada: evidence from sulfide textures, S/Se ratios, and PGE contents

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Abstract. Numerous Cu-Pd occurrences with variable ranges for Cu/Pd ratios occur throughout the Eastern Gabbro of the Coldwell Complex. Sulfides in the mineralized zones exhibit equilibrium textures, with rounded contacts between sulfides and silicates, and disequilibrium textures, with pyrrhotite replacement by chalcopyrite and the intergrowth of chalcopyrite with hydrous silicates. Disequilibrium sulfides are uncommon in the W Horizon of the Marathon deposit. Compositionally, these textual varieties of sulfide are similar and, except for Zn and Co, follow the trends expected according to MSS/sulfide melt partitioning. Chalcopyrite within different mineralized zones are also compositionally similar, except for Zn, which is depleted in Ccp from the W Horizon. This suggests that disequilibrium sulfides precipitated from a fluid that mobilized metals from Footwall Zone sulfides and into the Main Zone. The S/Se ratios of sulfides from Footwall and Main Zone, and W Horizon at Marathon decrease progressively from values greater than to values less than those of the mantle, whereas the ratios from the northern deposits are all less than mantle values. This suggests variable degrees of S contamination in the Footwall and Main Zone, higher R factors in the W Horizon than Footwall and Main Zone, and S loss in the northern deposits.

1 Introduction

Although numerous studies have described the occurrence of sulfides with different textural characteristics in Ni-Cu-PGE deposits, few have characterized the variations in their chemistry. Yet, correlations between the chemistry and texture of sulfides could yield important information regarding their mode of formation. In the Marathon Cu-Pd deposit, preliminary textural and chemical characterization of sulfides indicated differences between sulfides with different textural associations (Samson et al. 2008). No studies, however, have characterized the compositional variations in sulfides hosted in the different mineralized zones in this deposit. In this contribution, variations in the trace metal content, including PGE, and in the S/Se ratios of sulfides that exhibit various textures from the different mineralized zones in the low-sulfide, conduit-type Marathon Cu-Pd deposit are characterized in detail and used to assess the controls on low- to high-Cu/Pd mineralization. These data are used to assess i) the role of hydrothermal fluids in the redistribution of metals amongst and between the mineralized zones and ii) the role of multistage dissolution upgrading in the formation of the Pd-rich W Horizon.

Three Cu-Pd occurrences (Four Dams, Area 41, and Redstone) are located in the Eastern Gabbro Suite to the northwest of the Marathon deposit. To date, very little work has been carried out on these occurrences (McBride 2013). This study focuses on the detailed mineralogy, texture, and composition of sulfides and complements the detailed characterization of platinum-group minerals (PGM) in the W Horizon by Ames et al. (2017) and at Marathon, Geordie Lake, and Area 41 by Good et al. (2017). To develop well-constrained models for the mineralization hosted in the Eastern Gabbro Suite, it is important to understand their mode of formation and how they relate to the zones at Marathon. To do this, the mineralogy, texture, and composition of sulfides from Four Dams, Area 41, and Redstone are characterized and compared to those from the mineralized zones at Marathon.

2 Geological setting

The Eastern Gabbro Suite of the Coldwell Complex is subdivided into three genetically-distinct intrusive series, termed metabasalt, Layered Series, and Marathon Series (Good et al. 2015). The metabasalts and Layered Series predate the Marathon Series and, apart from minor secondary Cu mineralization in the latter series, are devoid of PGE mineralization. The Marathon Series is defined as including all mafic to ultramafic rocks that host Cu-PGE mineralization and consists largely of the Two Duck Lake gabbro, a coarse-grained ophitic to pegmatitic gabbro. This series is host to the Marathon Cu-Pd deposit, and to the Four Dams, Area 41, and Redstone occurrences (McBride 2013; Good et al. 2015).

Mineralization at Marathon occurs in shallow-dipping lenses that are texturally, mineralogically, and compositionally distinct from one another. At increasing distances from the footwall contact, these comprise the Footwall Zone, Main Zone, and W Horizon (Good et al. 2015). Sulfides in the Footwall Zone comprise semimassive to net-textured pyrrhotite (Po) > chalcopyrite (Ccp). In the Main Zone, sulfides are dominated by
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3 Analytical methods

The sulfide mineralogy was determined using a combination of reflected light microscopy and EDS. The major element composition of sulfides was primarily obtained using a FEI Quanta 200 FEG SEM equipped with an EDAX EDS x-ray detector at the University of Windsor. To verify the accuracy of the data obtained by EDS, the composition of a subset of sulfides was also obtained using a JEOL JXA-8530F field-emission EPMA at Western University.

The trace element composition of sulfides was obtained using laser ablation ICP-MS at the University of Windsor. The system comprises a Thermo X Series II ICP-MS coupled with a 193-nm excimer laser. Three external standards were used for calibration: MASS-1, Po725, and NIST610. Iron was used as the internal standard for all sulfides. Pure Cu and Zn foils were analysed to determine correction factors for the CuAr and ZnAr interferences on \(^{105}\)Pd, \(^{106}\)Pd, \(^{108}\)Pd, and \(^{103}\)Rh.

4 Results

4.1 Sulfide mineralogy and textures

Sulfide mineralization can be subdivided into semi-massive to net-textured and disseminated types. Semi-massive to net-textured sulfides occur in the Footwall Zone of the Marathon deposit and near the base of the Four Dams occurrence and are dominated by Po with minor Ccp. Mineralization elsewhere in the Eastern Gabbro occurs as disseminated sulfides. Sulfides in the Main Zone of the Marathon deposit consist primarily of comparable proportions of Ccp and Po with rare Cub and Bn, whereas those in the W Horizon consist primarily of Ccp and Bn with rare Po and Cub. The sulfides at Four Dams, Area 41, and Redstone differ from those in the Main Zone and W Horizon in that they contain noticeably more Cub and Po, and generally lack Bn. All of the mineralized zones contain minor pentlandite (Pn), either as grains associated with other sulfides or, more typically, as flames in Po (Fig. 1a).

Platinum-group minerals are more common in the W Horizon compared to the other zones and show a large diversity in mineralogy ranging from platinum-group sulfides, arsenides, bismuthides, tellurides, and alloys (Ames et al. 2017). A Co-rich (up to 5 wt. %) Pn occurs in some Ccp predominantly from Marathon.

Sulfides can occur as monomineralic grains or as aggregates that are interstitial to primary silicates and can either exhibit equilibrium or disequilibrium textures with silicate and sulfides. Equilibrium Ccp-Po assemblages are common in all of the mineralized occurrences and exhibit sharp, equilibrium boundaries with each other and with primary silicates (Fig. 1a). Bornite and Cub typically occur as wormy to tabular exsolution lamellae, but can also occur as monomineralic grains. Chalcopyrite and Po can also occur along the cleavage planes of plagioclase and within Ca-rich rims on plagioclase. Partial to complete replacement of Ccp by magnetite occurs in all of the mineralized zones apart from the Footwall Zone, and is most abundant in Four Dams, Area 41, and Redstone.

Interstitial disequilibrium sulfides comprise the replacement of Po by Ccp and the intergrowth of primarily Ccp with hydrous silicates. When Po has been replaced by Ccp, it occurs as optically-continuous islands with ragged boundaries in a matrix of Cep (Fig. 1b), suggesting that these islands of Po were originally larger, single crystals. Where sulfides are intergrown with hydrous silicates, the hydrous silicates typically comprise actinolite \(\pm\) chlorite that have partially to completely replaced pyroxene, olivine, and magnetite. There are several textural varieties of sulfide-hydrous silicate intergrowths: i) randomly-oriented euhedral actinolite within sulfides (Fig. 1c), ii) actinolite crystals that protrude from altered pyroxene into sulfides in the same orientation as the actinolite in the pyroxene (Fig. 1d), and iii) sulfides within altered pyroxene (Fig. 1e). Rarely, Ccp occurs along alteration fronts of hydrous assemblages (Fig. 1e). Where magnetite-ilmenite aggregates have been altered, magnetite is commonly replaced by an assemblage of hydrous silicates \(\pm\) Ccp. In one instance, an assemblage of magnetite+carbonate occurs as a pseudomorph in Ccp. Where the Co-rich sulfide is present, it typically occurs in aggregates of subhedral crystals within Ccp or is replaced by Ccp (Fig. 1f).

Replacement of Po by Ccp is common in all of the mineralized zones, except for the W Horizon, but intergrowths of Ccp with hydrous silicates is common in all zones.

4.2 Sulfide composition

Evidence from monosulfide solid solution (MSS)/sulfide liquid partitioning experiments (e.g., Liu and Brenan 2015) and natural examples (e.g., Dare et al. 2011) suggests that the Ir-group PGE (Os, Ir, Ru) and Co partition strongly into MSS, whereas the Pt-group PGE (Pt, Pd), Au, Ag, Zn, and heavy main group elements (As, Sn, Sb, Te, Pb, and Bi) strongly prefer to remain in the residual Cu-rich liquid, and either partition into intermediate solid solution (ISS) or form discrete phases. Selenium prefers the residual liquid, but has a D close to 1 (~0.6). Apart from Zn and Co, the concentration ranges of these elements largely overlap between sulfides that exhibit equilibrium and disequilibrium textures (Fig. 2a). Zinc is preferentially hosted in Ccp>Cub and shows no preference for either Po or Pn, whereas Co is preferentially hosted in Pn>Po and shows no preference for any of the Cu-rich sulfides (Fig.
2a). Palladium and Ru occur at higher concentrations in Pn and show no preference amongst the other sulfides, whereas Ag and Sn are preferentially enriched in the Cu-rich sulfides.

Chalcopyrite from the Main Zone exhibits a wide range in PGE, main group, and transition element concentrations that largely overlaps with the composition of Ccp from the Footwall Zone and W Horizon (Fig. 2b). The only notable difference between these zones is the lower Zn in Ccp from the W Horizon relative to those in Main and Footwall Zones and lower Co relative to the Footwall Zone (Fig. 2b). Chalcopyrite from the northern deposits display a limited range of Zn contents compared to Marathon deposits, but a similarly large range in Co (Fig. 2b). The Zn and Co contents of all of the northern deposits overlap with each other and with those from the Main and Footwall Zone at Marathon (Fig. 2b). Chalcopyrite from one sample from Area 41 zone 3 has notably lower Zn and Co than the other northern deposits and is similar to Ccp from the W Horizon (Fig. 2b).

**Figure 1.** Reflected light images of a) equilibrium Ccp, Po, and Pn b) replacement of Po by Ccp, c) Ccp intergrown with randomly-oriented blades of Act, d) Ccp intergrown with Act extending from altered Px, e) Ccp in altered Px and along and alteration front, and f) aggregates of a Co-rich Pn in replacement Ccp.

### 4.4 Variations in sulfide S/Se

Sulfide minerals from the Footwall Zone consistently have higher S/Se ratios (6,000-15,000) than the mantle range (Fig. 3). Sulfides from the Main Zone have S/Se ratios (1,400-20,000) that overlap with mantle values, with some exhibiting higher, and some lower, ratios (Fig. 3). Sulfide minerals from the W Horizon predominantly have S/Se ratios (300-16,000) that are less than mantle values, with some exhibiting ratios that are higher than mantle values (Fig. 3). Sulfide minerals from the northern deposits show less diversity in S/Se ratios and largely exhibit ratios that are less than, or within the range of, mantle values (Fig. 3).

**Figure 2.** Zn vs. Co between a) equilibrium sulfides (colored fields) and disequilibrium sulfides (data points) and b) chalcopyrite hosted in the zones at Marathon (colored fields) and northern deposits (data points).

**Figure 3.** S/Se ratio of sulfides from all occurrences vs. their corresponding whole-rock Cu/Pd ratio. Fields and arrows are modified from Queffurus and Barnes (2015). Mantle range from Eckstrand and Hulbert (1987).

### 5.1 Hydrothermal remobilization of metals

If Po formed from MSS and Ccp from ISS, then they should exhibit equilibrium textures as observed in many instances throughout the deposit (Fig. 1a) and chemistry that reflects MSS-ISS fractionation. Otherwise, the sulfides cannot represent MSS-ISS equilibrium. Chalcopyrite that has replaced pyrrhotite and/or are intergrown with hydrous silicates are clearly not in equilibrium with other sulfides and do not exhibit classic resorption textures. Therefore, these textures indicate the involvement of hydrothermal fluids in their genesis. Chalcopyrite that crystallized from a fluid should have a different chemistry from those which resulted from MSS-ISS fractionation. However, despite the textural evidence for the involvement of hydrothermal...
fluids in the genesis of the disequilibrium Ccp, there is no consistent difference in chemistry between equilibrium and disequilibrium Ccp (Fig. 2). If disequilibrium Ccp has replaced Po, then it could have inherited some of the chemical characteristics of the Po it has replaced (c.f. Li et al. 2004). The only element that is notably enriched in Po relative to Ccp is Co, however, the range of Co concentrations of equilibrium and disequilibrium Ccp overlap (Fig. 2). The similarity in composition between equilibrium Ccp, replacement Ccp, and Ccp intergrown with hydrous silicates can be explained if the metal content of a Cu-rich fluid was derived through its interaction with sulfide in the Footwall Zone prior to its migration and interaction with Po in the Main Zone (Shahabi Far 2016). The lack of Co enrichment in replacement Ccp relative to equilibrium Ccp can be explained either by sequestration of the inherited Co in a separate phase, the Co-rich Pn, or removal of Co during fluid-mineral interaction.

5.2 Affects of supra- and subsolidus processes in the formation of mineralization

If all sulfides are magmatic and are unaffected by subsequent supra- and subsolidus processes, then they should have S/Se ratios that fall within the range of mantle values. Ratios greater than mantle values could suggest low R factors and/or S contamination, whereas lower ratios could suggest high R factors, S loss, or hydrothermal alteration (Queffurus and Barnes 2015). The higher-than-mantle S/Se ratios and high Cu/Pd ratios in the Footwall Zone (Fig. 3) can be explained by the interplay of S contamination and a low R factor. Contamination by external S could have increased the S/Se ratio, and could also have led to the formation of the semi-massive mineralization, which is typically characterized by lower R factors than disseminated mineralization (Maier 2005). A large proportion of sulfides from the Main Zone have S/Se ratios that straddle the mantle range (Fig. 3), consistent with their origin from mantle-derived magmas. Few sulfides have S/Se ratios greater than the mantle range (Fig. 3), suggesting minor contamination by external S (Fig. 3). These observations are consistent with S isotopic evidence that suggests the different magma pulses that host the Marathon deposit underwent a progressive decrease in the degree of S contamination by Archean crust at depth with increasing distance from the Footwall contact, with the W Horizon showing very little evidence of contamination, possibly due to dilution by successive pulses of magma (Shahabi Far 2016). The W Horizon has the lowest S/Se and whole-rock Cu/Pd ratios of all the mineralized zones (Fig. 3). The low S/Se ratios can either be explained by a higher R-factor compared to other zones, or by su S loss. The lack of textural evidence to suggest S loss advocates for the high R factor model. This agrees with the multistage dissolution upgrading model that has been proposed for the formation of the W Horizon, whereby some volume of sulfide liquid is dissolved by influxes of S-undersaturated magma and the PGE content of the remaining sulfides is increased (Kerr and Leitch 2005). The lack of PGE enrichment in W Horizon sulfides relative to those from other zones suggests that most of the PGE exsolved from sulfides and occur as PGM (Ames et al. 2017). The mineral occurrences to the north of the Marathon deposit exhibit a vertical trend in Cu/Pd vs. S/Se with S/Se ratios that are mostly less than mantle values (Fig. 3). These ratios likely represent greater degrees of S loss compared to the other zones, consistent with the greater abundance of sulfide replacement by magnetite.

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Iron isotope systematics of the Panzhihua gabbroic layered intrusion associated with giant Fe-Ti oxide deposit in the Emeishan large igneous province, SW China

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Abstract. The Panzhihua mafic layered intrusion is unique to the layered intrusions worldwide as it hosts unusually thick stratiform Fe-Ti oxide ore layers in its lower zone. Here we present Fe isotopic compositions for 29 whole-rock samples and mineral separates (clinopyroxene, magnetite and ilmenite) along a cross section of the intrusion to investigate the formation of the intrusion and associated Fe-Ti oxide ore deposit. The whole-rock samples have \( \delta^{56}\text{Fe} \) ranging from 0 to 0.15‰, nearly identical to the range of 0.01 to 0.16‰ for clinopyroxene separates. Although the \( \delta^{56}\text{Fe} \) of magnetite separates (0.17 to 0.62‰) show a complementary trend with the values of coexisting ilmenite separates (-0.52 to -0.09‰) along the cross section, the bulk \( \delta^{56}\text{Fe} \) for the Fe-Ti oxides show a small range from 0.01 to 0.16‰ that is identical to the range for the clinopyroxenes and rocks. This indicates that the thick Fe-Ti oxide ore layers in the lower zone of the intrusion were unlikely to be produced by early crystallization of large amounts of Fe-Ti oxides. Based on Fe isotope data and the textural evidence, we propose a model of high-temperature silicate immiscibility of interstitial liquid for the formation of the Panzhihua intrusion and associated Fe-Ti oxide deposit.

1 Introduction

Mafic-ultramafic layered intrusions have been considered as prime examples of strong Fe enrichment because thick horizons dominated by Fe-Ti oxides are observed in various layered intrusions such as Bushveld, Duluth and Panzhihua (Eales and Cawthorn 1996; Ripley et al. 1998; Zhou et al. 2005). Among these intrusions, the Panzhihua gabbroic layered intrusion in SW China is special because it hosts a giant Fe-Ti oxide deposit (Pang et al. 2008; Song et al. 2013).

The origin of thick Fe-Ti oxide ore layers in the lower part of the Panzhihua intrusion has been debated over the last decade (Zhou et al. 2005; Pang et al. 2008; Song et al. 2013). Zhou et al. (2005) proposed a model involving the separation of immiscible oxide liquids from gabbroic magmas, whereas some workers favoured the more conventional model hinging on crystallization settling and sorting of early cumulus Fe-Ti oxides from silicate magma chamber (Pang et al. 2008; Song et al. 2013).

The Fe isotope systematics of intrusions or volcanic rocks are sensitive to the crystallization of Fe-bearing minerals during magma differentiation (e.g., Teng et al. 2008, 2013; Sossi et al. 2012). In this study, we report results for a suite of samples include gabbroic rocks and Fe-Ti oxide ores from a cross section in the Lanjiahuoshan open pit of the Panzhihua intrusion.

2 Geological background

The Panzhihua gabbroic intrusion is a part of the ~ 260 Ma Emeishan large igneous province (LIP). It is ~2 km thick with an outcrop area of ~30 km² (Zhou et al. 2005). The intrusion is in contact with Sinian dolomitic limestone of the Dengying Formation in footwall and overlain by coeval syenitic plutons. The hosted Fe-Ti oxide deposit contains the ore reserve of 1.333 billion tons at an average grade of ~33% FeO T and ~12% TiO₂ and it has been mined for over 60 years (Ma et al. 2003).

Based on internal structure and the extent of Fe-Ti oxide mineralization, the intrusion is divided into four zones from the base upwards, including a marginal zone (MGZ), lower zone (LZ), middle zone (MZ), and upper zone (UZ) (Zhou et al. 2005). The Middle zone is further divided into MZa and MZb by the appearance of apatite in MZb (Pang et al. 2008).

The Marginal Zone is considered as chilled margin and is mainly composed of microgabbro with small amounts of olivine gabbro (Fig. 1a). The lower zone consists of coarse-grained melagabbro and hosts the major Fe-Ti oxide ore (Fig. 1c) layers at the base. The thickness of Fe-Ti oxide ore layers ranges from a few centimetres to up to 60 m and can be traced in outcrop for a long stretch along the strike (Zhou et al. 2005; Pang et al. 2008). The MZa is mainly composed of prominently layered gabbro, i.e., the layers that are dominated by clinopyroxene and Fe-Ti oxides alternating with layers that are dominated by plagioclase (Fig. 1e). The MZb is composed of leucogabbro with 1-5%apatite. The upper zone is composed of leucogabbro with minor amounts of Fe-Ti oxides (Fig. 1g).
3 Petrography

Microgabbro in the MGZ is fine-grained (≈0.2 to 0.5 mm) and characterized by an equigranular texture consisting of ≈45 vol.% clinopyroxene, ≈40% plagioclase and <12% Fe-Ti oxides, with trace amounts of olivine (Fig. 1b).

Figure 1. Photographs (a, c, g, e) and photomicrographs (b, d, f, h) of rocks and ores in the Panzhihua intrusion.

Fe-Ti oxide ores in the LZ show both massive and disseminated texture. Massive ores contains >80% Fe-Ti oxides and <20% silicate minerals (Fig. 1c). The silicate minerals are isolated plagioclase and clinopyroxene grains that are completely enclosed by Fe-Ti oxides with most of them showing embayed margins and brown amphibole rims (Fig. 1d). Disseminated ores contain more silicate minerals than massive ores. Magnetite-rooted replacive symplectites are common in oxide gabbro and are composed of An-rich plagioclase (An$_{77-80}$) + amphibole that replaced plagioclase primocrysts (An$_{57}$) (Fig. 2). This texture is quite similar to the symplectite of An-rich plagioclase + clinopyroxene in the Skaergaard intrusion which was interpreted as the reaction of plagioclase primocrysts with immiscible Fe-rich melt due to the loss of Si-rich component from the interstitial liquid after the onset of silicate liquid immiscibility (Holness et al. 2011).

Melagabbro in the LZ and MZa is characterized by rhythmic layering with variable proportion of Fe-Ti oxides and silicate minerals (Fig. 1e). Medium-grained rocks contain 40-50% clinopyroxene, 20-40% plagioclase and 15-35% Fe-Ti oxides (Fig. 1f). Fe-Ti oxides are interstitial to silicate minerals (Fig. 1f).

Leucogabbro in MZb and UZ contains 60-70% plagioclase, 25-30% clinopyroxene and 5-8% Fe-Ti oxides (Fig. 1h). The rocks from MZb contain 1-5% apatite. Fe-Ti oxides occur as interstitial fillings between silicate minerals (Fig. 1g and h).

Figure 2. BSE images of the replacive symplectites in oxide gabbro in the Lower zone. a) Replicacive symplectites rooted in magnetite (or ilmenite), replacing adjacent primocryst plagioclase. b-c) Replicacive symplectites made of An-rich plagioclase (dark grey) intergrowth with amphibole (light grey), commonly with a biotite substrate at the inner edges.

4 Fe isotope systematics of the Panzhihua intrusion

Twenty-nine representative samples were collected from a cross section through the Lanzhiahuoshan open pit, which covers all common rock types of the Panzhihua intrusion. All samples for bulk rock analyses were ground into powder using an agate mortar. Mineral separates were cleaned in ultra-sonic bath with ethanol and Milli-Q water, then powdered prior to digestion for Fe isotope analysis. Sample purification for Fe isotope analysis was performed in clean laboratory at the State Key Laboratory of Isotope Geochemistry in the GIGCAS. Fe isotope ratios were measured at the Key Laboratory of Crust-Mantle and Environments (CAS) at the University of Science and Technology of China using a Thermo Scientific Neptune plus MC-ICP-MS at a high mass resolution mode (resolution >9000).

Whole-rock samples have δ$^{56}$Fe varying from +0.00 to +0.15‰ with an average of +0.08‰ ($n=29$), which fall into the range for terrestrial igneous rocks (Beard and Johnson 1999; Weyer et al. 2005). The whole-rock samples have a small variation in δ$^{56}$Fe through the cross section regardless of rock types, sample locations, and the proportion of Fe-Ti oxides in the samples (Fig. 3).
Clinopyroxene, magnetite, and ilmenite separates have $\delta^{56}$Fe ranging from +0.01 to +0.16‰, +0.17 to +0.62‰ and -0.52 to -0.09‰, respectively, defining a sequence of heavy Fe isotope enrichment trend of $\delta^{56}$Fe_Mt > $\delta^{56}$Fe_Cpx > $\delta^{56}$Fe_Ilm (Fig. 3). Clinopyroxene separates from each sample have $\delta^{56}$Fe values indistinguishable from the whole-rock value within analytical precision (Fig. 3). Magnetite and ilmenite from each sample have $\delta^{56}$Fe values quite different from the narrow range for the whole-rock and clinopyroxene values, displaying a remarkably complementary trend along the profile (Fig. 3). Coexisting mineral separates exhibit large fractionation of Fe isotopes with $\Delta^{56}$Fe_Mt-Cpx varying from +0.06 to +0.62‰, $\Delta^{56}$Fe_Mt-Ilm from +0.36 to +0.97‰ and $\Delta^{56}$Fe_Cpx-Ilm from +0.18 to +0.58‰. The bulk $\delta^{56}$Fe values for Fe-Ti oxides that were calculated based on the modes of magnetite and ilmenite in each sample, vary from 0.01 to 0.16‰, nearly identical to the values for the clinopyroxenes and rocks.

A striking feature of Fe isotope data in this study is that the whole-rock samples regardless of rock types define a narrow range of $\delta^{56}$Fe (Fig. 3). This is quite different from the trend caused by fractional crystallization of Fe-bearing silicate minerals or oxide in specific sequence in some intrusion such as the Red Hill intrusion, South Tasmania (Sossi et al. 2012).

Clinopyroxene, magnetite and ilmenite are dominant Fe-bearing minerals in the Panzhihua rocks. The Fe isotope composition of whole rock thus should conform to the mass balance results calculated for Fe isotope abundances in each phase assemblage. Clinopyroxene have $\delta^{56}$Fe values identical to the whole-rock values (Fig. 3). Consistently, previous studies suggested that Fe isotope fractionation factor between pyroxene and co-existing basaltic melt (1000ln$\alpha_{Cpx-Melt}$) is close to zero (e.g. Weyer and Seitz 2012). Therefore, if clinopyroxene is the only crystallized Fe-bearing phase from magma, Fe isotope compositions of the mineral and the melt should not be significantly affected by fractional crystallization. This explains the nearly uniform $\delta^{56}$Fe of the clinopyroxene separates and whole-rocks of the Panzhihua intrusion (Fig. 3). Textural relationship of the rocks also indicates that cumulus clinopyroxene crystallized earlier than Fe-Ti oxides and it is the dominant Fe-bearing silicate phase in the Fe-Ti oxide ores (Fig. 1d) and gabbroic rocks (Fig. 1f and h).

On the other hand, it is enigmatic that clinopyroxene and whole rocks have uniform $\delta^{56}$Fe, whereas the $\delta^{56}$Fe values of magnetite and ilmenite are highly variable (Fig. 3). We considered that insignificant Fe isotope fractionation of the whole rock samples is likely attributed to that magnetite and ilmenite crystallized in ratios that did not result in substantial variations in the bulk $\delta^{56}$Fe values of the rocks. A possible way to keep the Mt/Ilm ratio and bulk $\delta^{56}$Fe values of the rocks is that the magnetite and ilmenite may have crystallized nearly in situ from the melt and there was no whole-scale gravitationally driven compositional convection in the Panzhihua magma chamber.

Theoretically calculated $10^3$ln$\alpha_{Mt-Cpx}$ for Fe isotopes at 1200 to 900 °C is +0.15 to +0.23‰, $10^3$ln$\alpha_{Mt-Ilm}$ is +0.18 to +0.29‰ and $10^3$ln$\alpha_{Cpx-Ilm}$ is +0.07 to +0.12‰ (Polyakov and Mineev 2000; Polyakov et al. 2007). Apparently, the inter-mineral Fe isotope offsets of the minerals in our samples are displaced away from the calculated ranges for equilibrium fractionation, indicating Fe isotope disequilibrium amongst the minerals. We ruled out the possibility of kinetic processes, including chemical diffusion and thermal diffusion, as causes of disequilibrium offset of Fe isotopes. Instead, we calculated the bulk $\delta^{56}$Fe values for Fe-Ti oxides, ranging from 0.01 to 0.16‰, which is nearly identical to the values for the clinopyroxene separates. This can be explained if the Fe-Ti oxides crystallized from the interstitial liquid that had Fe isotope equilibrium with early crystallized clinopyroxene, then disequilibrium crystallization of magnetite and ilmenite from the interstitial liquid is likely the major reason for the disequilibrium fractionation of Fe.

5 Discussion
isotope in the two minerals.

Based on Fe isotope data and the textural evidence, we propose a model of immiscibility of interstitial liquid for the formation of the Panzhihua intrusion and Fe-Ti-V ore deposits. The nearly identical \( \delta^{56}\text{Fe} \) values of clinopyroxene and whole rock samples are attributed to the negligible Fe isotope differentiation between early crystallized clinopyroxene and parental high-Ti basaltic magma at high temperature. Nearly identical \( \delta^{56}\text{Fe} \) values of bulk Fe-Ti oxides and clinopyroxene at the same stratigraphic level along the cross section are attributed to the limited Fe isotopic fractionation between conjugate immiscible Fe-rich and Si-rich melts in the interstitial liquid. The complementary trend of \( \delta^{56}\text{Fe} \) values for the coexisting magnetite and ilmenite along the cross section indicates that the Fe-Ti oxides crystallized \textit{in situ} without large-scaled gravitationally derived migration and likely the late crystallization phases from interstitial liquid, rather than early crystallization phase from parental magma as proposed in earlier studies.

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References


Form and emplacement of chonoliths

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Abstract. Intrusion-hosted Ni-Cu-PGE magmatic sulphide deposits accumulate within crustal-scale magma plumbing systems that transport mantle-derived mafic and ultramafic magmas from mantle sources to the surface. Magmatic sulphide mineralization within such systems occurs in a variety of traps that form due to a combination of structural and fluid-mechanical processes. Ore-hosting structures include tubular chonoliths (e.g., Nebo-Babel and Limoiera), ribbon-shaped sills (e.g., Noril’sk and Nkomati/Uitkomst), funnel-shaped jogs within conduits (e.g., Voisey’s Bay Ovoid), elongate funnel-shaped flares within dyke-like intrusions (Eagle, Tamarack) and blade-shaped dykes (e.g., Expo-Ungava). Considerable research has been focused on the links between lithospheric architecture and Ni-Cu-PGE mineralization and the geochemical origins of sulphide mineralization. Far less work has addressed the physical processes involved in the transport of the host magmas, how high-flux channels develop, and where sulphide liquids separate and accumulate to form ore deposits. Here we discuss the form and emplacement mechanisms of pipe-, tube- and ribbon-shaped chonoliths. We hypothesise that chonoliths emerge from planar dykes and sills by elastic, viscous and thermal instabilities and then widen and elongate by thermo-mechanical erosion. We also suggest that chonoliths form linking conduits in crustal-scale sill systems, which explains the association between Ni-Cu-PGE sulphide deposition and high magma fluxes.

1 Chonoliths

Pipe-like chonoliths intrusions (Fig. 1A) are economically highly important with 58 of the 61 known examples in the world hosting Ni–Cu–PGE mineralisation, 26 of which are

![Figure 1](image-url)
producing mines (Beresford and Hronsky 2014). A major challenge for mineral explorers is that high-value mineralised pipes are exceedingly rare, making up <0.01% by volume of the magma plumbing systems in which they occur (Barnes et al. 2016). In other words, Ni–Cu–PGE deposits have a much smaller “footprint” compared to other base metal deposits. Narrowing down the search space for Ni–Cu–PGE mineralisation is further compounded by the fact that very little research has been carried out on the form, structure and emplacement of pipe-like intrusions. This is partly due to their rarity and also because their economic significance has only recently been realised by the mineral exploration community (Lesher and Keays 2002; Arndt et al. 2005; Beresford and Hronsky 2014).

The magma plumbing systems that host Ni–Cu–PGE sulphide mineralisation can be many thousands of kilometres wide. They transport enormous volumes of magma from the mantle through the crust via interconnected networks of sub-vertical and sub-horizontal dykes and sills. Their stair-stepping architecture can be focused above the mantle source or become laterally displaced from it over 100s to 1000s of kilometres (Magee et al. 2016).

In comparison to dykes and sills, very little research effort has focused on pipe-like magma conduits. Seminal work by Pollard et al. (1975) and Nicholson and Pollard (1985) showed that magma fingers form and grow by segmentation at the margins of propagating sills (Fig. 2A). These observations have been confirmed over the past decade by 3D seismic reflection images of sills, collected by oil and gas companies in offshore rifted volcanic margin basins, and complementary detailed outcrop studies of their onshore equivalents (Schofield et al. 2013; Magee et al. 2016). 3D seismic reflection surveys also reveal that sills have far more complex morphologies than previously thought, including a common tendency to develop saucer shapes. Many sills observed in 3D seismic images have lobate margins that resemble the fronts of lava flows (Magee et al. 2016), which in extreme cases evolve into narrow ribbon-like structures Miles and Cartwright 2010), resembling pipes in 3D (Figs. 2A,B). Magee et al. (2016) and others have suggested that prolonged and discrete pipe-like magma flow pathways develop within individual sill intrusions through the coalescence of magma segments or fingers and, on a larger scale, magma lobes (Fig. 1B) (Magee et al. 2016). The channeling of magma into one or several of these elongate zones can increase the segment thickness, allowing magma flow to be sustained while neighboring portions of the intrusion crystallize (Holness and Humphreys 2003). Flow of magma through thin channels, which then bud off to form larger sills, is supported by mapped magma flow patterns that suggest that sills are intruded from a pointlike source (Magee et al. 2016). This scenario of periodic transport of magma through sill complexes linked by high flow rate pipe- or finger-like conduits is similar to the conceptual model that Barnes et al. (2016) have proposed for Ni–Cu–PGE mineralisation.

2 Emplacement and growth of chonoliths

Dykes and sills are the fundamental building blocks of magma plumbing systems. We hypothesise that such plumbing systems develop by multiple linkages between these structures to form a stair-stepping architecture through the crust (Barnes et al. 2016; Saumur et al. 2015). Linkage or bridging between adjacent propagating dykes via their tips has been well documented in the field (Magee et al. 2016; Taisne and Jaupart 2009). Recent important theoretical and laboratory studies have investigated dyke-sill linkages (Kavanagh et al. 2015) and it is now thought that transition between the two occurs when a propagating dyke arrives at the interface between materials with different elastic properties, or where the interface itself is weak (Kavanagh et al. 2015). Field observations, laboratory experiments and theory confirm the influence that pre-existing country rock structures, including bedding, foliations, fractures and faults, have on magma plumbing system architecture (Taisne and Jaupart 2009; Le Corvec et al. 2013). This country rock control can also
promote the periodic development of pipe-like conduits within the plumbing system, which form high magma flux channels between dykes and sills, such as within the complex magma plumbing system of the Voisey’s Bay Ni–Cu sulphide deposit, which was influenced by pre-existing brittle and ductile structures (Barnes et al. 2016; Saumur et al. 2015).

2.1 Emergence of fingers from dykes and sills

Progress in understanding dyke and sill emplacement contrasts with very limited research on pipe-like intrusions. How pipe-like channels emerge from planar dykes and sills remains poorly understood but can be summarised as follows.

The leading edges of propagating dykes and sills can break down to form lobes and fingers due to the development of viscous instabilities, as originally postulated by Pollard et al. (1975). This processes is analogous to the well-known Saffman-Taylor instability in fluid mechanics, in which an originally linear interface between low and high viscosity fluids or between a fluid phase and a granular suspension breaks down into elongate, periodic fingers. Recent experimental work in which a low viscosity fluid is injected into fractional granular suspensions show the development of structures ranging from dendritic networks to elongate tubes, associated with fluidisation of marginal material (Fig. 2C) (Sandnes et al. 2011). The latter are particularly relevant to the formation of some magma fingers, which can also be associated with fluidisation when intruded into shales and partly consolidated rocks (Schofield et al. 2013). This scenario is relevant to the mineralised chonoliths of the giant Noril’sk-Talnakh Ni–Cu–PGE deposits, Russia, which is emplaced into weak shale and anhydrite layers (Czamanski et al. 1995; Naldrett 2004).

The leading edges of planar intrusions may break down into in-plane, periodically spaced fingers via an elastic instability, as observed in experiments of fluid-driven crack propagation in gelatine (an elastic crustal analogue) (Touvet et al. 2011). The leading edges of propagating dykes and sills are also known to break down into enechelon fingers that twist off the main crack (Fig. 2A) (Nicholsen and Pollard 1985). These eventually merge to form broken bridges and related features (Schofield et al. 2013). A variant to these mechanisms may occur when a propagating fluid-filled elastic crack intersects and then deviates along a pre-existing fracture to form an elongate structure (Valentine and Krogh 2006). Such elastic processes are relevant to the formation of pipe-like magma conduits in brittle host rocks, such as those associated with the Voisey’s Bay, Canada, and Nebo Babel, WA, Ni–Cu–PGE deposits, which occur in brittle crystalline host rocks (Seat et al. 2007; Saumur and Cruden 2016).

2.2 Growth of fingers into pipe- and ribbon-like chonoliths

In concert with the amplification of viscous and or elastic instabilities, variations in the degree of cooling and solidification may also result in the destabilisation of the edges of propagating dykes and sills and subsequent growth of the resulting perturbations to form lobes and fingers (Holness and Humphreys 2003), as recently observed in experiments in which molten paraffin wax is injected into gelatine (Fig. 3B) (Taisne and Tait 2011; Chanceaux and Menand 2016).

In extreme cases, and particularly in ore-hosting intrusions, pipe-like features may amplify due to thermo-mechanical erosion of the host rocks. Analogies for this process exist in the formation of erosional pipes in dams and or so-called wormholes formed during oil and gas reservoir stimulation (Richards and Reddy 2007; Ott and Oedai 2015). The former start out as planar hydrofractures and evolve into tubular conduits. The latter form by preferential dissolution of carbonate rocks during injection of CO₂ or weak acids. Research on these engineering problems may provide useful analogues for the formation and or modification of pipe-like magma conduits by thermal-mechanical erosion, such as the mineralised tube-shape Uitkomst chonolith, South Africa (Gauert et al. 1995; Barnes et al. 2016).

2.3 Preliminary laboratory experiments

We report on the results of preliminary 3D laboratory modelling of chonolith emplacement in which tanks of gelatine (and elastic crustal analogue), which can be isotropic, mechanically layered or pre-fractured, are injected by analogue magmas, fed via a peristaltic pump at constant flux or pressure (Taisne and Jaupart 2011; Kavanagh et al. 2015; Chanceaux and Menand 2016). High-speed imaging and particle imaging velocimetry (PIV) is employed to capture transient stress and strain.
perturbations in the analogue crust during the emplacement and growth of dykes, sills and chonolith-like intrusions (e.g., Kavanagh et al. 2015). Experiments using isothermal analogue magmas produce penny-shaped dykes and sills as predicted by elastic theory. They also demonstrate that transitions between dykes and sills occur at weak interfaces between mechanically contrasted layers. Considerable complexity emerges when isothermal analogues are replaced by molten materials that solidify under experimental conditions. A common observation of such experiments is the development of lobate dyke and sill margins, which in some cases amplify to form chonolith-like channels. Future work will focus on defining the parameters (e.g., driving pressure, flux, host material structure, temperature-dependent viscosity, analogue magma/host temperature differences, etc.) that favour growth of pipe-like chonoliths.

3 Conclusions

Chonoliths form within crustal-scale magma plumbing systems as rare pipe-like linking conduits between planar dykes and sills. The high magma flux in these conduits, in addition to their structural complexity makes them favourable sites for Ni–Cu–PGE sulphide deposition. Field, theoretical and laboratory research suggests that chonoliths form by the viscous or elastic destabilisation of propagating dykes and sills and coeval or subsequent amplification by the development of solidification instabilities and or thermo-mechanical erosion. This process-based understanding of chonolith development within magma plumbing systems should aid in the development of new exploration strategies for intrusion-hosted Ni–Cu–PGE sulphide deposits.

References

Valentine G, Krogh K (2006) Emplacement of shallow dikes and sills. The high magma flux in these conduits, in addition to their structural complexity makes them favourable sites for Ni–Cu–PGE sulphide deposition. Field, theoretical and laboratory research suggests that chonoliths form by the viscous or elastic destabilisation of propagating dykes and sills and coeval or subsequent amplification by the development of solidification instabilities and or thermo-mechanical erosion. This process-based understanding of chonolith development within magma plumbing systems should aid in the development of new exploration strategies for intrusion-hosted Ni–Cu–PGE sulphide deposits
Arrested in the Ivrea Zone: Ni sulfide mineralisation in lower continental crust, La Balma igneous complex (NW Italian Alps)

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Abstract. Our understanding of how mantle-derived magmas are transferred to sites of ore formation is limited by the accessibility of intrusion networks at crustal roots. The Ivrea Zone (NW Italian Alps) represents a largely intact section of lower to middle continental crust modified in composition and structure by voluminous mantle melts. Exhumation and tilting of the Ivrea Zone reveals an elongate mafic-ultramafic intrusive complex in cross section that hosts Ni-Cu-PGE-sulfide mineralisation, termed here the La Balma igneous complex, where we investigate mechanisms of magma arrest and sill formation. The complex comprises one or more sills with a cumulative length of at least 9 km and thickness of 400m. New mapping suggests the mineralised intrusion post-dates voluminous plutonism of the well-studied Mafic Complex and ascended at least 2 km through mafic lower crust. A comparison of the parental melt density with bulk densities for the host rocks under lower crustal conditions shows that buoyancy force is the first order control on the structural level of magma arrest and subsequent sill emplacement.

2 Geologic setting

The Ivrea Zone is among the most extensively exposed sections of underplated continental crust and exemplifies the abrupt structural transition from mafic rocks to overlying metasedimentary rocks at paleodepths of 20±5 km (Demarchi et al. 1998). Magmatic underplating has resulted in the emplacement of a large (>200 km³) mafic pluton into lower crustal metasediments, commonly referred to as the Mafic Complex and Kinzigite Formation, respectively. The Kinzigite Formation comprises metapelites, marble, and calc-silicate paragneiss. Within the tilted crustal section, metamorphic grade increases with paleodepth from southeast to northwest from amphibolite to granulite facies (Fig. 1). Westernmost (i.e., deepest) exposures of granulite facies metapelites are strongly restitic, retaining only small amounts of migmatite. The Mafic Complex is considered to be the result of prolonged mantle magmatism from 288 Ma to 259 Ma (Peressini et al. 2007).

Figure 1. Generalised geologic map of the west-central Ivrea Zone, showing the intrusive contact between the Mafic Complex and overlying Kinzigite Formation, as delineated by Quick et al. (2003). The La Balma igneous complex lies along the margin of the northernmost exposed portion of the Mafic Complex, as mapped by us. Southern extent of the La Balma igneous complex is modified from Ferrario et al. (1984) and Brodie et al. (1992). Map is oriented such that the approximate regional paleo-up direction is toward the top. Metamorphic isograds (dashed lines) denote increasing metamorphic grade.

It is a composite pluton dominated by gabbros and norites. Ultramafic cumulates occur as small, isolated horizons, comprising <1% of the Mafic Complex. The maximum...
exposed thickness of the Mafic Complex is ~10 km. The roots of the Mafic Complex and underlying mantle peridotite are concealed in the footwall of knappes of the Alpine Orogeny. The boundary between Ivrea Zone and supracrustal Alpine rocks is referred to as the Insubric Line (Schmid et al. 1989). However, in the region between Val Strona and Val Mastallone, the Insubric line is a diffuse zone 10-200 m thick characterised by slivers of mafic rocks tectonically interleaved with mylonitised schists of overlying Alpine knappes. The northern extent of the La Balma igneous complex is overridden and by mylonite of the Insubric Line. Thus our estimate of 9 km for the length of the La Balma igneous complex is a minimum.

Key events in the evolution of the Ivrea Zone through time include: peak metamorphism, timing of mantle-derived magmatism, exhumation, and tilting. P-T conditions of these events are reasonably constrained by a range of geo-barometers and chronometers. Regional metamorphic isograds (Fig. 1) were established during peak granulite-amphibolite facies metamorphism at 299±5 Ma (Vavra et al. 1999). Notably, emplacement of the Mafic Complex post-dates peak metamorphism, with inception of mafic plutonism at 288±4 Ma (Peressini et al. 2007). Garnet and orthopyroxene mineral chemistry show equilibration temperature and pressure within the Mafic Complex increases with paleodepth (Demarchi et al. 1998). Garnet gabbro in the structurally deepest zone yields equilibration estimates of 730-810°C at 0.7-0.9 GPa, corresponding to a depth of 20-25 km. Granulite-facies kinzigites cooled slowly to background temperatures of 600°C at 180 Ma (Ewing et al. 2015), suggesting the westernmost Ivrea Zone remained at mid-to-lower-crustal depths at least until the early Jurassic. Assuming tilting accompanies exhumation, a range of thermochronometers track extension from 25-30 km depth to surface between the Jurassic and Miocene in the val Strona section of the Ivrea Zone (Wolff et al. 2012).

### 3 La Balma ultramafic intrusive complex

#### 3.1 Internal architecture

The La Balma igneous complex is a sill or collection of sills with a combined lateral outcrop extent of ca. 9-10 km and thickness of the order of 100s of m. The northern half of the La Balma igneous complex is tilted 70-80° SE, roughly concordant with overlying igneous and metasedimentary rocks of the val Strona section. From northwest to southeast, the sill comprises a gradational succession from olivine adcumulate to pyroxenitic orthocumulate (Figure 2). The uppermost portion of the sill is olivine websterite that intrudes overlying amphibole gabbro. The intrusive is contact is complex: blocks of amphibole gabbro roof rocks meters to tens of meters in length are incorporated into pyroxenitic orthocumulates. Partial melting of the gabbroic xenoliths is evident from invasion of ultramafic melt along foliation planes in xenoliths and delicately crenulated intrusive contacts. Late veins of feldspar pegmatoid originate from the partially melted xenoliths and propagate 10s of cm into adjacent pyroxenitic cumulates. The basal contact of the sill is tectonically modified everywhere it has been observed. Brittle shear is focused along the inferred floor of the sill where basal dunite lies adjacent to (Fe)garnet-bearing gabbro in the footwall. Shear fabrics and cataclasite lenses penetrate basal dunite up to 1 m from the contact. The footwall gabbro is injected by cm-scale ultramafic pseudotachylite veins, presumably derived from slip along the contact with adjacent dunite. Deformation along the base of the sill and in the adjacent footwall rocks are the result of brittle-elastic mechanisms at conditions after solidification of the sill complex.

![Figure 2](image_url) **Figure 2.** The present structural setting of the La Balma igneous complex preserves a window into primary intrusive relationships related to sill emplacement and differentiation. Amphibole gabbro of the Mafic Complex is partially incorporated into olivine websterite of the La Balma body. Geologic map is oriented such that the approximate inferred paleo-up direction is toward the top.
3.2 Fe-Ni-Cu sulfide mineralisation

Nickel sulfides occur as disseminated, intercumulus phases. Concentrations of 1-3% occur mainly in lherzolite and harzburgite toward the core of the sill. Pyrrhotite and pentlandite are the dominant sulfide phases with lesser chalcopyrite, mackinawite, and cubanite. Minor disseminations away from the middle of the sill include small (<10 m) pods with 1-3% disseminated sulfides in the basal dunite. WW-II-era adits toward the core of the sill exploit disseminated sulfides and concentrations up to 10% and sparse zones of massive sulfide. These historic ore-crystallisation.

emplacement and during late stages of magma suggests sulfur saturation was reached after sill composition. Ubiquitous interstitial texture of sulfides consistent with the gradational succussion in overall sill mineralogical horizons, reefs, or abrupt textural changes is concentration are diffuse. The absence of sharply defined mineralogical horizons, reefs, or abrupt textural changes is consistent with the gradational succussion in overall sill composition. Ubiquitous interstitial texture of sulfides suggests sulfur saturation was reached after sill emplacement and during late stages of magma crystallisation.

4 Magma-rock density contrasts

4.1 Rationale

To evaluate the role of pre-existing crustal layering in the emplacement of the La Balma igneous complex, we model a 1D density profile of the Ivrea Zone lower crust around the La Balma igneous complex. The model incorporates mean bulk densities for the Mafic Complex and overlying granulite-facies pelitic gneiss of the Kinzigite Formation. We compare these results with the calculated density for an estimated primary melt of the La Balma igneous complex. Pressure-Temperature (P-T) conditions for the entire system are assigned according to published thermobarometry for the westernmost Ivrea Zone prior to onset of exhumation.

4.2 Host rock densities

For given P-T conditions, in situ density of crustal rocks is a function of bulk composition and modal mineralogy. We use Gibbs free minimization and thermodynamic modelling to determine rock densities based on the above parameters using Perple_X (Connolly, 2009) with internally consistent thermodynamic data for solids (Holland and Powell, 1998; rev 2002). Representative average densities for the two host rock units at 740°C and 0.82 GPa are reported in Table 1. Mean density is estimated for an average bulk composition compiled from new and previously published bulk rock geochemical data from val Strona, val Mastallone, and val Sesia (n=76). The modelled mineral assemblage is characteristic of restitic granulite-facies metapelites (Schnetger, 1994). Phases present in trace amounts are excluded to retrieve rock densities irrespective of small (<10%) variation in P, T, and composition for granulite-facies metasedimentary rocks. The average density of the gabbroic host rocks is calculated from a mean composition compiled from new and published bulk compositions of gabbro of the Mafic Complex from val Strona and val Sesia (n=21).

Table 1

<table>
<thead>
<tr>
<th>Representative host rocks</th>
<th>Representative primary melts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granulite-facies metapelite</td>
<td>Gabбро, garnet-bearing</td>
</tr>
<tr>
<td>0.8 GPa, 750°C</td>
<td>Primary melt (24% MgO)</td>
</tr>
<tr>
<td></td>
<td>melt</td>
</tr>
<tr>
<td>Ksp + Qt + Gt + An</td>
<td>w% SiO2</td>
</tr>
<tr>
<td>1.0</td>
<td>46</td>
</tr>
<tr>
<td>1.0</td>
<td>46</td>
</tr>
<tr>
<td>Gt(Fe)+Cpx</td>
<td>w% H2O</td>
</tr>
<tr>
<td>4.28</td>
<td>3.28</td>
</tr>
<tr>
<td>2.836</td>
<td>0.065</td>
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</tbody>
</table>

Representative rock and silicate melt densities for the west-central Ivrea Zone. Thermodynamically-derived densities for lower crustal Ivrea Zone rocks are greater than global averages for equivalent rock types reported by Rudnick and Gao (2003). 5 Discussion and implications

5.1 Buoyancy force

A wide range of aethenospheric melt compositions are capable of ascending through the lower crust, but only the most mafic, anhydrous endmember (45 wt% SiO2, 0.1% H2O) is predicted to reach a level of neutral buoyancy at
the base of the Kinzigit Formation. Higher silica contents of primary mafic melts reduce density and increase buoyancy contrasts between melt and host rock. The mean density of the granulite-facies Kinzigit Formation is just 1% more than the global average of Rudnick and Gao (2003). Garnet-bearing gabbroic rocks exceed the global average by 6%. Preliminary results reveal the sensitivity of density to small changes in composition at fixed P-T conditions. Such variation is expected in natural systems is exceptionally well characterised in the Ivrea Zone. Future thermodynamic modelling should consider this chemical heterogeneity and uncertainties in empirically determined P-T conditions posed in the literature.

5.2 Magma transfer through evolved lithosphere

The composition of post-Archaean lower continental crust is commonly bimodal, consisting of peraluminous granulites and mafic rocks. These compositional differences result in density and rheological contrasts. In the Ivrea Zone, the physical contrast is abrupt between metasedimentary granulite and gabbroic rocks. The La Balma igneous complex is a sill or suite of sills resulting from the arrest and differentiation of asthenospheric melt within the lower crust. This process can be understood in terms of density differential by taking into account the bimodal composition and structure of the Ivrea Zone lower crust. Abrupt density contrasts in the lower crust are reasonable in the context of magmatic underplating. Moreover, magmatic underplating is widely documented in a range of tectonic settings also conducive to formation of orthomagmatic ore deposits. We suggest pathways for mantle melts to sites of sulfide accumulation are not only controlled by deep continental crust, such as density. Such insights are useful in moving from 2D to 3D characterisation of lithospheric- and camp-scale magma pathways.

Acknowledgements

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References

Processes controlling the distribution of Te, As, Bi, Sb, and Sn, and the formation of platinum-group minerals in sulphide ores in the Noril’sk mining district (Russia)

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Abstract. The distribution of TABS (Te, As, Bi, Sb, and Sn) in magmatic sulphide ore deposits have been neglected despite their critical role in forming platinum-group minerals (PGM). Investigating the primary processes controlling the TABS distribution is a challenge as TABS are generally volatile, present at low levels, and mobile with alteration. Magmatic sulphide ore bodies in the Noril’sk mining district (Siberia, Russia) offer an exceptional opportunity to investigate the behaviour of TABS during fractional crystallisation of sulphide liquids and PGM formation as the primary features of the ore bodies have been relatively well preserved. We show that the distribution of Pt, Pd, and TABS is controlled by their partitioning behaviour during sulphide liquid fractional crystallisation, prior to PGM formation. In Cu-poor massive sulphides the PGM formed as the result of exsolution from sulphide minerals, whereas in Cu-rich massive sulphides the PGM formed by crystallisation from late-stage fractionated liquids.

1 Introduction

The distribution of platinum-group elements (PGE) within zoned magmatic ore bodies has been extensively studied and appears to be controlled by the partitioning behaviour of the PGE during fractional crystallisation of magmatic sulphide liquids (monosulphide solid solution (MSS) – intermediate solid solution (ISS) crystallisation sequence). However, other chalcophile elements, especially TABS (Te, As, Bi, Sb, and Sn) have been neglected despite their critical role in forming platinum-group minerals (PGM). TABS are considered to be mobile elements so investigating their primary distribution may be challenging in magmatic ore bodies that have been somewhat altered. Furthermore, determining their concentrations is a challenge as they are generally volatile and present at low levels.

Magmatic sulphide ore bodies in the Noril’sk mining district (Siberia, Russia) offer an exceptional opportunity to investigate the behaviour of TABS during fractional crystallisation of sulphide liquids and PGM formation as the primary features of the ore bodies have been relatively well preserved. In contrast to a number of previous studies on specific aspects of the geology, petrography, platinum-group mineralogy, whole-rock and isotopic compositions of the ores in the Noril’sk mining district, our study focusses on integrating the textural, mineralogical, and geochemical variations. We combine optical and secondary electron microscopy, electron probe micro-analysis (EPMA) of PGM and precious metal minerals (PMM), high-resolution X-ray computed tomography (HRXRCT), and whole-rock geochemical analyses to address the main differences between the various ore types. We show that textural, mineralogical, and geochemical variations are consistent with variable interaction of sulphide liquid droplets with silicate magma followed by sulphide liquid ponding, MSS-ISS fractional crystallisation, and in some cases injection of Cu-rich liquid into surrounding rocks. Using the median disseminated sulphide composition as initial sulphide liquid composition and recent partition coefficients (D_{MSS}^{liq} and D_{ISS}^{liq}), numerical modelling predicts the compositional variations observed in the massive sulphides, especially in terms of Pt, Pd, and TABS. We also discuss the origin of PGM and PMM (i.e., exsolution versus crystallisation).

2 Petrography and geochemistry of the sulphide ores

Based on textures, sulphide-mineral proportions, and whole-rock compositions, the sulphide ores were divided into four main groups. The main characteristics of these groups are described below.

**Disseminated sulphides:** This ore type essentially consists of millimetric to centimetric spherical to ellipsoidal droplets in olivine-gabbronorites. The typical droplets are characterized by a pyrrhotite-rich base and a chalcopyrite-rich top with pentlandite in-between (Fig. 1). Recalculated to 100% sulphides, disseminated sulphides have primitive mantle normalized multielement patterns enriched in most elements (Fig. 1). The petrography and geochemistry suggest that disseminated sulphides have initial sulphide liquid compositions and higher concentrations in most elements can be explained by strong interaction of sulphide liquid droplets with silicate magma.

**Cu-poor massive sulphides:** This ore type essentially consists of accumulation of sulphides at the base of the intrusions and is characterized by high abundances of pyrrhotite (>70%), variable abundances of pentlandite, and low abundances of chalcopyrite (<10%). Pyrrhotite occurs as centimetric anhedral patches. Pentlandite occurs in...
three forms: as large subhedral grains (a few hundred μm to a few mm in apparent diameter), as chain-like polycrystalline aggregates around Po grains, and as exsolution flames within Po grains (Fig. 1). Chalcopyrite occurs either as small anhedral grains randomly dispersed between pyrrhotite and pentlandite grains or as centimetric patches. The Cu-poor massive sulphides have primitive mantle multielement patterns (Fig. 1) depleted in elements incompatible with MSS (Sn, In, Ti, As, Sb, Pb, Bi, Cd, Ag, Cu, Au, Te, Pd, Pt) and enriched in elements compatible with MSS (Mo, Re, Rh, Ru, Ir, Os, Co). The petrography and geochemistry suggest that Cu-poor massive sulphides consist of cumulus MSS ± Cu-rich fractionated liquid.

**Cu-rich massive sulphides:** This ore type essentially consists of accumulation of sulphides at the base of the intrusions or of sulphide impregnations in surrounding rocks (veins and breccias). Most Cu-rich massive sulphides are characterized by high abundances of chalcopyrite (>50%; Fig. 5a-i) and variable abundances of pentlandite and pyrrhotite, with pyrrhotite being minor (<10%) or absent. Chalcopyrite occurs as centimetric anhedral patches and in some samples, it hosts cubanite exsolutions. Cubanite exsolutions either occur as large bands (Fig. 1) or as tiny patches. Pentlandite mainly occurs as large grains (hundreds of μm to several mm in apparent diameter) associated with chalcopyrite and/or with pyrrhotite where present. Despite the texture variability observed in the Cu-rich samples, the geochemical compositions are the same. Similar geochemical compositions are suggestive of a common origin for all the Cu-rich samples. Differences in textures may simply reflect variations in kinetic processes. In contrast to Cu-poor massive sulphides, the Cu-rich massive sulphides have primitive mantle multielement patterns (Fig. 1) enriched in elements incompatible with MSS (Sn, In, Ti, As, Sb, Pb, Bi, Cd, Ag, Cu, Au, Te, Pd, Pt) and depleted in elements compatible with MSS (Mo, Re, Rh, Ru, Ir, Os, Co). The petrography and geochemistry suggest that Cu-rich massive sulphides represent cumulus ISS ± late-stage fractionated liquid.

**Transitional massive sulphides:** The transitional massive sulphides have the appearance of a mixture between Cu-poor and Cu-rich sulphides. Pyrrhotite proportions vary between 40 and 60%, chalcopyrite proportions vary between 10 and 50%, and pentlandite proportions vary between 10 and 30%. Pentlandite occurs as exsolution flames in pyrrhotite (Fig. 1) and/or as polycrystalline aggregates at the pyrrhotite/chalcopyrite interface (Fig. 1). The transitional massive sulphides have intermediate primitive mantle multielement patterns (Fig. 1) in that they share geochemical characteristics with both Cu-poor and Cu-rich ores. The petrography and geochemistry suggest that transitional massive sulphides represent accumulation of sulphides in which MSS, ISS, and late-stage fractionated liquid have not been dissociated.

3 Platinum-group and precious-metal mineralogy

In our investigated samples PGM and PMM consist of Pt-, Pd-, and Au-bearing minerals. No IPGE-, Rh-, or Re-bearing minerals were observed. The PGM and/or PMM were identified in all ore types, however the vast majority were found in the Cu-rich samples. In the disseminated sulphides and Cu-poor and transitional massive sulphides, the PGM and PMM essentially consist of Pt-PGM (Fig. 2) and minor electrum. No Pd-PGM was observed in these ore types. In the Cu-rich massive sulphides, Pt only-PGM were rarely observed. Most PGM in this ore type consist of Pt-Pd-PGM and Pd-PGM. Composite grains consisting of stannides and/or bismuthotellurides and/or arsenides and/or alloys were also commonly observed. Most grains were observed at sulphide grain boundaries (sulphide-sulphide, sulphide-silicate, sulphide-carbonate interfaces) or included within sulphide grains. The texture of the PGM and PMM varies from euhedral grains with well-defined crystal faces to anhedral grains with ragged boundaries.

High-resolution X-ray computed tomography (Fig. 2)
performed on samples from each ore types shows that PGM and PMM from the disseminated sulphides have the highest median sphericity (0.677) followed by those from the Cu-rich massive sulphides (0.669), transitional massive sulphides (0.584), and Cu-poor massive sulphides (0.569). This indicates that in general the PGM and PMM in disseminated sulphides and Cu-rich massive sulphides have more rounded shapes, whereas those in transitional and Cu-poor massive sulphides have more elongated shapes. The PGM and PMM from the Cu-rich massive sulphides have the highest median specific surface area (9.851 mm$^{-1}$) followed by those from the transitional massive sulphides (4.780 mm$^{-1}$), disseminated sulphides (2.874 mm$^{-1}$), and Cu-poor massive sulphides (1.893 mm$^{-1}$). This indicates that in general the PGM and PMM in Cu-rich and transitional massive sulphides have rougher surfaces whereas those in disseminated sulphides and Cu-poor massive sulphides have smoother surfaces.

Considering that Cu-poor ore crystallized early, when the sulphide liquid was likely unsaturated in Pt, Pd, Au, and TABS, PGM and PMM in this ore type could not have crystallized from sulphide liquids. Elongated morphologies and smooth crystal faces rather suggest that PGM and PMM in the Cu-poor ore formed by exsolution from the sulphide minerals. Ballhaus and Ulmer (1995) showed that at high temperature, Pt and Pd could substitute for Fe in MSS when vacancies surround the Fe sites, and that solubilities of Pt and Pd drastically decrease with decreasing temperature and f$S_2$, leading to exsolution of Pt and Pd initially present in solid solution in MSS as it recrystallized to form Po and Pn (< 650°C). The lack of Pd-PMM in the Cu-poor ore also suggests that Pd did not exsolve from MSS along with Pt and was rather incorporated into Pn as demonstrated by Barnes et al. (2006). In contrast to the Cu-poor ore, the Cu-rich ore crystallized later and late-stage fractionated sulphide liquids enriched in Pt, Pd, Au, and TABS formed after ISS crystallisation (< 880°C). Such liquids have low melting points and droplets of these residual liquids were likely trapped among ISS grains in the late stages of crystallisation prior to crystallize as composite PGM and PMM. This interpretation is supported by the spherical morphology of composite grains. As transitional massive sulphides represent mixtures of Cu-poor and Cu-rich ores, the intermediate median sphericity and specific surface area suggest that in this ore type PGM and PMM consist of a combination of exsolutions and trapped droplets of late-stage fractionated sulphide liquid.

### 4 Modelling the composition of massive sulphides

Upon sulphide segregation from, and interaction with silicate liquid, sulphide liquid droplets tend to accumulate downwards due to higher density relative to silicate liquid. Once pools of sulphide liquid have accumulated, the composition of massive sulphides is believed to be controlled by the partitioning behaviour of the elements during the course of fractional crystallisation of sulphide liquids (i.e., D$^{\text{MSS/Liq}}$ and D$^{\text{ISS/Liq}}$; see discussion in Liu and Brenan (2015) for further insights). To test whether the partitioning behaviour of the elements is the essential parameter in controlling the composition of massive sulphides, compatible elements in MSS (e.g., Ir and Rh) and incompatible elements in MSS (e.g., Pt, Pd, and Cu) have been plotted against each other. Commonly, massive sulphides lie along the evolution lines of predicted MSS and complementary fractionated liquid calculated from assumed initial liquid composition on the basis of Rayleigh fractionation.

To further assess the role of fractional crystallisation, we present the massive sulphide data and the result of the modelling on Pd, Pt, and TABS versus Cu plots (Fig. 3), in which Cu is used as an index of sulphide evolution. For clarity and due to limited massive sulphide samples from Noril’sk’s I, we only present the data from Kharaelakh and Talnakh. Assuming that disseminated sulphides represent initial sulphide liquids from which massive sulphide accumulated, the composition of the modelled MSS and complementary fractionated liquids derived from these initial liquids can be calculated using the Rayleigh fractionation equations:

$$C_L = C_0 * F^{(D-1)}$$  \quad (1)

$$C_S = C_L * C_0 * F^{(D-1)}$$  \quad (2)
in which \( C_L \) is the concentration of an element in the fractionated sulphide liquid; \( C_S \) is the concentration of an element in the solid crystallizing from the sulphide liquid; \( C_0 \) is the concentration of an element in the initial sulphide liquid; \( F \) is the fraction of liquid; and \( D \) is the partition coefficient between the solid and liquid. In addition, the modelled ISS and fractionated liquid after ISS crystallisation are plotted. The same Rayleigh fractionation equations were used and in this case \( C_0 \) was assumed to be the composition of the fractionated liquid after reaching >20 wt.% Cu (i.e., after ca. 60% fractionation), which is consistent with the experimental work of Ebel and Naldrett (1996) and Liu and Brenan (2015). The modelling was performed using the experimental range of partition coefficients for Pd, Pt, and TABS, and the best fits for the evolution lines were obtained with the lowest partition coefficients (Barnes and Ripley 2016).

Most Cu-poor and transitional massive samples plot between the evolution lines of modelled MSS and sulphide liquid crystallizing MSS, whereas most Cu-rich massive sulphides plot along the evolution lines of modelled ISS and fractionated liquid crystallizing ISS. Overall, the Pd, Pt, TABS, and Cu compositions of the massive sulphides from Kharaelakh and Talnakh are in agreement with the MSS-ISS crystallisation sequence and sulphide liquid enrichment in incompatible elements. The fact that TABS are concentrated in evolved sulphide liquids along with Pt and Pd is of high importance for magmatic sulphide deposits, as these elements play a role in the formation of PGM and PMM. The partitioning behaviour of these elements during sulphide liquid differentiation was likely the main parameter driving the changes in composition observed in massive sulphides, leading to concentration of these elements in the residual liquids until PGM and PMM crystallisation in the Cu-rich ore.

5 Concluding remarks

The petrographic and geochemical variations in sulphide ores from the Noril’sk mining district are consistent with fractional crystallisation of sulphide liquids. Platinum-group minerals mainly exsolved from sulphide minerals in the Cu-poor ore whereas in the Cu-rich ore PGM mainly crystallised from late-stage fractionated liquids. Numerical modelling predicts the compositional variations observed in the massive sulphides, especially in terms of Pt, Pd, and TABS, in agreement with our observations and interpretations.

Acknowledgements

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Figure 3. Binary diagram of Cu versus Pt and Te for massive sulphides from Kharaelakh and Talnakh (recalculated to 100% sulphides). The purple lines represent model compositions of the evolving MSS and liquids. The numbers represent the degree of fractionation in percent. After 60% fractionation, ISS would crystallise (i.e., when the liquid reaches reached ca. 20 wt.% Cu). The pink lines represent the compositions of the evolving ISS and liquids. Note that Pd, As, Bi, Sb, and Sn show the same distribution.

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Fe-Ni-Cu sulfide – evaporite association at Munali, Zambia

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Abstract. The Munali nickel-copper deposit occurs as Fe-Ni-Cu sulfide mineralization hosted in a megabreccia at the margins of a lens-like gabbroic intrusion. It was intruded within Neoproterozoic passive margin metasediments of the Zambezi belt of southern Zambia. Geologic and petrographic evidence suggests that the sediments contained evaporite layers, associated with red-beds, limestone and siliceous cherts. The intrusive breccia matrix associated with the Fe-Ni-Cu sulfides includes minerals that are enriched in Na and Cl, such as scapolite, chloroapatite, chloropargasite and biotite. These can be divided on petrographic grounds into high-temperature and low-temperature parageneses. Scapolite of the high-temperature paragenesis is intergrown as euhedral needles within chloroapatite and olivine, whereas low-temperature scapolite pseudomorphically replaces igneous plagioclase. It is proposed that a gabbroic sill was emplaced within and reacted with evaporite beds at the time of mineralization. A lower temperature metasomatic overprint resulted from metamorphism during the Zambezi orogeny. Sulfur saturation of the magma probably occurred before this emplacement and was not induced by evaporite digestion, but the contact reaction processes probably helped to physically trap and collect sulfide liquid at the margins of the intrusion.

1 Introduction

It has been recognized that subvolcanic sill-like intrusions of large igneous provinces (LIPs) often preferentially intrude within or at the contacts with physically distinct sedimentary units of passive margin sequences, such as coal seams, limestones or evaporite beds, all of which may contribute volatiles and result in complex and dynamic intrusion morphologies (Schofield et al. 2014; Warren, 2016).

The Munali nickel-copper deposit in southern Zambia shows many characteristics of the highly dynamic emplacement of sulfide liquid and of interaction between magma and sedimentary host rocks (Holwell et al. 2017). Mineralization takes the form of a sulfide-matrix megabreccia situated at the margins of an unmineralized sill-like gabbroic lens that is emplaced within a marble-graphitic schist-chert package. These metasediments show evidence, such as widespread scapolite porphyroblasts, for the former presence of evaporitic beds that have now largely disappeared due to basal halokinesis or later orogenic deformation and metamorphism. Field and petrographic evidence presented here suggests that the Munali intrusive complex was emplaced into a package containing such evaporitic rocks and that this resulted in physical and chemical activity that may have enhanced the Fe-Ni-Cu sulfide mineralization.

2 Geological setting

The infracrustal basement of Zambia can be divided along a WSW-ENE-trending reactivated tectonic zone, the Mwembeshi Lineament (Fig. 1), into the Paleoproterozoic to Archean aged Likasi terrane to the north, and a Southern Irumide terrane to the south (De Waele et al. 2008). Deformation and granite intrusion partially overprinted both areas in the Mesoproterozoic (Irumide orogeny) and the Neoproterozoic (Lufilian Arc and Zambezi Belt orogenies; De Waele et al. 2008). Neoproterozoic-aged supracrustal sequences cover this basement both north and south of the Mwembeshi Lineament (Fig. 1) and contain similar continental rift to passive margin lithologies, but detailed correlation between these sequences is not possible. We are here concerned with the Zambezi Supracrustal sequence (ZSS), occurring to the south of the Mwembeshi Lineament, and whose stratigraphy and chronology has been updated by Johnson et al. (2007).

The ZSS comprises two or three fault and/or unconformity-bounded volcano-sedimentary packages. These are best developed in the Lusaka-Kafue area (Fig. 1), where a package of metarhyolites and schists, dated at 880 Ma, is overlain unconformably by a sequence of shallow-marine silicilastic and carbonate metasediments (Johnson et al. 2007). In the Munali area south of Kafue, the early volcanosedimentary package has not been recognized, but a similar shallow-marine sedimentary sequence exists: the basal Nega Formation of metasandstones, thin marbles and schists being overlain by the carbonates of the Muzuma Formation (Johnson et al. 2007).
In detail, the Nega Formation comprises basal metaconglomerates overlain by interlayered hematitic quartzites, kyanite-biotite-schists and scapolite-biotite schists. Over this siliciclastic unit is an extensive unit of marble, calc-silicate, graphitic schist and cherts of variable thickness and interbanding, often showing rapid lateral variations. This marble-dominated unit is overlain by hematitic quartzite or metasiltstone with abundant carbonate schlieren and then by a thick unit of dark biotite schist. Locally in the marble unit and the dark biotite schist there are cherty bands, sometimes containing irregular, nodular to rounded or cubic-shaped aggregates of dolomite and quartz, possibly pseudomorphs after anhydrite or halite (Fig. 2).

The Munali Igneous Complex (MIC) is an elongate lozenge-shaped composite body composed of a Central Gabbro Unit (CGU) making up the bulk of the intrusion, and a Marginal Ultramafic Breccia Unit (MUBU) along the margins (Evans 2011; Holwell et al. 2017). Sulfide mineralization is contained within the MUBU, as a breccia matrix and as later veins. Some sparse narrow veins of sulfide penetrate the CGU, but otherwise this unit is unmineralized. The MUBU occurs on both SW and NE sides of the CGU, but is thickest on the SW side, which is the upper (hangingwall) side of the CGU. It is composed of breccia clasts of poikilitic gabbro and a coarse-grained annealed olivine-magnetite-apatite (phoscorite or OMA) rock, within a sulphide-magnetite-rich matrix (Holwell et al. 2017). Irregular fine-grained dolerite dykes are present in the MUBU and appear to be coeval with or just postdate the sulfide breccia.

Whereas the poikilitic gabbro clasts and dolerite dykes rarely contain unequivocal magmatic-textured sulphides, the OMA rock clasts often contain interstitial-textured sulphides that wrap around euhedral olivine grains. The assemblage pyrrhotite-pentlandite-chalcopyrite dominates the sulfide mineralization and is usually associated with abundant magnetite. This magnetite contains Ti and often shows oxy-exsolution of ilmenite lamellae. Other gangue minerals sometimes associated with the sulphidic breccia matrix are apatite, scapolite and carbonate. Olivine of the OMA rock is usually partly to wholly altered to serpentine or talc-carbonate assemblages.

3 Methods

41 samples representative of the MIC and surrounding rock types have been examined petrographically. These include 16 samples of mineralized ultramafic or vein rock, 7 samples of Munali gabbro, 5 samples of Munali dolerite, and 12 samples from the surrounding region. These have been classified according to their degree of alteration, based on textural modification and growth of overprinting hydrous or metasomatic minerals.

Olivine, magnetite, apatite, scapolite, amphibole and biotite were analysed by electron probe microanalysis (EPMA) to understand their relationship and variation within 18 of the Munali and other rocks. The EPMA was carried out by wavelength dispersive X-ray emission spectrometry on Cameca SX50 and Cameca SX100 instruments at the Natural History Museum, London, using standard analysis procedures.

4 Petrography and mineral chemistry

Schists and marbles in the Nega formation have a moderate to strong planar foliation subparallel to their original bedding planes. Biotite schists below the MIC contain porphyroblasts of kyanite, albite and scapolite, whereas biotite schists above the MIC contain garnet and andalusite porphyroblasts. Amphibolite bodies within the basement gneissic granites contain a dark blue-green amphibole and abundant scapolite poikiloblasts replacing original plagioclase grains. Textures are granular to gneissic, but relic gabbroic textures can also be discerned.

The Munali dolerite rocks are mostly altered to a fine-grained mat of blue-green amphibole with poikiloblastic scapolite replacing groups of adjacent plagioclase laths of the primary igneous assemblage. The subophitic texture is usually preserved without much deformation, but growth of the scapolite and amphibole results in fine-scale intergrowth of grain margins. Gabbro and microgabbro from the CGU is always at least partly altered to either a scapolite-amphibole-bearing or an epidote-carbonate-amphibole alteration assemblage, often with poor textural preservation due to recrystallization. Coarse-grained
Poikilitic leucogabbros of the MUBU are often altered to a scapolite-amphibole-biotite assemblage (Fig. 3), with moderate to good textural preservation. Locally this rock type is only weakly altered with excellent textural preservation and minimal alteration of euhedral plagioclase chadacrysts to scapolite along grain boundaries and fractures.

Figure 3. Photomicrograph of proximal scapolite (Sc) alteration of poikilitic gabbro (now hornblende-plagioclase Hbl-Pl) in the MUBU: field of view 4mm; MAD046.

Figure 4. Euhedral scapolite (Sc) needles associated with brown hornblende (Hbl) within serpentinized olivine (Ol, Se): MAD020.

Mineralized ultramafic and related rocks in the MUBU are also variably altered from partial serpentinization of olivine and uncommon orthopyroxene to total alteration by talc-carbonate assemblages, often associated with through-going carbonate veins and ductile deformation. The talc-carbonate alteration and deformation is inferred to be related to later greenschist to greenschist-amphibolite boundary metamorphism during the Zambezi orogeny, whereas serpentinization is retrogressive and not associated with deformation. Serpentinitized olivine usually retains its original igneous shape, especially in contact with sulphides, with which it presents sharp contacts with euhedral shapes. Importantly, weakly-serpentinized olivine also retains clean, euhedral boundaries with coarse apatite and Ti-magnetite, which wrap around the euhedral olivine grains in the same fashion as the sulfides.

Petrographic examination has shown that, in contrast to the scapolite present in the dolerite and gabbro rocks of the MIC, which is anhedral to poikiloblastic (Fig. 3), the scapolite present in the ultramafic and mineralized rocks of the MUBU is euhedral, having an elongate prismatic habit, often enclosed partly or wholly within olivine, apatite or sulphide (Fig. 4 & 5). This scapolite sometimes has fringes of a dark brown hornblende. The euhedral shape and intergrowth with apparently igneous minerals suggests that this scapolite belongs to a high-temperature paragenesis, as opposed to the poikiloblastic scapolite in gabbro and dolerite, which is part of the greenschist-lower amphibolite metamorphic assemblage. This latter can be divided into a proximal alteration facies relative to mineralization within the MUBU, and a distal facies mainly within the CGU.

Figure 5. Euhedral scapolite (Sc) within semi-massive sulphides (Po): MAD047.

The EPMA analyses indicate that both scapolite and brown hornblende of the high-temperature paragenesis are Na and Cl-rich. The composition of euhedral scapolite within apatite, olivine and sulfide clusters at around the meionite-(Me)30 mark, with enough Cl to almost completely fill the anion site (Fig. 6a). Associated brown hornblende has the composition of a chloropargasite. The lower-temperature paragenesis is also Na and Cl-rich, but shows a much wider range of compositions. Proximal low-temperature scapolite (poikiloblastic replacement of plagioclase chadacrysts of poikilitic gabbro in the MUBU) has compositions varying from Me18 to Me35 (Fig. 6a). Associated amphibole varies from a tschermakitic chloropargasite to a less Cl-rich common hornblende (Fig. 6b). In the distal suite, scapolite ranges from Me25 to Me45 and has lower Cl content than the high-temperature paragenesis and the proximal low-temperature paragenesis. The amphiboles of the distal suite vary from low-Cl pargasite through common hornblende to close to actinolite (Fig. 6b). Scapolite found in the regional amphibolites and in the metasedimentary biotite...
schist have even higher meionite contents – Me35 to Me65 and their Cl contents are correspondingly lower.

![Diagram](image)

**Figure 6.** Composition of a) scapolite and b) amphiboles in the MIC and adjacent regional rocks.

### 5 Discussion

The presence of scapolite and pargasite as regional metamorphic minerals both within sedimentary and enclosed intrusive rocks has long been noted in the Zambian and Congolese copperbelt area and presented as evidence for the former presence of evaporites (Jackson et al. 2003). More recently, widespread scapolite has been recognised within the Zambezi supracrustal sequence and its immediate basement (Katongo et al. 2011). The sedimentary lithologies and textures observed around the Munali intrusion are permissive of the former presence of evaporites in the sequence.

Scapolite and amphibole in the metasedimentary sequence and in amphibolite bodies in the basement to this sequence have moderately sodic compositions, consistent with a regional Na-Ca-Cl metasomatic event. This is likely to have originated as Na-Ca-Cl-rich brines derived from deformation and metamorphism of residual evaporite layers in the metasediments during regional metamorphism (Katongo et al. 2011).

The high-temperature and proximal low-temperature alteration parageneses of scapolite-amphibole in the mineralized MUBU of the MIC have more sodic and chlorine-rich compositions than those found in the regional rocks. This implies either that a hotter and more strongly saline brine passed through the MUBU as part of the regional metasomatic event, or that an earlier high-temperature alteration event has locally been preserved in the mineralized environment. I propose that the latter is more likely, and that given the paragenetic association of these metasomatic minerals with olivine and igneous apatite, they record locally well-preserved evidence of magmatic or late-magmatic interaction of a Mg-rich, Ni-Cu-PGE sulfide mineralized magma with salt in evaporite beds within the host marble-chert sequence. Note that the composition, textures and distribution of sulfide mineralization indicates that S saturation occurred before this unusual sediment interaction. The reaction of magma with evaporite beds may have caused brittle fracturing of pre-existing rocks by generation of volatiles, enhancing the scale and volume of the megabreccia emplacement at Munali.

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PGE-fertile magmatism in the Carajás Mineral Province, Brazil: evidence from the Serra Leste Magmatic Suite

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Abstract. The scale of the 2.75 Ga mafic-ultramafic magmatism in the Carajás Province is comparable with those attributed to Large Igneous Provinces. This large magmatic event includes the Serra Leste Magmatic Suite, a cluster of small- to medium-size PGE-mineralized intrusions. Except for widespread PGE mineralization and anomalously high Ni content of olivine (up to 7,500 ppm) in cumulates of the Luanga Complex, mafic-ultramafic intrusions from the Serra Leste Suite have geochemical features similar to those described in other layered intrusions in the Carajás Province. High Ni contents in olivine occur in distinctively PGE enriched (> 1 ppm) zones of the Luanga Complex. They are interpreted as the result of dissolution of previously formed magmatic sulfides, a process that may promote the enrichment of PGE and Ni in the parental magma. This interpretation implies that the suggested PGE- and Ni-rich composition of the parental magma is not an original feature of the melt, but results from later interaction of the primary melt with magmatic sulfides. Therefore, the PGE "fertile" Serra Leste Magmatic Suite may result from high-MgO primitive magmas that became variably enriched in PGE and Ni due to interaction with sulfides in hidden lower magma chambers.

1 Introduction

Magmas with distinctive geochemical characteristics that enhance the origin of Ni-Cu-PGE deposits are commonly designated as "fertile" magmas, but how they originate and whether such compositions are systematically associated with Ni-Cu-PGE deposits is a debated issue. Some studies have proposed that Large Igneous Provinces (LIP; Ernst et al. 2005) containing large Ni-Cu-PGE deposits originated from magmas with distinctive geochemical compositions, usually attributed to specific characteristics of the subcontinental lithosphere (e.g., Zhang et al. 2008; Griffin et al. 2013). However, other studies suggest that a systematic association of unusual magmas and magmatic Ni-Cu-PGE deposits is not supported by current data (e.g., Fiorentini et al. 2010; Barnes et al. 2015).

The spatial association of PGE-mineralized intrusions in the Carajás Mineral Province led to the suggestion that they originated from a PGE-fertile magmatic suite (i.e., Serra Leste Magmatic Suite; Ferreira Filho et al. 2007). Recent petrological and metallogenic studies indicated that PGE-mineralized intrusions in the Serra Leste Magmatic Suite host different styles of PGE mineralization (Teixeira et al. 2015; Mansur 2017). These results, together with anomalously high Ni contents in olivine associated with PGE mineralization in the Luanga Complex, suggest that they originated from Ni- and PGE-rich parental magmas (Mansur and Ferreira Filho 2016). In this study we review the data supporting the existence of a PGE-fertile magmatism in the Carajás Mineral Province.

2 Neoarchean mafic-ultramafic magmatism

The Carajás Mineral Province (CMP), located in the southeastern portion of the Amazonian Craton (Fig. 1A), is one of the most important mineral provinces of the South American continent. The CMP is subdivided in two Archean tectonic domains: the older Mesoarchean Rio Maria Domain to the south and the younger Neoarchean Carajás Domain to the north (Fig. 1B; Vasquez et al. 2008). The Carajás Domain is best known for hosting several world-class deposits, including the largest iron ore deposit in the world, as well as several Cu-Au and Ni laterite deposits.

Several Neoarchean (ca. 2.75 Ga) mafic-ultramafic layered intrusions occur in the Carajás Domain (Ferreira Filho et al. 2007; Vasquez et al. 2008). They include large intrusions characterized by thick piles of olivine cumulates (e.g., dunite, harzburgite) that developed world-class Ni laterite deposits (e.g., Onça-Punha, Vermelho, Jacaré). Significant differences in the magmatic structure and petrological evolution of the layered intrusions suggest that they belong to distinct Neoarchean magmatic suites (e.g., Ferreira Filho et al. 2007; Teixeira et al. 2015). The ages of the layered intrusions of the CMP (e.g., 2763 ± 6 Ma Luanga Complex: Machado et al. 1991; 2766 ± 6 Ma Serra da Onça Complex: Lafon et al. 2000) overlap with ages of bimodal volcanism in the Grão Pará Group (e.g., 2759 ± 2 Ma: Machado et al. 1991; 2760 ± 11 Ma: Trendall et al. 1998), supporting the interpretation that mafic volcanics and mafic-ultramafic layered intrusions resulted from coeval major magmatic events in the Carajás Domain (e.g., Machado et al. 1991; Ferreira Filho et al. 2007). The scale of the ca. 2.75 Ga basaltic volcanism and mafic-ultramafic intrusions is comparable with those attributed to LIP (Ernst et al. 2005). The bimodal volcanism in the Carajás Domain shows lithogeochemical and isotopic evidence for significant contamination of mantle-derived melts by continental crust, supporting the interpretation that they originated in a continental rifting setting (e.g., Olszewski et al. 1989). Magmatic structures and compositions of the layered intrusions are also consistent with a Neoarchean rifting environment in Carajás (e.g., Teixeira et al. 2015).

3 The Serra Leste Magmatic Suite

The Serra Leste Magmatic Suite (Ferreira Filho et al. 2007) consists of a cluster of small- to medium-size layered...
mafic-ultramafic intrusions located in the northeastern portion of the CMP (Fig. 1B; see location of Luanga and Lago Grande intrusions). Mafic-ultramafic complexes are intrusive into gneissic rocks of the Xingu Complex and/or volcanic-sedimentary rocks of the Grão Pará Group. This cluster of layered intrusions returned abundant PGE anomalies or mineralized zones during exploration for PGE deposits, a distinctive feature compared with layered intrusions from other portions of the CMP (Ferreira Filho et al. 2007). Recent studies of the Lago Grande (Teixeira et al. 2015) and Luanga (Mansur and Ferreira Filho 2016) Complexes provided constraints for the composition of their parental magmas and fractionation processes. The compositional range of cumulus olivine of the Luanga (Fo78.9-86.4) and Lago Grande (Fo80.0-84.7) Complexes suggests moderately primitive parental magmas. The crystallization sequence of both complexes is similar to those of the major PGE-bearing intrusions (e.g., Bushveld, Stillwater, Great Dyke) in which orthopyroxene precedes clinopyroxene (Eales and Cawthorn 1996). The early crystallization and predominance of orthopyroxene indicate that the primary magma was silica saturated, a feature commonly interpreted as the result of crustal assimilation (Campbell 1985). Mantle-normalized trace element patterns for gabbroic rocks of the Luanga and Lago Grande Complexes show characteristic negative Nb and Ta anomalies with relative enrichment in LREE and Th. These geochemical
features may be interpreted as the result of crustal assimilation during ascent and/or emplacement of the parental magmas. Additional evidence for crustal contamination of the parental magma of the Lago Grande Complex is provided by Nd model ages between 2.94 and 3.56 Ga, with variably negative εNdT values (Teixeira et al. 2015). Together with the crystallization sequence, geochemical results obtained for layered intrusions of the Serra Leste Suite are consistent with primitive mantle melts contaminated with gneisses and migmatites of the Xingu Complex (ca. 3.0 Ga). Although the lithogeochemical and isotopic results are consistent with contamination of a primitive mantle melt with continental crust, they may also be interpreted as the result of melting an old lithospheric mantle (Zhang et al. 2008).

4 Olivine compositions

The compositional range of cumulus olivine from several layered intrusions of the CMP, reviewed by Mansur and Ferreira Filho (2016), indicates that some intrusions have olivine with highly primitive compositions (Fig. 2A). The composition of the most primitive olivine from the Jacaré (up to Fo93), Serra da Onça (up to Fo92) and Vermelho (up to Fo90) Complexes are comparable with the highest values reported for mafic-ultramafic layered intrusions (Fig. 2). These results, together with their emplacement into older gneiss-migmatite terrains, are consistent with very primitive (i.e., high MgO) mantle-derived magmas being transferred through and emplaced into older continental crust in the CMP. The compositional range of cumulus olivine in the Luanga (Fo78.9-86.4) and Lago Grande (Fo82.5-85.7) Complexes, is comparable to those reported for layered intrusions originated from moderate primitive parental magmas. Compared with other layered intrusions in the CMP, olivine from ultramafic rocks of the Luanga Complex has significantly higher Ni content (Fig. 2A). Ni contents in olivine from the Luanga Complex (up to 7,500 ppm) are particularly high when similar Fo contents are considered. In fact, Ni contents in the Luanga Complex stand among the highest values ever reported in layered intrusions, with higher Ni contents only reported in olivine from the Ni-PGE sulfide orebodies of the Kevitsa intrusion (Yang et al. 2013). High Ni contents in olivine of the Luanga Complex occur in distinctively PGE enriched (Pt+Pd > 1 ppm) zones. This connection of high Ni contents in olivine with PGE-enriched rocks led to the interpretation that the parental magma of the Luanga Complex became PGE- and Ni-rich due to the “cannibalization” of previously formed sulfides (Mansur and Ferreira Filho 2016), following the model proposed by Kerr and Leitch (2005). The unusually high contents of Ni obtained in olivine of the Luanga Complex do not occur in the Lago Grande Complex (Fig. 2A). Considering the petrological similarities of these closely located complexes (Fig. 1B), the distinct Ni contents in olivine are significant for the interpretation of the primitive magma associated with the Serra Leste Magmatic Suite.

Figure 2. Plot of Ni versus forsterite contents of olivine crystals from mafic-ultramafic complexes and komatiites. A) Data for layered intrusions of the CMP. B) Data for Jinchuan Complex, the Bushveld Complex, the Sandsloot section below the Platreef, the Uitkomst Complex, the Luanga Complex and the Munro Township komatiites. C) Data for several Brazilian layered intrusions. Partially modified from Mansur and Ferreira Filho (2016). See also Mansur and Ferreira Filho (2016) for references regarding olivine data.

5 Discussion

The Serra Leste Magmatic Suite was originally grouped based on abundant PGE mineralization within a cluster of layered intrusions, disregarding any geological, stratigraphic or petrological consideration (Ferreira Filho et al. 2007). Following this development, a debate has opened up over whether this cluster of intrusions...
originated from parental magmas with geochemical characteristics that enhance the origin of PGE deposits. Geochemical studies in the Lago Grande (Teixeira et al. 2015) and Luanga (Mansur and Ferreira Filho 2016; Mansur 2017) Complexes indicate that they have very similar petrological features that generally match the characteristics described in layered intrusions from different portions of the CMP. However, the anomalously high Ni content of olivine in the Luanga Complex is a remarkable distinctive feature. Mansur and Ferreira Filho (2016) interpreted the high Ni contents in olivine as the result of dissolution of previously formed magmatic Ni-Cu-PGE sulfides. The authors suggested that this process promoted the enrichment of PGE- and Ni in the parental magma of the Luanga Complex. This reasoning implies that the PGE- and Ni-rich parental magma suggested for the Luanga Complex is not linked to the primary mantle-derived magma, but results from later interaction of the primary magma with magmatic sulfides accumulated in the crust. This interpretation does not demand a distinctive composition of the primitive magma to generate the PGE deposit. On the other hand, it is consistent with the absence of significant evidence for unusually PGE-rich primitive magmas (e.g., Fiorentini et al. 2010; Barnes et al. 2015). Therefore, the PGE "fertile" Serra Leste Magmatic Suite may result from high-MgO primitive magmas that became variably enriched in PGE and Ni due to interaction with sulfides in hidden lower magma chambers.

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Low $\delta^{18}$O magma and Cu-PGE mineralization in the Coldwell alkaline complex, Midcontinent Rift, Ontario

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Abstract. Cu-Pd mineralized troctolite and magmatic breccia located near the base of the Geordie Lake intrusion in the Proterozoic Coldwell Alkaline Complex are characterized by anomalously low $\delta^{18}$O values (0.8 to 3.8 ‰). Moving away from mineralization into either the overlying homogeneous gabbro or underlying syenite, the $\delta^{18}$O values gradually increase to the range expected in magmatic systems (>5.5). Two packages of basalt, located close to the Geordie Lake intrusion have similarly low $\delta^{18}$O values (0.37 to 3.9 ‰). Mineralized and barren gabbros and ultramafic rocks of the Eastern Gabbro Suite, located around the north and eastern margin of the Complex, and basalt of the Osler Volcanic Group, located 125 km west of the Complex, have $\delta^{18}$O values typical of igneous rocks of a mantle origin.

Low $\delta^{18}$O whole-rock values commonly result from high temperature exchange with meteoric waters depleted of $^{18}$O. Less commonly, rocks with $\delta^{18}$O values < 5.5 ‰ derive from a magma depleted of $^{18}$O relative to average mantle values. We present evidence here that the contribution of low-$^{18}$O magma to the Geordie Lake intrusion reinforces trace element chemistry that suggests two distinct but co-genetic magma pulses were involved in the genesis and mineralization of the deposit. Possible sources of low-$^{18}$O magma in this Midcontinent rift setting, and implications for volatile content are explored.

1 Geological background

The Geordie Lake intrusion and co-genetic Wolf Camp basalt are located in the north-central portion of the Midcontinent rift related Coldwell Alkaline Complex (Fig. 1). The intrusion and basaltic unit were cut by Centre I syenite. The Geordie Lake intrusion extends for 4 km along strike, is up to 600 m thick, and dips moderately to the west. It consists of an upper unit of homogeneous gabbro and a lower unit of magmatic breccia comprising olivine gabbro fragments within augite troctolite. Cu-Pd mineralization consists of disseminated bornite and chalcopyrite, concentrated mostly within augite troctolite near the base of the intrusion. The augite troctolite is characterized by abundant skeletal olivine crystals that are up to 3 cm in length. Syenite was intruded approximately parallel to the mineralized zone and cuts across the northern part of the intrusion. Partially assimilated gabbroic fragments occur within syenite close to the contact. The Geordie Lake intrusion is also cut by thin porphyritic syenite dikes with chilled margins.

Field evidence, such as that presented by Good and Crocket (1994) and Meghji (2016), suggests that units of the Geordie Lake intrusion underwent diverse physical processes during emplacement, as follows: (1) homogeneous gabbro crystallized with minimal crystal sorting but with flow alignment of plagioclase in the uppermost zones, (2) magmatic breccia formed by mixing of augite troctolite magma and partly crystallized homogeneous gabbro and basal gabbro; and (3) augite troctolite crystallized during conditions of under-cooling related to breccia formation. All units of the Geordie Lake intrusion are partially altered to albite, chlorite, actinolite, and biotite. Magmatic breccia includes small irregular-shaped pods that consist of greater than 80-90% albite. The albite pods are typically surrounded by a coarse-grained gabbro that includes fresh and zoned olivine crystals, implying a close spatial and temporal relationship between metasomatism and magma at a high temperature, and low water to rock ratio.

Figure 1. Simplified geological map of the Coldwell Alkaline Complex highlights the distribution of gabbroic (dark blue) and basaltic (dark green) rocks that were cut by syenitic intrusions (beige), and locations of the Marathon and Geordie Lake deposit host intrusions (purple) and Area 41, Four Dams and Redstone Cu-Pd occurrences. Orange triangles indicate $\delta^{18}$O
The Eastern Gabbro Suite is represented by the dark blue gabbro along the eastern and northern margins of the complex. Geology after Walker et al. (1993) and Stillwater Canada Inc.

2 Methods

The study comprises 204 whole rock δ18O determinations for sample sites located within the Coldwell Alkaline Complex, as follows: 176 at Geordie Lake; 20 from barren and mineralized units in the Eastern Gabbro Suite; 4 of Coubran basalt; and 4 of Wolf Camp basalt. An additional 6 samples from the Midcontinent rift-related Osler volcanic group, located 125 km to the west of the complex were analysed for comparison. All samples were analysed at the Laboratory for Stable Isotope Science at the University of Western Ontario.

Whole-rock powders were reacted with an excess of ClF3 at 580°C in nickel reaction tubes. The resultant O2 gas was converted to CO2 for isotope analyses by reaction with incandescent graphite. During the course of the experiments, the average precision on standard quartz was ±0.2 ‰ (n = 21). A total of 90 samples of whole rock powder were analysed by XRD to estimate the relative proportions of primary and secondary mineral phases.

3 Results

A summary of δ18O values for the Coldwell Alkaline Complex and Osler volcanic group is presented in figure 2. The low δ18O values for augite troctolite and basal gabbro in the Geordie Lake Intrusion are comparable to those for the Wolf Camp and Coubran basalts. Samples from the syenite and upper unit of the Geordie Lake intrusion have a wide range of δ18O values from 1.5 to 7.7 ‰. In contrast, all of the mineralized gabbro samples located around the outer rim of the Coldwell Alkaline Complex have δ18O values greater than about 5.8 ‰. Three porphyritic syenite dikes that cross-cut the Geordie Lake mineralization have an average δ18O value of 5.7 ‰.

A longitudinal section of the Geordie Lake intrusion showing contoured δ18O values relative to geology is presented in figure 3. Note that drill holes are shifted vertically in figure 3 to enable constant elevation relative to the syenite contact. There is a systematic decrease in δ18O from ~6 ‰ near the top of the intrusion to 0.8 ‰ within the basal augite troctolite. The δ18O values of syenite increase from 1.5 ‰ at the contact to 7.7 ‰ away from the contact. Low δ18O values (>3) at the base of drill holes G-00-03 and G-01-14 in the lower right hand corner of figure 3, suggests mineralized gabbro is located at depth below the section. ANOVA statistical tests reveal that δ18O for the augite troctolite, basal gabbro and albite pods are similar (P = 0.81), but these units are distinct from the homogenous gabbro and breccias (P <0.0002).

Figure 2. Summary of δ18O values in the Coldwell Alkaline Complex and Osler volcanic group. Numbers in parentheses indicate number of determinations. Grey band represents normal δ18O for magmas of between 5.5 and 5.9 (after Bindeman, 2009).

Figure 3. Longitudinal section parallel to strike of the Geordie Lake Intrusion showing contoured δ18O values determined for samples in 9 drill holes. The black line represents the contact between homogenous gabbro (above) and augite troctolite plus breccia (below). Cu-Pd mineralization is most concentrated in the augite troctolite above the syenite contact. Drill holes shifted vertically to enable constant elevation relative to the syenite contact.

Figure 4 presents results of a detailed study for heterogeneous (breccia) gabbro marginal to two zones of intense albite alteration. The figure illustrates the relationship of increasing δ18O values with decreasing Rb. The abundance of Rb is a proxy for intensity of albite alteration. The δ18O of the most altered, albite-rich samples is higher than for relatively unaltered samples adjacent to the pod and which contain fresh olivine.

Figure 4. Plot of δ18O (‰, VSMOW) vs. Rb for samples in a transect from weakly altered heterogeneous gabbro to albite pod at the pod 3 and discovery pod study locations. Increasing albite abundance correlates with Rb loss and increasing δ18O.
4 Discussion and conclusions

Based on geological relationships, there are two possible scenarios to explain the very low $\delta^{18}O$ values in the gabbro and syenite located at the base of the Geordie Lake Intrusion. First, it is possible that hydrothermal alteration by meteoric fluids migrating along the gabbro/syenite contact reduced whole rock $\delta^{18}O$ values. In this case, alteration must have occurred after crystallization of the gabbro and before the end of Coldwell magmatism to account for the porphyritic syenite dikes with normal $\delta^{18}O$ values. This explanation is problematic given that there is no apparent relationship between intensity of alteration, as inferred from the abundance of secondary hydrothermal minerals such as actinolite and biotite, and $\delta^{18}O$, and that other similarly altered mineralized gabbros located near the outer margin of the Coldwell do not have depleted $\delta^{18}O$ signatures. In addition, the co-genetic Wolf Camp basalt has a similar range of low $\delta^{18}O$ values and it is reasonable to expect a common origin to explain such values for both basalt and gabbro. However, given the time constraints, the hydrothermal alteration would need to occur simultaneously and to a similar extent at depth for the gabbro and near the surface for basalt and it is difficult to envisage how this could have happened.

An alternative model to explain the low $\delta^{18}O$ for the augite troctolite and co-magmatic Wolf Camp Lake basalt is that these magmas all had low $\delta^{18}O$ values prior to crystallization. One mechanism that would explain magmas with low $\delta^{18}O$ values is anatexis and assimilation of previously altered basalt by a process similar to that described by Bindeman et al. (2008) or Pope et al. (2013) for low-$\delta^{18}O$ basalts in Iceland. The possible assimilation by the troctolite magma of, for for the alteration assemblage, including albite, that is observed throughout the Geordie Lake intrusion, and the gradual increase of $\delta^{18}O$ values in the homogeneous gabbro moving away from the troctolite. Low $\delta^{18}O$ values in the mineralized magmatic breccia zone could be due to a combination of alteration by the low $\delta^{18}O$ volatiles and mixing of the low $\delta^{18}O$ troctolite magma with the nearly crystallized and normal $\delta^{18}O$ homogeneous gabbro. Low $\delta^{18}O$ values in the syenite could be explained by a combination of assimilation of the gabbro and the migration of the low $\delta^{18}O$ volatiles away from the crystallizing gabbro. instance, a hydrous altered hyaloclastite formed at depth during the early stages of the Coldwell caldera-formation event could result in low $\delta^{18}O$ values. Such magma would presumably be hydrous, and crystallization of this hydrous magma would result in exsolution of low $\delta^{18}O$ volatiles near the end of crystallization. Reaction of this low $\delta^{18}O$ fluid with the surrounding rocks could account

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A new reef-type PGE-enriched zone in the early Paleoproterozoic Näränkävaara Layered Intrusion, north-eastern Finland

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Abstract. The Näränkävaara Layered Intrusion is one of the several Finnish 2.45-2.43 Ga layered mafic intrusions. It occurs in Kuusamo, north-eastern Finland and contains a new type of PGE-enriched reef in the Finnish 2.45-2.43 Ga layered intrusion province. The internal structure of the intrusion is divided into four principal units: I) dunitic, II) peridotitic-pyroxenitic, III) gabbroidic-granodioritic and IV) granophyre. The PGE-enriched zone is situated in the border zone between the units II and III. The sulphur content of the PGE-enriched zone is low. The maximum observed thickness of this zone is about 25 m and the highest analysed 2PGE+Au content is 0.39 ppm. The lithology of this PGE-enriched zone is very similar to the PGE-deposit in the Munni Munni Complex, Western Australia.

1 Introduction

The 2.45-2.43 Ga magmatism generated several metal-rich layered intrusions in the Fennoscandian Shield. They host significant metal resources such as Ni-Cu-PGE and Cr-V-Ti-Fe.

The Näränkävaara Layered Intrusion is located in north-eastern Finland near the Russian border, about 100 km south of the Arctic Circle. It belongs to a discontinuous 2.45-2.43 Ga layered intrusion belt about 300 km in length which begins in Sweden (Kukkola/Tornio) and continues eastwards via Penikat, Portimo Complex and Western Koillismaa intrusions to Näränkävaara and from there into Russia.

These intrusions contain different types of PGE-(±Ni-Cu) deposits: the contact-type, the reef-type and the offset-type (Rasilainen et al. 2010 and references therein).

2 Samples and analytical techniques

This study is based on four diamond drill holes (KSM/MUV-16, -19, -20 and -22) made by Outokumpu Mining Oy during years 2002-2003 (Lahtinen 2005). The whole-rock analyses have been made in the Geolaboratory of Geological Survey of Finland. In the elements, presented in Figures 2 and 3, the chromium and zinc were determined by XRF from pressed powder pellets (analytical method 175X), copper, nickel, sulphur and cobalt by aqua regia digestion ICP-OES (analytical method 510P), and gold, palladium and platinum by Pb-fire assay ICP-OES (analytical method 705P).

3 Geology

The Näränkävaara layered Intrusion is about 30 km long and up to 5 km wide. Its footwall and hanging wall rocks consist of Neoarchaean intrusive (tonalite-trondhjemite-granodiorite (TTG) and migmatites) and subcrustal (intermediate-mafic metavolcanic) rocks. The original intrusion was tilted by tectonic movements and now consists of two blocks, a northwest block dipping to northeast about 25 degrees and a southeast block dipping to the southwest 5-15 degrees (Alapieti 1982).

The internal structure of the intrusion may be divided into four principal units: I) dunitic, II) peridotitic-pyroxenitic, III) gabbroidic-granodioritic and IV) granophyre. The average stratigraphic thickness of the dunitic unit is about 2 km, the peridotitic-pyroxenitic unit about 700 m and the gabbroidic-granodioritic unit about 600 m. The total stratigraphic thickness is then about 3.3 km.

According to whole rock chemistry the composition of the parental magma of the dunitic part seems to be of komatiitic affinity whereas the rest of the Näränkävaara Intrusion is of boninitic or siliceous high-magnesian basalt (SHMB) affinity.

4 PGE-enriched Zone

Only one PGE-enriched zone has been found in the Näränkävaara Intrusion. Stratigraphically it is situated in the border zone between the peridotitic-pyroxenitic and gabbroidic units and it has been observed for at least the length of 5 km (Figures 1, 2 and 3). The sulphur content in the PGE-enriched zone area is quite low. The highest analysed sulphur and copper contents are 2440 ppm and 262 ppm, respectively (Figures 2 and 3). The maximum
observed thickness of this PGE-enriched zone is about 25 m and the highest analysed 2PGE+Au content is 0.39 ppm (one meter long drill core sample). The PGE-enriched zone is enriched in Pd over Pt and in the PGE-richest samples its Pd/Pt ratio varies between 2.5 and 8.7.

5 Discussion and conclusion

The PGE-enriched reef in the border zone between the ultramafic unit and gabbroidic unit is a new type of PGE-enriched zone in the Finnish 2.45-2.43 Ga layered intrusions. This type of deposit has not yet been found from other Finnish intrusion of this age group (e.g. Halkoaho et al. 1990a, 1990b, Huhtelin et al. 1989, 1990, Iljina et al. 1989, Mutanen 1997 and Karinen 2010). The host rock lithology of the PGE-enriched zone resembles greatly the platinum-group element mineralisation in the Munni Munni Complex, Western Australia (see Barnes and Hoatson 1994 and Barnes et al. 1990). The next task is to study in detail this PGE-enriched deposit type and its genesis.

Figure 1. Simplified geological map of the 2.45-2.44 Ga Näränkävaara Layered Intrusion in the north-eastern part of Finland. Figure modified after Alapieti (1982).

Figure 2. Rock type column and variations in Cr, Zn, Cu, Ni, S, Co, Au, Pd and Pt contents of the diamond drill hole KSM/MUV-16. The PGE-enriched zone in the diamond drill hole KSM/MUV-16 is about 16 m thick and its average 2PGE+Au content is 0.27 ppm.
Figure 3. Rock type column and variations in Cr, Zn, Cu, Ni, S, Co, Au, Pd and Pt contents of the diamond drill hole KSM/MUV-22. The PGE-enriched zone in the diamond drill hole KSM/MUV-22 is about 25 m thick and its average 2PGE+Au content is 0.17 ppm.

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Controls of ‘proto-craton’ boundaries and deep faults on the intrusion of mafic-ultramafic complexes hosting Ni-PGE-Cr mineralisation, Kaapvaal and Superior cratons

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Abstract. Margins of hitherto unrecognised cratonic nuclei or ‘proto-cratons’ with deep SCLM keels, intersected by crustal to lithospheric faults, control intrusion of mafic-ultramafic complexes hosting Ni-PGE-Cr mineralisation. 3D seismic tomographic and gravity data suggest that the Bushveld Complex and related intrusions in the Kaapvaal Craton (RSA) were emplaced along opposite NNE-SSW margins to a discrete nucleus with a deep keel, that existed prior to mantle plume impingement, and represents a separate proto-craton or a remnant left after delamination of SCLM on its margins. Similarly, Archean mafic-ultramafic intrusions in the N Superior Craton (Canada) occur at intersections of proto-cratons with deep faults. The Ring of Fire is only a small part of a deeper, elliptical feature on whose margins other mafic-ultramafic intrusions of the same age are localised at its intersection with deep N-S faults. The 1311 Ma Soisson Complex in the Paleoproterozoic SE Churchill also intrudes at the E margin of the underlying N Superior Craton SCLM mantle keel at fault intersections. Identification of cryptic ‘proto-craton’ boundaries within Archean cratons and SCLM keels beneath their Proterozoic margins is thus important in Ni-PGE-Cr exploration.

1 Controls of lithospheric keels on mafic-ultramafic complexes

Deep (generally Archean) lithospheric keels control the migration of magma produced by plume-related melting, localising the emplacement of mafic-ultramafic complexes hosting magmatic Ni-Cu-PGE mineralization on their margins (Kerrich et al. 2005; Hronsly 2007; Begg et al. 2010; Griffin et al. 2013). Whilst Kerrich et al. (2005) highlight the transition from thick Archean to thinner Proterozoic SCLM as localising mafic-ultramafic intrusions, the margins of cryptic proto- (or paleo-) cratons within cratons (Begg et al. 2010; Mole et al. 2013; Barnes et al. 2016) or the margins of Archaean deep SCLM keels preserved beneath bounding Proterozoic orogens are equally important. Crustal-scale faults are also required to focus magma migration (Naldrett 1989; Lesher and Houle 2015).

This contribution presents integrated geophysical and geological interpretations that highlight both previously unrecognised Archaean proto-cratons with deep lithospheric keels within the Kaapvaal Craton of South Africa and the northern Superior Province of Canada and an extension of the NE Superior province beneath the Paleoproterozoic New Quebec orogen that localise mineralised mafic-ultramafic complexes at their intersection with crustal- to lithospheric-scale faults.

2 Kaapvaal Craton, RSA

2.1 Conventional terrane interpretation

Although late Archean granitoids and sedimentary cover sequences make recognition of terrane boundaries difficult, the Kaapvaal Craton, South Africa, is traditionally subdivided into the ENE-WSW trending Southern, Central, and Pietersburg terranes with sinistral shear zones along their margins (apparent in both gravity and aeromagnetic images), separated by the generally N-S trending Colsesberg lineament or suture from the Western terrane on their W margin (Eriksson et al. 2009).

A NNE-SSW trending high-Vp mantle nucleus (i.e. oblique to conventional terranes) is suggested from seismic tomography by James et al. (2001). Griffin et al. (2003) interpret lateral heterogeneity of SCLM beneath the Kalahari Craton (of which the Kaapvaal Craton is a constituent) and surrounding orogenic belts as a product of metasomatism related to Bushveld (2.05 Ga) and Karroo (ca. 180 Ma) intraplate magmatism.

2.2 The Bushveld and related mafic-ultramafic complexes

The 2.06–2.05 Ga Rustenburg Layered Suite mafic rocks of the Bushveld Complex in the northern Kaapvaal Craton, South Africa, the world’s largest layered mafic intrusion, hosts PGE-Cu-Ni-rich sulphides, chromite and Fe-Ti-V oxides and is the largest PGE deposit in the world, containing half the world’s resources in chromite (Groves and Bierlein 2007). The Bushveld Complex and associated A-type/anorogenic alkaline granites are attributed to mantle plume magmatism.

ENE-WSW striking structures, especially the Thabazimbi–Murchison Lineament, a regional feature that separates the northern from southern lobes, are generally interpreted as controlling main dyke-like feeders for the Bushveld Complex and for focussing of hydrothermal fluid flow during further mineralization. It has also been suggested that the NE-striking Steelpoort Fault may have acted as a magma conduit. Modelling of gravity data and analysis of kimberlite xenoliths (Webb et al. 2011) and shear wave velocity models (Kgaswane et al. 2012) show that western and eastern lobes of the Bushveld Complex are connected at depth.
2.3 Geophysical interpretations

3D visualisation of S-wave seismic tomographic isosurfaces calculated from data described by Fishwick (2010) in our study clearly portrays the form of the South African lithosphere, highlighting a NNE-SSW central region with a deep lithospheric keel that plunges northwards beneath the Limpopo Belt (consistent with petrological whole rock major element and mineral chemical analysis of mantle xenoliths presented by van der Meer et al. 2013). The area E of its boundary shows no such deep keel and is interpreted as a (or several) younger Archaean accreted terrane(s).

The margins of this central SCLM block with a deep keel portrayed by seismic tomography are sub-parallel to deep gravity ‘worms’ (i.e., edges to the horizontal gradient calculated for different depths) suggesting this is also a crustal feature and a likely ‘proto-craton’ core to the Kaapvaal Craton, and not simply the result of mantle metasomatism as suggested by Griffin et al. (2003). The SW part of the Inyoka shear or fault system parallels the interpreted craton margin but turns away from the margin to a more NE orientation in the Barberton greenstone belt. Its western margin generally coincides with the Colseberg lineament. A NW-SE oriented continuation of Archaean SCLM is suggested on the W side of the Colseberg lineament, possibly extending slightly beyond the mapped margin of the Kaapvaal Craton. The Bushveld and Molopo Farms (Prendergast 2012) layered intrusions occur on opposite margins of the interpreted ‘proto-craton’ at the intersections with the Thabazimbi–Murchison Lineament. The 2055 Ma Lindeques Drift and Heidelberg intrusions and the Roodekraal Complex in South Africa (de Waal et al. 2006) and the Okwa basement complex in southern Botswana, coeval with Bushveld intrusion, also occur on the interpreted ‘proto-craton’ margin, as does the 1915±6 Ma Trompsburg intrusion (Maier et al. 2003). Most diamondiferous kimberlites in South Africa (from the database of Faure 2010) are located within the central ‘proto-craton’, consistent with its deep lithospheric keel. Some more isolated diamondiferous kimberlites in younger terrains, however, appear to occur within areas above SCLM fragments rifted from this central ‘proto-craton’, hence mapping these blocks provides targets for diamond exploration.

3 Superior Province, Canada

3.1 Proto-craton margin controls on mafic-ultramafic intrusions

Cr-PGE, Fe-Ti-V, Ni-Cu-(PGE) mineralization in the ‘Ring of Fire’ in the Superior Province of N Ontario is hosted by mantle derived peridotite and other large mafic to ultramafic intrusions in the 2828-2702 Ma McFaulds Lake greenstone belt (Metsaranta and Houle 2013). Enhanced long wavelength aeromagnetic and pseudogravity images show a horseshoe-shaped features corresponding to the Ring of Fire is located off-centre within a much larger concentric elliptical structures in a zone of N-S faults; both elliptical features and faults are not apparent in short wavelength and total field aeromagnetic images, implying a deep crustal source. Mapped mafic-ultramafic intrusions of the same age as those in the Ring of Fire (Houlé et al. 2015; Sappin et al. 2015) occur within or on the margins of the elliptical feature at the intersection with N-S faults.

The elliptical features and the Ring of Fire occur on the SW margin of the middle of 3 distinct domains (each with deep, ca. 230 km SCLM keels) in 3D S-wave seismic tomographic images produced from data by Godey et al (2003) of the northern Superior craton. Central & E domains (Fig. 1) are interpreted as early proto-crats that were accreted E-W to form a ‘Superior 1’ craton. ‘Superior 1’ was subsequently fragmented into ribbon-continent fragments upon and between which E-W trending greenstone belts and sedimentary basins were developed and reassembled during ensuing N-S shortening (Bédard and Harris 2014). This model supported by a change in Hf zircon model ages from 3.5 Ga to 3.1 Ga (Lu et al. 2013) across this interpreted N-S early terrane boundary in the Wabigoon Subprovince.

The ca. 2.83 Ga (Thurston et al. 1991) Big Trout ultramafic complex and the 2.75 Ga Menarik Complex, (Houlé et al. 2015) occur in the same position on the margin of accreted proto-crats with deep keels (Fig. 1).

Figure 1. Map (top) and section between the Ring of Fire (ROF) and Soisson (bottom; 2x vertical exaggeration) of a 3D S-wave seismic tomographic isosurface model. The ROF occurs within a larger elliptical feature interpreted from ‘deep-source’ aeromagnetic data, shown in dark green. The outer, pale pink region (6% dVs) marks the limit to N Superior craton with a deep keel (c.f. Faure et al 2011). Red lines = terrane boundaries (Stott et al. 2007). Archaean and Mesoproterozoic mafic ultramafic intrusions occur on of close to the margins of the N Superior Province SCLM keel at the intersection with cross-cutting faults.
3.2 Archaean SCLM controls on emplacement of the Mesoproterozoic Soisson suite (Papavoine showing), Core Zone, SE Churchill

The 3D seismic tomographic image for the N Superior Province shows that Archaean SCLM continues beneath the Paleoproterozoic Labrador Trough and Core Zone to the SE Churchill Province in NE Quebec. The 1311 Ma (Corrigan et al. 2015) Soisson mafic-ultramafic suite, where Western Mining Corporation’s Papavoine ‘showing’ contains pyrrhotite, chalcopyrite, pentlandite and, locally, violarite, projects on the E margin of the SCLM Archaean keel (Fig. 1). The Soisson suite is only slightly younger than Voiysey’s Bay (1332-1313 Ma; Kerr and McNicol 2010); both are intruded along E-W structures, with Voiysey’s Bay occurring on the margin of the Archean Nain Craton. The Soisson suite also occurs at their intersection with a NWW-ESE trending fault, the same structure along which the 1240 ± 2 Ma (Miller 1997) Strange Lake peralkaline complex is located (at the intersection with another E-W fault).

4 Discussion and conclusions

A schematic 3D model summarising the factors controlling magma genesis and the emplacement mafic-ultramafic intrusions in the Kaapvaal and Superior cratons is shown in Figure 2.

Geophysical data suggests that, as for the Archaean Yilgarn Craton in Western Australia (Mole et al. 2013), proto-craton margins within both the Kaapvaal and Superior cratons control the emplacement of mafic-ultramafic intrusions that host Ni-PGE-Cr mineralisation. Further isotopic studies to those undertaken by Mole et al. (2013) are, however, required to validate interpretations that:

- The greater Ring of Fire elliptical features occur above a preserved paleo-craton SCLM boundary (as proposed by Bédard and Harris 2014).
- ENE-WSW trending domains (presently interpreted as terranes) in the Kaapvaal developed upon or were accreted to an older, composite craton whose keel is imaged through seismic tomography, instead of the young, metasomatism models of Griffin et al. (2003).

Deep structures intersecting paleo-craton margins that also provide pathways for magma emplacement are only seen on enhanced, long wavelength components of aeromagnetic data and on enhanced pseudogravity images. Integrating such aeromagnetic processing with enhancement and 3D visualisation of gravity and seismic tomographic data and mapping the boundaries of Archaean SCLM keels beneath Proterozoic orogens and deep crustal to lithospheric-scale structures are shown to be a valuable approaches in regional target generation in Ni-PGE-Cr exploration.

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Figure 2. Model for the controls of SCLM proto-craton keels and deep crustal structures on localising magma generated above a mantle plume and the emplacement of mafic-ultramafic intrusions (modified after the 2D section by Griffin et al. 2013).
The Munali Ni-sulfide deposit, southern Zambia: a multi-stage mafic-ultramafic magmatic sulfide megabreccia with a carbonatite component?

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Abstract. The Munali Intrusive Complex (MIC) is a flattened tube-shaped, mafic-ultramafic intrusion located along the southern Congo Craton margin in the Zambezi belt of southern Zambia. It is made up of a Central Gabbro Unit (CGU) core, surrounded by a Marginal Ultramafic-mafic Breccia Unit (MUBU), containing magmatic Ni-Cu-PGE sulfide mineralisation. Munali has many of the characteristics of craton-margin, conduit-style, dyke-sill complex-hosted magmatic sulfide deposits. It was intruded ~860 Ma, during rifting of the Zambezi ocean. The MUBU was intruded 4.5 Ma after the CGU and is a highly complex, multi-stage megabreccia made up of mafic and ultramafic rocks (including phoscorites). The breccia matrix is largely made up of pyrrhotite-pentlandite-chalcopyrite-pyrite with variable amounts of magnetite, apatite and carbonate. Late stage sulfide-carbonate-magnetite veins cut the rest of the MUBU. The strong carbonate signature is likely due, in part, to contamination from the surrounding marbles, but may also be linked to a carbonatite melt related to the phoscorites and a number of similarly aged carbonatites are present in the region. Munali is an example of a complex conduit-style Ni-Cu-PGE sulfide deposit formed from multiple stages and sources of magmatism during rifting near a craton margin.

1 Introduction

The Munali Ni-sulfide deposit is a magmatic sulfide deposit, located in the ultramafic portion of the mafic-ultramafic Munali Intrusive Complex (MIC) in the Zambezi Supracrustal Sequence (ZSS), southern Zambia, 75 km south of Lusaka. This general setting is consistent with the well-established spatial link between Ni-Cu-PGE sulfide deposits and craton margins (e.g., Begg et al. 2010).

The characteristics of the deposit, as a flattened tube-shaped, zoned and composite intrusion, with marginal sulfide breccias, is typical of many conduit-style magmatic sulfide deposits (e.g., Barnes et al. 2016), though we show a significant difference here in that the gabbroic rocks are intruded by a later, ultramafic episode of atypical composition. Furthermore, the sulfide mineralisation itself contains unusually high proportions of magnetite-apatite and carbonate of primary magmatic origin (Holwell et al. 2017).

The MIC is intruded along a major crustal fault zone (the Munali Fault), which runs NW-SE and separates granitic basement (1090 Ma), and early rift sediments metamorphosed to amphibolite facies, from slightly older rift sediments of the Nega Formation of greenschist facies (>880 Ma). The immediate host rocks to the MIC are marbles of the Nega Formation (Fig. 1). The intrusion is hosted within this unit and dips, along with the metasedimentary sequence, steeply to the SW. Other units that make up the hangingwall to the SW include biotite, graphitic, garnet and scapolite schists.

Magmatic Ni-Cu-PGE sulfide mineralisation is hosted by a Marginal Ultramafic-mafic Breccia Unit (MUBU), which was emplaced around the margins of a Central Gabbro Unit (CGU). The MUBU is thickest on the southwestern edge of the MIC and comprises three main sulfide deposits/prospects: Enterprise (the site of the Munali Ni mine), Voyager and Intrepid (Fig. 1).

Here we present the results from the first detailed mapping of the underground sections through the deposit and supporting geochronology (from Holwell et al. 2017) to construct a framework of multi-stage magmatic emplacement and sulfide mineralisation.

Figure 1. Geological map of the Munali Igneous Complex, showing the unmineralised CGU, and later, sulfide-hosting MUBU. Coordinate system: UTM, WGS84.
Figure 2. A: phot montage of a strike-perpendicular cross cut through the MUBU at Munali. Dolerite units are highlighted as markers. B: underground face map of A showing multiple stage of magmatic rocks (poikilitic gabbro, ultramafic and olivine basalt) and breccia textures with fill comprised of sulfide.

2 Field relationships

Detailed underground face mapping (Fig. 2 and 3) has allowed us to define a robust chronology of events within the MIC. Clear cross cutting relationships indicate that the ultramafic rocks were intruded after the mafic rocks. The MUBU is a megabreccia, with clasts of mafic and predominantly ultramafic rocks on decimetre to metre scales. The matrix of the breccia is made up of magmatic sulfide with variable amounts of silicate clasts, but also abundant magnetite, carbonate and, in places, apatite. Olivine dolerite dykes are intruded into the MUBU after the main stage of sulfide brecciation, but show some evidence of being brecciated themselves (Fig. 2), indicating a prolonged history of intrusion, brecciation and sulfide emplacement. The final stage identified by our mapping is the injection of sulfide-carbonate-magnetite veins that cross cut all rock types.

2.1 Central Gabbro Unit

The CGU is made up of variably textured gabbros and forms the immediate footwall to the mineralised MUBU along the SW-dipping southwestern margin of the MIC. There is no Ni-Cu-sulfide mineralisation in this unit.

2.2 Poikilitic Gabbro

This is present within the MUBU and around the margins of the CGU. It is much coarser, with plagioclase chadacrysts and clinopyroxene and magnetite-ilmenite oikocrysts. It is interpreted to be cogenetic with the CGU, though does occasionally contain some minor magmatic sulfide blebs. Holwell et al. (2017) report a high precision CA-TIMS U-Pb zircon age of 862.39 ± 0.84 Ma.

2.3 Ultramafic rocks

The ultramafic rocks are present only within the MUBU, sometimes as intrusions into the footwall CGU, but mostly as large clasts within the megabreccia (Fig. 2). They are unusual in their composition, being comprised of very coarse olivinites, olivine-magnetite cumulates, and phoscorites (olivine-magnetite-apatite rocks). The interstitial assemblage to the olivines consists of magnetite ± sulfide ± apatite. There is no chromite at all and only very rare clinopyroxene.

Sulfides in the interstitial portion are pyrrhotite-pentlandite-chalcopyrite. Zircons in sulfide-bearing phoscorite yielded a U-Pb CA-TIMS age of 857.9 ± 2.1 Ma (Holwell et al. 2017). This is marginally, but distinctly younger than the poikilitic gabbro. This confirms the geological relationships that indicate the ultramafic rocks intruded the gabbro. As such, Munali is not a conventionally zoned intrusion with an ultramafic rim and more fractionated mafic core, but a multi-stage intrusion. Furthermore, the ultramafic clasts contain sulfide mineralisation, but are themselves intruded by the main stage of sulfide mineralisation.

2.4 Sulfide mineralisation and brecciation

Massive to semi-massive sulfides make up the matrix to the megabreccia (Fig. 2) and are most massive and in greatest abundance at the footwall contact, where they are seen to intrude into the footwall CGU (Fig. 3). Detailed description of the sulfides can be found in Blanks et al. (2017). Magnetite reaction rinds are observed at many sulfide-silicate contacts (Fig. 3). The macrotextures shown in Figure 3 indicate that sulfide liquids intruded the footwall and are analogous to textures from other deposits that show sulfide liquids intruded and ‘rafted off’ xenoliths of floor rocks (Barnes et al. 2016). On a smaller scale,
sulfide is observed to inject along grain boundaries and fractures in the xenoliths, disaggregating the silicate rocks.

### 2.5 Olivine basalt/dolerite dykes

Barren olivine dolerite/basalt dykes intrude the MUBU and contain some sulfide clasts, but are themselves brecciated and infilled by sulfide (Fig. 1), indicating intrusion after the first stages of sulfide intrusion, but before the final stages of brecciation and sulfide injection.

### 2.6 Sulfide-carbonate-magnetite injections

Late stage sulfide-magnetite-carbonate veins and injections cut through the MUBU and appear to be the final stage of mineralisation. The carbonate is largely dolomite and is present in a magmatic texture. Detailed description of this stage can be found in Blanks et al. (2017).

### 2.7 Ductile deformation and talc-carbonate alteration

Sheared talc-carbonate altered ultramafic rocks are present in irregular zones within the MUBU (Fig. 1), indicating some late stage ductile deformation that focussed strain in the least rheologically competent rocks. The talc-carbonate alteration is interpreted to be the result of CO$_2$-rich fluids interacting with serpentinitised ultramafic rocks.

### 3 Multi-stage emplacement

The underground mapping clearly shows multiple stages of magmatism (gabbro > poikilitic gabbro > ultramafic > olivine dolerite), and multiple stage of sulfide injection (as a cumulus phase in the poikilitic gabbros and ultramafic rocks, as breccia fills, and as late stage veins). This is not unusual for conduit-style deposits, but what is unusual is the clear geological and geochronological evidence for ultramafic emplacement several million years after emplacement of the gabbro. As such, Munali is not a conventional zoned ultramafic intrusion and the CGU and MUBU must be considered separate intrusions and may have different sources.

### 4 Magmatic versus tectonic brecciation

One of the major questions regarding magmatic sulfide breccias is whether they are truly magmatic breccias, or tectonic breccias infilled by sulfide melts, or even fully tectonic breccias (with durchbewegung textures). The ultramafic rocks and poikilitic gabbro clasts are juxtaposed next to each other in the MUBU and so must have undergone some amount of transport. Both may have formed in situ and then been subject to dynamic brecciation, but the large grain size of the ultramafic rocks would imply slow cooling, perhaps in a much bigger chamber elsewhere.

The abundant magnetite reaction rinds at massive sulfide-silicate rock boundaries are interpreted to be analogous to the chromite rinds seen in komatiites that are thought to form from interaction between sulfide liquids and films of silicate melt (Frost and Groves 1989). This, along with the injection into, and rafting off of, the footwall, supports the presence of high temperature sulfide liquids at least in part, causing brecciation.

### 4 A carbonatite influence?

Whilst the abundant carbonate content of the Munali ores is likely to be at least in part due to assimilation of carbonate wall rock, a number of lines of evidence present a compelling argument for the presence of carbonatite melts in the development of the Munali deposit. There are many Ni sulfide deposits around the world intruded into
carbonate rocks (e.g., Jinchuan), and whilst they do contain carbonate veins, they do not show many of the unusual features that Munali does, such as the primary magmatic carbonate-sulfide-magnetite veins, and the association with phoscorites.

Phoscorites are rare, and are not known as hosts to major magmatic sulfide mineralisation (minor sulfides are present in some of the phoscorites of the Kola peninsula, e.g., Kovdor). They are, however, almost always related to carbonatites, which are commonly associated with rifting in intraplate settings. This is consistent with a syn-rift emplacement age for the phoscorites of 858 Ma. The phoscorites (and carbonatites by extension) raise the possibility that some, if not the majority, of the carbonate in the MIC may be of a primary magmatic source. Carbonatite intrusions are present sporadically throughout the Zambezi belt and form a linear trend that runs ESE from the Munali area into northern Zimbabwe at Kesya, Marindagomo, Dande-Doma and Kapfrugwe. All of these share some similarities in texture and mineralogy to Munali; in particular the presence of carbonate together with apatite and magnetite (Walsh et al. 2001). None of these intrusions have been dated, although they have been deformed at around 800 Ma (Walsh et al. 2001). Therefore, the 858 Ma phoscorite event may be related to this carbonatite magmatism, and that intra-plate rifting at the time was associated with carbonatitic as well as mafic magmatism.

The association of abundant apatite and Fe-Ti oxides with Ni-Cu-Fe-sulphides and mafic silicates seen at Munali is rare. Only the Babbit deposit of the Duluth Complex, Minnesota (Ripley et al. 1998), and the Isindro Gabbro Complex, Madagascar (Augé et al. 2015) are known to show this and have been interpreted to be the result of the presence of immiscible sulfide and Fe-Ti-P liquids. This may be a plausible mechanism for the presence of abundant apatite and magnetite in some of the massive sulfides at Munali.

Alternatively, and an explanation that also goes a way to explaining the carbonate association as well, lies in the similarity between the sulfide-apatite-carbonate textures seen in the ores at Munali and recently recognised sulfide-apatite-carbonate assemblages in melt veins in mantle xenoliths, interpreted to represent sulphide-carbonate-phosphate immiscibility (Hughes et al., 2016). This is further demonstrated by Blanks et al. (2017). If they are comparable, the origin of the apatite may be primary carbonate-rich magmatic melts, and would provide a stronger case for a carbonatitie influence at Munali.

5 Summary

The Munali Ni sulfide deposit conforms to many of the classic features of magmatic sulfide deposits formed in conduit systems: a near-craton margin location, emplacement coincident with intraplate-rifting as a dyke-sill complex along a major crustal lineament, a chonolith-like morphology of a mafic-ultramafic complex, and massive sulfide in a magmatic breccia. Breciation appears to be primarily magmatic and in places, there is abundant evidence that sulfide liquids have been instrumental in causing brecciating. However, the deposit shows a highly complex and unusual multi-stage history that shows a clear temporal distinction between an early mafic phase, and a later, mineralised phoscoritic ultramafic intrusion with a characteristic apatite-magnetite-carbonate character of the ore. These two aspects may be related and Munali could represent an example of a magmatic Ni sulfide deposit with a significant phoscorite-carbonatite influence, and as such may represent an unusual style of mantle-derived magmatic sulfide deposits.

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References


The redistribution of platinum-group elements and platinum-group minerals in the weathered chromitites of the Lower and Middle Group chromitites of the Bushveld Complex and the mineralogical siting of Ru

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Abstract. The chromitite seams of the Lower Group (LG) and Middle Group (MG) of the Bushveld Complex in South Africa contain elevated Pt and Pd concentrations. So far, only limited work has been done on the distribution of platinum-group elements (PGE) and platinum-group minerals (PGM) in these ores. In particular, the knowledge about the effects of weathering of PGM and the redistribution of PGE in these ores are rare. Previous studies showed that the main PGM are PGE-sulfides (cooperite-braggite, malanite, laurite), followed by PGE-sulfarsenides, sperrylite and Pt-Fe alloys. During weathering PGM are largely destroyed and only relict PGM are observed. Platinum-group minerals are weathered along small cracks and neo-formation of PGM may take place. Additionally, the mineralogical siting of Ru within chromitites is studied here. It was shown by LA-ICP-MS work that chromite can host some 100s-ppb of Ru.

1 Introduction

The mineralization of economically important platinum group elements (PGE) mainly occurs in mafic-ultramafic intrusions such as the Bushveld Complex in South Africa. The 2,054.89 ± 0.37 Ma old (Zeh et al. 2015) Bushveld Complex is the largest layered mafic-ultramafic intrusion on Earth and hosts about 70% of the world’s platinum (Vermaak 1995, Zientek et al. 2014). Platinum-group elements are currently mined from the Merensky Reef, the Platreef and the UG-2 chromitite. The UG-2 is the only chromitite layer mined for PGE as the primary economic metal, however, the Lower Group (LG) and Middle Group (MG) chromitites are mined for Cr and V but not for PGE, although all chromite seams within the Critical Zone contain significant PGE concentrations ranging from 0.5 to 9 g/t (e.g. Naldrett et al. 2012).

In the pristine chromitite ores of the Bushveld Complex, PGE occur both as discrete platinum-group minerals (PGM) and included within sulphides – mainly pentlandite (Junge et al. 2014, 2016, Oberthür et al. 2016). The mafic-ultramafic rocks in the Bushveld Complex are strongly weathered down to 10 to 40 m below the surface (Wagner 1929, Buchholz & Foya 2015, Junge et al. 2015). During weathering, sulfides and PGM are largely destroyed and PGE are mobilized and redistributed in the near-surface ores (Locmelis et al. 2010, Junge et al. 2015, Kraemer et al. 2015). The redistribution and mobility of PGE under supergene conditions was discussed in rocks from the Bushveld Complex and the Great Dyke in Zimbabwe that are mined for PGE (Hey 1999, Locmelis et al. 2010, Oberthür et al. 2013, Junge et al. 2015) and on laterites worldwide (Bowles 1986, Aiglsperger et al. 2015, 2016).

In this work the distribution of PGE and PGM in weathered LG and MG chromitites is studied by electron microprobe analyses (EPMA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Additionally, the mineralogical siting of Ru in chromitites is studied by scanning electron microscopy (SEM) and LA-ICP-MS.

2 Samples and analytical methods

Near-surface chromitite seams of the LG and MG of the western Bushveld Complex at the Thaba Mine are studied for the distribution of PGE.

For the silicates in the oxidized ore the following elements were analysed by EPMA: Mg(Kα), Al(Kα), Si(Kα), S(Kα), Ca(Kα), Cr(Kα), Mn(Kα), Fe(Kα), Co(Kα), Ni(Kα), Cu(Kα), As(Lα), Se(Lα), Rh(Lα), Pd(Lβ), Ag(Lβ) and Pt(Lα). The analytical conditions employed for silicates were: 20 kV acceleration voltage, 120 nA beam current, focused beam, and up to 360 s measuring time. Synthetic metals (Rh, Pd, Ag, Pt, Se, Mn, Fe, Co, Ni, Cu, Se, Si), natural chromite (Al, Mg) and natural pentlandite (S) are used as standards. Mean detection limits were 130 ppm for Mg, 100 ppm for Al, 100 ppm for Si, 175 ppm for S, 130 ppm for Ca, 85 ppm for Cr, 160 ppm for Mn, 325 ppm for Fe, 100 ppm for Co, 145 ppm for Ni, 150 ppm for Cu, 90 ppm for Se, 85 ppm for Rh, 70 ppm for Pd, 325 ppm for Ag and 200 ppm for Pt.
Laser ablation-inductively coupled plasma-mass spectrometry measurements on chromite and secondary alteration minerals were carried out on a ThermoScientific Element XR (HR-ICP-MS) coupled with a femtosecond laser ablation system. The following isotopes were measured: $^{25}\text{Mg}$, $^{27}\text{Al}$, $^{28}\text{Si}$, $^{30}\text{Si}$, $^{34}\text{Ca}$, $^{47}\text{Ti}$, $^{51}\text{V}$, $^{53}\text{Cr}$, $^{55}\text{Mn}$, $^{57}\text{Fe}$, $^{60}\text{Ni}$, $^{63}\text{Cu}$, $^{65}\text{Zn}$, $^{67}\text{Zn}$, $^{77}\text{Se}$, $^{89}\text{Y}$, $^{99}\text{Ru}$, $^{101}\text{Ru}$, $^{103}\text{Rh}$, $^{105}\text{Pd}$, $^{106}\text{Pd}$, $^{111}\text{Cd}$, $^{113}\text{Ba}$, $^{139}\text{La}$, $^{140}\text{Ce}$, $^{147}\text{Sm}$, $^{153}\text{Eu}$, $^{167}\text{Yb}$, $^{175}\text{Lu}$, $^{181}\text{Re}$, $^{189}\text{Os}$, $^{193}\text{Ir}$, $^{195}\text{Pt}$, $^{197}\text{Au}$, $^{207}\text{TI}$. NIST610 (Jochum et al. 2011) and a piece of the Lombard iron meteorite (Gilbert et al. 2012) were used as reference materials. Laser spot size was about 40 μm and chromite grains are analyzed in raster mode. Rasters were positioned in the largest part of the grain and had a diameter of about 100 μm. 12 analyses on sample material were preceded by 4 analyses on NIST610 and 4 analyses on Lombard. The raw data were exported to a data-handling software tool implemented in JAVA using the libraries JFreeChart (JFree 2009), commons Math (Commons 2009) and POI (POI 2009).

3 Distribution of platinum-group elements in weathered chromitites

3.1 Platinum-group minerals

Previous studies showed that in the LG-6 and MG-1/2 of the eastern and western Bushveld Complex, PGE-sulfides (cooperite-braggite, malanite, laurite) are the dominant PGM, followed by PGE-sulfarsenides, sperrylite and Pt-Fe alloys (Junge et al. 2016, Oberthür et al. 2016). Within the near-surface weathered chromitite seams, only relict PGM can be observed. Figure 1 shows BSE images of weathered LG-6 and MG-1 chromitites at Thaba Mine from the western Bushveld Complex. Chromite grains are partly zoned with Fe-rich core and Fe-poor rim (Figure 1A). Chromite grains can be fractured or remain relatively unaffected. Fracturing usually takes place at grain contacts of chromite grains, however, chromite grains within secondary silicates are typically intact. Relict PGM are observed within silicates or as inclusions in chromite – typically laurite. Former grains of PGM are observed in secondary Fe-silicates showing larger shapes but are locally redistributed along small cracks (Figure 1B,C) and Pt-Fe-(oxides) are observed as well, arguing for the neoformation of PGM (Figure 1D).

3.2 Platinum-group elements in secondary minerals

Secondary minerals in weathered PGE ores can show concentrations of Pt and Pd in the 100s-ppm range (Locmelis et al. 2010, Junge et al. 2015). Similarly, secondary minerals in the weathered chromitites of the Thaba Mine were analysed here by EPMA and LA-ICP-MS. For the LA-ICP-MS work, a normalization of MgO, Al$_2$O$_3$, SiO$_2$, CaO, MnO, FeO to 100% was used, because these oxides comprise the major compounds of the analyzed phases.

Maximum values of Pd in these secondary minerals are 155 ppm (median 10 ppm). The concentrations of Rh, Ir and Pt are in the ppm-range. A good correlation can be observed with Ni and Pd, arguing for the weathering of pentlandite, which hosts Pd in the pristine PGE ore. Palladium and Ni partly remained and were incorporated into secondary silicates while S is largely lost.


3 Mineral chemistry of chromite

Chromite grains within MG-2 chromitite of the western Bushveld Complex at Thaba Mine were analyzed for PGE and trace elements concentrations. A normalisation of MgO, Al$_2$O$_3$, TiO$_2$, V$_2$O$_5$, Cr$_2$O$_3$, MnO, FeO, NiO and ZnO to 100% was used, because these oxides comprise the major oxides. The ablation spectrum was typically flat and no inclusions of laurite were identified (Figure 2A). All PGE are below the detection limit but $^{99}$Ru shows median values (n=18) of 264 ppb (total range from 171 to 365 ppb). In-situ LA-ICP-MS measurements of komatiitic chromite grains carried out by Locmelis et al. (2011) showed that Ru has concentrations of 220 to 540 ppb. Pagé & Barnes (2016) showed similar values of Ru contents in chromites of the Bushveld Complex (maximum values of 548 ppb). In some cases zones with larger enrichment of Ru are observed (Figure 2B). However, no correlation with S was detected arguing for a heterogeneous distribution of Ru in chromite rather than the incorporation of laurite [RuS$_2$]. These zones may be associated with the different zones of chromite grains shown in Figure 1A.
Figure 2. LA-ICP-MS spectra of chromite grains. A: Flat pattern showing homogenous distribution of Ru. B: Zones with elevated concentrations of Ru with is not in correlation with sulphur (no inclusions of laurite [RuS₂]).

4 Summary and conclusions

In pristine LG and MG chromitites, PGE contents can vary up to 4 g/t (Cawthorn 1999). Similar concentrations are observed in chromitite seams close to the surface. Ruthenium contents are typically large, whereas Pt and Pd are lower in the near surface ore than in the pristine ore. Laurite, as the main carrier of Ru, is often observed as inclusions within chromite grains. During weathering PGM are largely destroyed and only relict PGM are observed. PGM are mainly destroyed and redistributed within the weathered ore and may show neoformation of PGM and PGE-oxides along small cracks. Ruthenium can occur as solid solution within chromite with median values of 260 ppb. Laurite [RuS₂] is the main carrier of Ru.

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Orthopyroxene mineral chemistry of the Mafic Norite, Sudbury Igneous Complex: further insights into the formation of the Sudbury Ni-Cu-PGE sulphide deposits

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Abstract. The contact Ni-Cu-PGE sulphide ores of the Sudbury Igneous Complex (SIC) are associated with the “Sublayer”, a fragment-rich unit that occurs in “embayments” at the base of the SIC. The compositions of orthopyroxene (Opx) in the Mafic Norites, the unit that caps the Sublayer, were determined to establish whether Opx chemistry can be used to discriminate between well-mineralized and poorly-mineralized embayments; Opx from the fine grained fragment-free margins of the Foy Offset Dyke were also analysed. With the exception of one sample from the well-mineralized Levack embayment, all of the Opx have considerably lower Ni contents than the Opx in the least fractionated Foy offset sample. However, the Opx in the well-mineralized embayments have, in general, higher Ni than Opx from the poorly-mineralized embayments. Whereas the marginal facies of the Offset Dykes were formed from the sulphide-undersaturated parental SIC magma, all of Mafic Norites were formed from magma that had been Ni-depleted due to formation of the Ni-Cu-PGE ores. A $D_{\text{Ni}}$ (Ni in Opx/Ni in melt) value = 6.5 was determined from the Opx and whole rock compositions of the Foy Offset samples and used to calculate the compositions of the melts that formed the Mafic Norites.

1 Introduction

Approximately 60% of the Sudbury Igneous Complex (SIC) Ni-Cu-PGE sulphide deposits lie within “embayment” structures at the base of the Sublayer, a laterally discontinuous fragment- and sulphide-rich unit that occurs exclusively within the embayment structures. The Sublayer is overlain by the Mafic Norite, which is also discontinuous along strike and localized above and close to the embayments. Whereas some of the embayments contain economic grades and tonnages of Ni-Cu-PGE sulphides, other embayments only contain sub-economic amounts of sulphides. The compositions of orthopyroxene (Opx) in the Mafic Norite collected from the embayments shown Figure 1 were determined to ascertain if it was possible to use the compositions of the Opx in combination with whole rock analyses of the Mafic Norite to discriminate between well-mineralized and poorly-mineralized embayments. Using appropriate mineral/silicate melt partition coefficients, the mineral chemistry of the Opx can also be used to determine the trace element contents of the magmas from which the Mafic Norite formed. A partition coefficient, $D_{\text{Ni}}$ (=Ni in Opx/Ni in melt) appropriate for Sudbury was obtained by measuring the Ni contents of Opx in the fine-grained, fragment-free margins of “Offset Dykes” and the whole rock Ni contents of the rocks that host the Opx.

2 Geology of the Sudbury Igneous Complex

The Main Mass of the SIC, from the top down, consists of the Granophyre, Transition Zone Quartz Diorite, and the Felsic Norite. The Mafic Norite occurs at the base of the Felsic Norite, but is restricted to areas above and immediately adjacent to the embayments where it overlies the Sublayer in the North Range. In addition, Quartz Diorite occurs in the radial and concentric “Offset” dykes. All rock types are believed to have formed from a single melt sheet produced by the impact of a large meteorite (Lightfoot et al. 1997). The fragment- and sulphide-free fine grained margins of the offset dykes are believed to be representative of the bulk composition of the melt sheet (Keays and Lightfoot 2004); the chilled margins of the Offset Dykes indicate that the initial Ni and Cu contents of the SIC were 83 and 98 ppm, respectively. The extreme Ni, Cu and PGE depletion of the Felsic Norite provides compelling evidence that all the metals in the Ni-Cu-PGE sulphide ores were sourced from the overlying Felsic Norite (Lightfoot et al. 2001). An important feature of the Sudbury ores is that they segregated from the melt sheet...
before crystallization of any silicates commenced and that all of the rocks, except the fragment-free margins of the Offset Dykes, formed from sulphide-saturated magma (Keays and Lightfoot 2004). Another important feature is that the noritic rocks are significantly thicker over well-endowed embayments compared to poorly-endowed embayments (Lightfoot 2016).

3 Methods

The compositions of the Opx in the Mafic Norite were determined using electron microprobe analysis followed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the University of Melbourne. The cores of the Opx were selected for analysis; this was necessitated in some cases due to alteration of the Opx. Also, only Opx grains that were well removed from sulphides were analysed. The whole rock compositions of the samples in which the Opx occurred were also determined. Because of the wide range in the D_Ni values published in the literature, it was necessary to establish a D_Ni appropriate for the SIC. To this end, the Ni contents of the Opx in the fine grained, sulphide- and fragment-free margins of the Foy Offset Dyke were measured together with Opx in inclusion-rich quartz diorite from the Ministic Offset; the whole rock analyses of the Foy QD hosting the Opx were taken to represent the composition of the melt. The Ni contents of the melts from which the Opx crystallized were calculated by dividing the Ni contents of each of the Opx by the calculated partition coefficient.

4 Results

The data plotted in Figures 2, 3 and 5 are analyses of individual grains of Opx whereas the points plotted in Figure 4 are the primitive mantle normalized averages of the Opx analyses in a single thin section. In most cases, the analytical data for Opx from each sample cluster together (cf Fig. 2); for example, the data for the Opx in the two different Ministic Mafic Norite samples analysed plot in two distinct clusters. The Ni contents of the Opx in the Mafic Norites range from 84 to 1142 ppm with samples from the best mineralized embayments (Levack and Victor) having significantly higher Ni contents than those from the embayments that are less well mineralized such as Foy and Trill, with the exception of the Sultana sample and one of the Victor samples (Fig. 2). The Opx from the poorly-mineralized embayments generally have a narrow range in Ni contents, whereas those from well-mineralized embayments display a much broader range in Ni contents. For example, the average Ni contents of the Opx in the five Foy Mafic Norite samples range from 108 to 121 ppm; on the other hand, the average Ni contents of the Opx in the ten Levack Mafic Norite samples vary from 184 to 1052 ppm (Fig. 2). With the exception of the Opx in one sample, the Levack Opx exhibit a distinct trend of increasing Ni contents with increasing Mg#.

The Ni contents of the Opx in the two Foy Offset Dyke samples are higher than those in all the Mafic Norite samples with the exception of the Opx in one of the Levack samples; the Opx in the two Foy Offset Dyke samples also have the highest Mg# of any of the Opx. Whereas there are large variations in the Cr contents at constant Ni in most samples, some of the Levack samples exhibit a trend of increasing Ni at constant Cr (Fig. 3); the Levack samples with the highest Ni contents have the lowest Cr contents (Fig. 3). The Opx in the Offset Dyke fine-grained margins exhibit a trend of increasing Cr contents with increasing Mg# (Fig. 3).

On an extended spidergram, there is a decrease in primitive mantle normalized values from Lu through to La (Fig. 4); Sr, Zr and Eu exhibit prominent negative anomalies. Although the patterns of all samples from all the embayments are broadly similar, the Levack samples have lower HREE and elevated Zr and Ti relative to samples from the other embayments (Fig. 4).

The Opx used to calculate a D_Ni suitable for the SIC were those from the fine-grained and fragment-free marginal Quartz Diorite phase of the Foy Offset Dyke. The rationale for this was that these Opx had the largest Mg# and were therefore most likely to have crystallized from the most primitive SIC melt. The average Ni content of the Opx in the two Foy Offset samples is 540 ppm. As the average whole rock Ni content of these samples is 81, the calculated D_Ni = 6.5. The calculated Ni contents of the melts in equilibrium with the Opx in the Mafic Norites are all less than that of the initial SIC magma with the exception of the Opx in equilibrium with one of the Levack samples (Fig. 5). It is acknowledged that because of the small number of samples, the calculated D_Ni is not robust and therefore the melt compositions are estimates only.
5 Discussion

Lightfoot et al. (2001) demonstrated that the upper part of the Felsic Norite is strongly depleted in Ni, Cu and the PGE, containing much less of these metals than both intraplate basalts and the fragment-free fine grained margins of the Offset Dykes. They proposed that the metals stripped out of the Felsic Norite formed the Ni-Cu-PGE sulphide deposits at the base of the Sublayer. Lightfoot et al. (2001) also argued that the marginal Quartz Diorite phase of the Offset Dykes formed prior to sulphide-saturation of the impact melt sheet and that its Ni and Cu contents, which average 83 and 97 ppm Ni and Cu, respectively, represent the Ni and Cu contents of the impact melt which formed the SIC. The significantly lower Ni contents of Opx in the Mafic Norite samples relative to those of the Foy marginal Quartz Diorite is consistent with the Mafic Norite having been formed from a sulphide-saturated magma that had been depleted in Ni, as argued by Keays and Lightfoot (2004). As a result, the calculated Ni contents of the melts from which the Mafic Norites crystallized are all less than that of the initial Ni content of the SIC melt (Fig. 5). The amount of melt depletion appears to have been highly variable, with the melts that formed the Foy embayment Mafic Norite having a calculated Ni content of only 16 ppm Ni whereas the melts that formed most of the Levack embayment Mafic Norites exhibit very little Ni depletion relative to that of the sulphide-undersaturated initial SIC melt (Fig. 5). Indeed, the melt that formed some of the Levack Opx contained more Ni than that of the initial SIC melt. The very low calculated Ni content of the Foy melt can not be due to fractionation as the Foy Opx have higher Mg# than most of the other Opx grains (Fig. 5).

Figure 3. Scattergram of Cr$_2$O$_3$ vs Ni in individual grains of Opx in Mafic Norite from different embayments.

The fact that the embayment structures that are the least prospective for Ni sulphide mineralization host rocks that were formed by strongly Ni-depleted melts is counter intuitive as one may have expected that the embayment structures containing the most Ni-depleted melts would have been the best mineralized. However, the opposite is true. A pertinent question is: where is all the Ni that was stripped out of the melt that formed the Mafic Norite in the Foy embayment? If the embayment is situated in a trough, it may be that the missing Ni is in Ni-Cu-PGE sulphides at depth in that trough (similar to the low Ni-tenor WD150 and 155 deposits in the funnel of the Foy Offset). Another possibility is that there was vigorous convection in the SIC melt sheet during ore formation and immiscible magmatic sulphides dropped out of the convecting magma in the well mineralized embayments and then the melt, which was now depleted in the chalcophile elements, was swept along the bottom of the chamber and came to rest in the poorly mineralized embayments.

Figure 4. Extended spidergram of average primitive mantle-normalized concentrations of elements in the Opx in individual thin sections. The Levack-Lo-Ni sample has the lowest Ni content of the Levack samples and vice versa for the Levack-Hi-Ni sample. The primitive mantle values are from McDonough and Sun (1995).

A question that needs to be addressed is why do the Opx in the well-mineralized embayments have a much wider range in Ni than those in the less well-mineralized embayments? Also, why is it that the most of the Opx in the Mafic Norites in the well-mineralized intrusions embayments contain higher Ni than those in the poorly mineralized embayments?

Lightfoot et al. (2001) used the R-factor equation of Campbell and Naldrett (1979), $Cs = Cs \cdot D \cdot (R+1)/(R \cdot D)$, in which $Cs =$ metal in sulphide, $Co =$ metal in initial silicate melt, $D =$ partition coefficient of metal, and $R =$ ratio of silicate melt to sulphide melt, to calculate the chalcophile element contents of the magmas that formed the ore deposits. For the Ni-Cu-PGE sulphide ores of the Creighton embayment, which average ~7 % Cu and ~5% Ni, Lightfoot et al. (2001) determined that the Cu and Ni contents of the magma from which the sulphides segregated must have been 172 and 265 ppm, respectively. However, this means that the magma from which the sulphides had more than double the Cu and Ni contents of...
the initial SIC melt. To explain this enrichment, Keays and Lightfoot (2004) suggested that sulphides formed in the upper part of the SIC melt sheet were dissolved when they reached the base of the Felsic Norite, thereby enriching the basal depleted melt in Ni.

We suggest that segregation of Ni-Cu-PGE sulphides from thin parts of the SIC melt sheet and settling of these sulphides to the base resulted in the formation of small mineral zones in embayments like Foy and Trill. In contrast, over the well-mineralized embayments, where the norites are thickest (Lightfoot 2016), sulphides from the upper part of the melt sheet continued to rain down and be re-dissolved in the magmas from which the Mafic Norites were formed, thereby enriching it in Ni and the other chalcophile elements. Support for this interpretation is provided by the wide range in the Ni contents of Opx in the Mafic Norite samples in the well-mineralized Levack and Victor embayments (Fig. 2). This wide range in Ni contents would have been produced by heterogeneous addition of the settling sulphides to the depleted magma in the embayment.

The differences in the trace element contents of the Opx in the Mafic Norite samples from different embayments demonstrates that there were subtle variations in the composition of the magmas that formed the Mafic Norite and, presumably Sublayer, in these embayments (Fig. 4). These observations are consistent with those of Darling et al. (2010) who concluded from a Pb isotope study of the SIC that the melt sheet was heterogeneous from an early stage.

Figure 5. Scattergram of the calculated Ni contents of the melts from which the Opx crystallized plotted against the Mg# of individual grains of Opx. The Ni content of the initial SIC melt is from Keays and Lightfoot (2004); melt compositions were calculated using an Opx/melt partition coefficient for Ni of 6.5 (see text).

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References


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Petrogenesis of PGE reefs in the Penikat intrusion, Finland

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Abstract. The 2444 Ma Penikat layered ultramafic-mafic intrusion in northern Finland contains at least six platinum-group element (PGE) enriched horizons, including the SJ, AP and PV reefs, each with 4 to >10 ppm Pt+Pd over a width of between <1 and > 10 m. The mineralisation formed by orthomagmatic processes as indicated by strong positive correlations between Pt and Ir contents. Subdued stratigraphic variation in incompatible trace element ratios and Nd isotope ratios indicates that mixing of magmas of distinct lineage, or in situ contamination with country rocks, was not required to form the PGE reefs. There is also no evidence for addition of external sulphur to the magma, based on S/Se ratios at, or below, primitive mantle levels. Instead, sulphide melt saturation was likely reached in response to silicate fractionation of a siliceous high-magnesium basalt. We propose that the SJ reef formed through hydrodynamic sorting of crystal mushes, whereas the AP and PV reefs formed through tectonically induced injection of evolved, PGE- and volatile-rich, plagioclase-charged melt into bedding-parallel dilational zones within the semi-consolidatedcumulate pile.

1 Introduction

The northeastern part of the Fennoscandian Shield hosts more than two dozen Palaeoproterozoic (~2440 Ma, Huhma et al. 1990) layered mafic-ultramafic intrusions. Their compositions vary from ultramafic dominated (Tornio and Näränkävaara) to mafic-ultramafic interlayered (Kemi, Penikat, Portimo, Koitelainen, Akanvaara), to predominantly mafic (Koillismaa). Based on similarities in their stratigraphy, some of the intrusions may represent dismembered fragments of larger magmatic bodies. The footwall to most of the intrusions is Archaean granite gneiss whereas the hanging wall rocks consist of older Palaeoproterozoic metavolcanics or younger supracrustal sequences deposited on a Palaeoproterozoic erosional unconformity (e.g., Alapieti et al. 1990). None of the intrusions is currently exploited for PGE, but an exploration programme in the Suhanko block of the Portimo intrusion is at an advanced feasibility stage.

2 Lithostratigraphy of the Penikat intrusion

The exposed portion of Penikat is 23 km by 1.5-3.5 km. It has been delineated to a depth of 0.5-2.5 km by drilling and seismic reflection data. The intrusion is sub-divided into 6 megacyclic units (MCU I-VI). As a whole, it is relatively mafic, with ultramafic rocks making up <10% of the stratigraphy (Fig. 1). Most rocks are gabbronorites with 40-60% plagioclase, 10-20% orthopyroxene and clinopyroxene each, as well as accessory oxides, quartz, and phlogopite. In comparison to the nearby Kemi intrusion, Penikat is poor in ultramafic rocks (Alapieti et al. 1990), contains only thin chromitite (cm - dm, vs 10s of metres at Kemi), and is enriched in PGE (up to 10s of ppm, vs <200 ppb at Kemi)(Halkoaho et al. 1990a,b; Huhtelin et al. 1990).

3 Description of the PGE-reefs

3.1 The SJ (Sompujärvi) reef

The mineralisation occurs within the lowermost ultramafic rocks of MCU IV, but may extend, in patchy form, for several decimeters or meters into the footwall where it can be associated with chromite disseminations and pyroxenite lenses, or into the peridotitic hanging wall. In many cases, the lowermost ultramafic rock of MCU IV is a cm-to-m-thick chloride schist enriched in disseminations or stringers and schlieren of chromite. This is overlain by orthopyroxenite and/ or lherzolite. The basal contact of MCU IV ultramafic rocks is undulating and irregular, showing a transgressive relationship with regard to the footwall norite. The MCU IV ultramafic rocks are laterally of variable thickness, and they may pinch out and form channels and potholes, enriched in disseminated chromite. The SJ reef has average grades (normalised to 1 m) of between 4-10 ppm PGE. Grades are locally variable, but regionally broadly consistent; Of 400 holes drilled through the SJ reef along the strike of the intrusion, only 20 (5%) contained less than ~100 ppb PGE. Highly enriched grades
occur at Kirakkajuppura, e.g., 46.4 ppm Pd and 18 ppm Pt over 11.2 m. The published mineral resource (to a depth of 100 m) for the Sompujärvi block stands at 6.7 mt at a grade of 5.36 ppm Pd and 3.08 ppm Pt over 0.97 cm (Eerola et al. 1990). Average sulphur contents are < 0.13% (Halkoaho et al. 2005). Sulphur loss related to Svecofennian metamorphism is considered to have been insignificant, judging from broadly mantle-like S/Se ratios.

Figure 1. Stratigraphy, CIPW norms and modified differentiation index in a profile through the Penikat intrusion in the Ala-Penikka block (modified after Alapieti and Halkoaho, 1995). Rock types: 1 = peridotite+pyroxenite, 2 = gabbro-norite (with cumulus opx and cpx), 3 = gabbro-norite (with intercumulus augite), 4 = transition zone, 5 = contact zone, 6 = anorthosite, 7 = bronzite cumulate layer.

3.2 AP (Ala-Penikka) reefs

Analogous to the SJ reef, the AP1 and AP2 reefs are present along most of the strike length of the intrusion. They are located 250 and 340 m above the base of MCU IV, respectively. The AP1 reef is normally 20-40 cm thick and of erratic grade. The mineralisation is closely associated with sulphides (0.52% S) in a 3- to 30-cm-thick mottled anorthosite which is underlain by gabbro-norite and overlain by norite (Fig. 2b). Average grades are 7 ppm Pd and 2 ppm Pt (Halkoaho et al. 2005). The mineral resource stands at 3.5 mt @ 6.16 ppm Pd and 1.68 ppm Pt, 0.11 ppm Rh, 0.28 ppm Au, and 0.21 wt.% Cu (average reef thickness 0.73 m; Eerola et al. 1990). The AP1 anorthosite may locally transgress across the layering in the footwall gabbro-norite. In the Ala-Penikka block, this has resulted in a 250-m-wide pothole (Fig. 3) in which the AP1 reef is up to 20 m thick at an average grade of 4 ppm Pt+Pd+Au. The pothole is characterised by abundant lenses of pegmatoid, several faults, a dolerite dyke, and Cl-rich apatite. Some 200 m directly above the pothole occur sub-vertical pegmatoidal veins and anorthosite fragments. These observations suggest that the pothole formed through slumping of semi-consolidated cumulates and enhanced percolation of sulphur-bearing fluids or melts.

Figure 2: (a) Layered anorthosite and gabbro-norite, ~ 100m above base of MCU IV. This interval forms the most prominent marker horizon across the Penikat intrusion. (b) The AP1 reef, Ala-Penikka block. (c) The AP 2 Reef anorthosite, Ala-Penikka block. Length of the white plates are 10 cm in each case.
Analogous to the AP1 reef, the AP2 reef is equally hosted within a narrow (~5 cm) anorthosite (Fig. 2c). It contains 11.4 ppm Pd and 3.4 ppm Pt. AP2 has less base metal sulphides (0.35 wt% S) than AP1, but sulphide-rich patches may locally contain several 10s of ppm PGE. The sulphides in both AP reefs have Cu/Ni 1.4-2.7, Pd/Pt 3.7, and Pd/Ir 170-240, i.e., the mineralisation is of a more differentiated composition than that of the SJ reef.

Figure 3: Map of the large pothole of the AP1 reef. Note cross-cutting relationship of the pothole across several gabbronorite and anorthosite layers, and thickening of sulphidic anorthosite in the centre of the pothole.

### 3.3 The PV (Paasivaara) Reef

The PV reef is located within a broad (10-40 m wide) zone of mineralisation hosted by the so-called “Transition Zone”, a heterogeneous interval immediately below MCU V, 700-1000 m above the AP reefs. The Transition Zone is characterised by strong lithological and chemical variation, expressed by interlayering of mela- and leucogabbroic rocks, anorthosite and pegmatoids. The abundance of anorthosite is particularly noteworthy; There are 3 layers, each 1-2m wide, whereas anorthosite is rare in the underlying rock formations. All 3 anorthosite layers are directly overlain by melanocratic rocks suggesting a genetic relationship between anorthosite and the melanocratic layers. Locally, the anorthosite may be enriched in chromite. Many of the Transition Zone rocks show a strong enrichment in highly incompatible elements such as K and P. The PGE and Cu are enriched in the anorthosites and in pegmatoid that is usually closely associated with the anorthosites. The best PGE grades are found within the uppermost mottled anorthosite (average thickness of mineralisation: ~1m, 2.3 ppm Pd and 3.9 ppm Pt). The mineral resource is 5 mt @ 2.58 ppm Pd, 4.04 ppm Pt, 0.08 ppm Rh, 0.61 ppm Au, 0.28 wt.% Cu, and 0.63 wt.% S over a reef thickness of 1.09 m. P/Pd is ~2, the highest in the intrusion. The primitive mantle-normalised metal patterns resemble those of the SJ Reef, i.e., are less fractionated than those of the AP reefs.

### 4 Discussion

It is proposed that the four Penikat PGE reefs (SJ, AP1, AP2, PV) formed through different processes. The SJ reef bears many similarities to the Merensky Reef of the Bushveld Complex. Both are proposed to have formed via hydrodynamic sorting of crystal slurries (cf Maier et al. 2013; Forien et al. 2015). This model is consistent with field and compositional evidence, e.g., the abundance of schlieren and lenses that we interpret as flow structures, the highly irregular enrichment of chromite and PGE along strike, the presence of potholes, and the paucity of PGE-bearing sulphides in the rocks above the reef.

Compared to most other PGE reefs globally, the AP and PV reefs are unusual in that the mineralisation is largely hosted by anorthosite seams. The PV reef is additionally highly enriched in incompatible trace elements, magmatic breccia and pegmatoidal lenses. We propose that readjustments in the subsiding semi-consolidated cumulate package locally caused bedding-parallel shearing and pull-apart structures, both at the top of and within the cumulate pile. Evolved melt enriched in incompatible elements, volatiles and PGE-rich sulfides, derived from the underlying compacting cumulate package was filter pressed into the shear planes and pull apart structures (Fig. 4). Downward draining of dense Fe-rich residual liquid towards the centre of the intrusion resulted in the formation of residual anorthosite (cf Scoates et al. 2010).

### 5 Summary and conclusions

The Penikat intrusion contains several PGE reefs, analogous to many other layered intrusions. Though all reefs have been traced along much of the strike length of the intrusion, they show slightly less continuity and lower grade than the Bushveld or Great Dyke reefs, possibly due to faster cooling resulting from smaller intrusion size. However, grades are locally extremely high, notably in potholes. It is proposed that the SJ reef formed by magma replenishment followed by hydrodynamic crystal sorting during subsidence of the intrusion. The AP and PV reefs formed through upward emplacement of PGE-rich residual liquids induced by structural readjustments.
Figure 4: Schematic model for formation of the Penikat PGE reefs. The SJ reef formed by hydrodynamic sorting of the MCU IV magma influx leading to concentration of chromite, sulphide and olivine-pyroxene. Note abundance of potholes and localised injections into floor. The AP reefs formed through tectonically induced mobilisation of sulphide rich melt layers within MCU IV, upwards into dilatational zones including major potholes that formed as pull-apart structures. The PV reefs formed through a combination of processes instrumental in the formation of SJ and AP reefs; Initially, ultramafic cumulates formed through hydrodynamic sorting of MCU V magma influx. The resulting chamber subsidence and tectonism led to mobilisation of sulphide-rich residual melt from within MCU IV which ascended to the base of MCU V (possibly by exploiting major syn-magmatic normal faults) where the melt spread out in a sill-like manner, locally inducing partial melting of the host rocks, to form a heterogenous package of anorthosites, pegmatoids, and (mela)gabbroic rocks.

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References


Crustal level of the 1.88 Ga Svecofennian Ni-Cu bearing intrusions

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Abstract. Svecofennian 1.88 Ga Ni-Cu deposits are hosted by mafic-ultramafic intrusions, which occur in terrains of variable metamorphic grade likely to represent different crustal levels. More accurate data on the crystallization conditions and thus on the crustal intrusion level are provided by thermobarometric studies. Based on the recent study of the contact aureole of the small Ni-Cu hosting Särkiniemi intrusion in the Kotalahti area, central Finland, an estimate of 15 – 20 km (4.5 - 6 kbar) for the crystallization depth is indicated. Combined with the earlier studies for the Svecofennian intrusions the study result indicates a favourable crustal level for nickel sulphide deposition at 1.88 Ga.

1 Introduction

Nickel sulphide deposition took place in the Fennoscandian and similarly in the Canadian Shield at 1.88 Ga. Examples include the Kotalahti and Vammala Nickel Belts in Finland, the Västerbotten Nickel Belt in Sweden (Weihed et al. 1992) and the Thompson and Cape Smith Nickel Belts in Canada (e.g. Hulbert et al., 2005; Lesher, 2007; Layton-Matthews et al. 2011; Naldrett 2011). Many of the 1.88 Ga intrusive Svecofennian nickel deposits occur in the Kotalahti Ni Belt, which is located close to the Archaean craton margin, similar to the settings of the Thompson and Cape Smith Belts. Margins of ancient Archaean cratons are favourable places for Ni-Cu-PGE concentrations (Begg et al. 2010) and can develop into rift zones with transcrustal fault zones, along which the mafic-ultramafic magma ascends (Hagemann et al. 2011). For the magma to ascend a melt transport network is developed. According to Barnes et al. (2016) the key elements in development of the network are 1) the transition whereby dykes reorient into sills; 2) emergence of dykes from sills; and 3) interaction of propagating dykes and sills with existing mechanical anisotropies (fractures, foliations, lithological contacts). The resulting transport network thus enables magmas to form intrusions at different levels within the crust.

Some studies have been made to this topic earlier in Finland. Tuisku and Makkonen (1999) estimated, on the basis of the crystal chemistry of orthopyroxene-clinoamphibole-spinel coronas between plagioclase and olivine, that the crystallization depth for the Saarjärvi intrusion in south eastern Finland was 17 – 20 km (900 °C, 5 – 6 kbar). Here we present new data on the crystallization conditions of one small, Ni deposit hosting intrusion near the Kotalahti deposit, central Finland and discuss how the estimated intrusion depth and the compositions of the host intrusion and the ore correlate with the Svecofennian ore model (mineral system).

2 Kotalahti area and the Särkiniemi Ni-Cu deposit

The Kotalahti area is characterized by the Kotalahti Dome, which is composed of Archaean gneiss surrounded by a Palaeoproterozoic craton-margin supracrustal sequence of quartzites, limestones, calc-silicate rocks, black schists and banded diopsite amphibolites. Metamorphism reached the amphibolite facies, causing gneissose and migmatitic textures in the supracrustal rocks. Several nickel deposits have been found in the Kotalahti area and in its close vicinity. The most important deposits include Kotalahti, Rytky, Särkiniemi, Sarkalahti and Hanhisaalo. The Särkiniemi intrusion lies within mica gneiss, higher in the stratigraphy than Kotalahti and Rytky, which occur in the contact zone of Archaean gneiss and Proterozoic schists (Fig. 1). In total, 12.35 Mt of ore at 0.66% Ni and 0.26% Cu was mined at Kotalahti during 1959–1987 (Puustinen et al. 1995). Exploration at Rytky continues.

The Särkiniemi intrusion is located within schollen-schlieren migmatites between major shear zones. As a result of shearing competent rocks like mafic-ultramafic intrusion bodies have been split into smaller pieces from their original forms. In Särkiniemi area numerous small gabbro fragments are found (from centimetre scale upwards), while the largest one forms the Särkiniemi intrusion and covers an area of around 100 x 200 m at the surface section (Fig. 2). It is composed of the western peridotite and eastern metagabbro, which both host a Ni-Cu ore body. The western, peridotite-hosted ore body in Särkiniemi was mined during 2007-2008 totalling 0.12 Mt at 0.92% Ni and 0.44% Cu. The gabbroic, eastern part of the Särkiniemi intrusion extends to the 120 m level, while the western, peridotitic part is shallow and restricted to faults on each side. A distinct contact metamorphic aureole, especially around the eastern gabbro body, is represented by a several meters thick hornfels between the intrusion and the migmatites (Kontoniemi and Forss 1997). This kind of contact aureole is very rare within the Svecofennian intrusions.

The hornfels differs from the migmatitic wall rock
gneiss by the almost total absence of neosome material. Different types of hornfels include 1) biotite–amphibole gneiss, 2) pyroxene-cordierite gneiss and 3) pyroxene gneiss (Kontoniemi and Forss 1997). The following main mineral assemblages have been generated (Suvanto 2015): bt-pl-opx-qz-crd, hbl-pl-bt, bt-crd-opx-aph, bt-opx-aph and aph-crd-bt. Pyrrhotite dissemination is common within the hornfels.

Figure 1. The main domains of the Svecofennian Ni deposits on the simplified lithological map (Bedrock of Finland-DigiKP, Geological Survey of Finland). Särkiniemi deposit locates within the Kotalahti Ni Belt close to the Kotalahti and Rytky deposits. Red squares indicate the most important Ni deposits and red dots the minor deposits. Modified from Makkonen (2015).

3 Thermobarometry

The TWQ software package of Berman (1991, 2006) was used to calculate PT-conditions of crystallization of the host migmatites and the contact metamorphic hornfelses at Särkiniemi (Fig. 3). The Berman (1988) dataset with the update by Berman and Aranovich (1996) was used for the calculations. Error was estimated from the intersections of 3 or 4 independent equilibria by exclusions of intersections outside of 1.5σ and parallel (< 20°) equilibria. The bulk composition of the samples was used to calculate isochemical phase diagrams in order to test the consistency of the results with the observed mineral assemblage, and possible influence of disequilibrium in the results. The datasets used were the same as in the PT-calculations but we also tested the Holland and Powell (1998) dataset. Generally the calculated P and T of the hornfelses were within the fields of observed assemblages in the phase diagram, which is interpreted to reflect achievement of equilibrium and minor re-equilibration during cooling. The migmatites, however, gave lower T than expected from the observed assemblage, which might indicate re-equilibration during cooling combined with the prolonged cooling due to extra heat from the intrusion.

Figure 2. Kotalahti Dome geology and location of the most important Ni deposits. Modified from Mäkinen and Makkonen (2004). In the Kotalahti deposit the ore bodies are marked: M = Mertakoski, V = Välimalmio, H = Huuhtijärvi.

4 Implications for the mineral system

The Svecofennian bedrock geology in Finland suggests several intrusion levels for the 1.88 Ga intrusions. These observations include 1) the correlation of the metamorphic grade with the amount and composition of the intrusions and 2) the form of the intrusion bodies. The Svecofennian mafic–ultramafic intrusions occur throughout the Svecofennian of central and southern Finland, but most of the nickel-bearing intrusions occur within the Kotalahti and Vammala nickel belts to the south and east of the Central Finland Granitoid Complex (Fig. 1). The
metamorphic grade within these two belts is high-amphibolite to granulite facies (low P, high T, Bedrock of Finland-DigiKP 2017) and the magmatic mineralogy of the intrusions is often destroyed or even recrystallized. Intrusions outside these belts and within a lower metamorphic grade areas are better preserved in their primary magmatic features. Comagmatic volcanic rocks (tholeiites-picrites) also occur within the areas of lower metamorphic grade, suggesting shallower crustal depth than the areas of high-amphibolite to granulite facies metamorphism.

Figure 3. Thermobarometry of the hornfelses and garnet-bearing gneisses and migmatites near the Särkiniemi intrusion (ellipses) indicating 4.5 – 6 kbar pressure for the hornfels formation. Stars give, for comparison, initial subsolidus and cooling stage conditions of the Saarijärvi intrusion (in the igneous body itself) in Juva area 65 km south of Särkiniemi (Tuisku and Makkonen 1999). Some key equilibria of melting or dehydration are given for reference.

Shallow intrusions are expected to have a more sill-like form than those crystallized at a greater depth as a result of sub horizontal magma flow because of the smaller density difference. This is seen e.g. in southern Savo province in SE Finland where gabbro-diorite intrusions form sills that were later folded upright outcropping now as narrow and long bodies. These intrusions can be interpreted to represent the most fractionated and high-level melts (low Ni/Cu in related sulphide ores), whereas the peridotite and peridotite-gabbro bodies outside the gabbro-diorite belt occur as more rounded and less elongated bodies (Makkonen 1996, 2015).

The P-T determinations of the crystallisation conditions for the intrusions provide more accurate crustal depth estimate than the comparative geological observations. The crustal depth estimations of 15 – 20 km (4.5 – 6 kbar) for the Särkiniemi intrusion and 17 – 20 km (5 – 6 kbar) for the Saarijärvi intrusion are similar within errors. Both intrusions host nickel mineralization, which indicates that this crustal level at 1.88 Ga was favourable for magmatic nickel sulphide ores to form.

Särkiniemi intrusion has crystallized from a relatively fractionated parental magma (MgO ~ 8 w%) resulting in low Ni/Cu value (1.7) of the related sulphide ore. The intrusions located within the Archaean gneiss or in the contact zone of the Archaean gneiss and Palaeoproterozoic rocks in the Kotalahti area (e.g. Kotalahti and Rytky) have a more primitive parental magma (MgO ≤ 15 w%) and distinctly higher Ni/Cu value (2.5) of their related sulphide ore (Mäkinen and Makkonen 2004; Makkonen 2015). This suggests a correlation between the crustal depth and primitiveness of the parental magmas for the intrusions. However, to study this correlation carefully data from larger amount of deposits should be gathered.

Ascending magma will meet several kinds of wall rocks, physical environments and possibly sulphur-rich rocks to assimilate. At Särkiniemi the R-factor is low, around 200, which suggests effective assimilation of sulphur-bearing crustal rocks. The spatially closely associated sulphide-rich black schists of the Kotalahti area are good candidates for a sulphur source.

In conclusion, if the intrusion level can be defined and the critical parameters for ore formation at that depth and below can be mapped or estimated the ore potential evaluation has a good basis. In Figure 4 the proposed relative levels of the Särkiniemi and Saarijärvi intrusions are marked.

Figure 4. Schematic model for the magma ascend and the intrusions forming at different crustal levels, with the proposed relative levels of the Särkiniemi and Saarijärvi intrusions. Numbers 1–4 refer to (1) Kotalahti-type intrusions, where differentiation produced layered ultramafic to gabbroic rocks; (2) Vammala-type intrusions, representing ultramafic, weakly differentiated magma conduits; (3) ultramafic cumulate bodies from which the residual melt has been efficiently expelled upward; (4) gabbroic intrusions, with or without peridotite as a result of later pulses of olivine-bearing melt from lower magma chambers. Modified from Makkonen (2015).
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The Luanga deposit, Carajás Mineral Province, Brazil: the origin of different styles of PGE mineralization

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Abstract. The Neoarchean Luanga Complex, located in the eastern portion of the Carajás Mineral Province, hosts the largest Brazilian PGE deposit. The deposit is hosted by a sequence of layered ultramafic and mafic cumulates and has two distinct styles of significant PGE mineralization. The first, referred as Sulfide Zone, consists of a 10-50 m thick interval of disseminated base metal sulfides. The second, referred as silicate-related PGE, consists of several 2-10 m thick stratabound zones of cumulate rocks without associated sulfides and/or chromite. The Sulfide Zone hosts the bulk of PGE resources of the Luanga Complex (142 Mt at 1.24 ppm Pt+Pd+Au and 0.11% Ni). The Sulfide Zone has Pt/Pd ratios of 0.55 and a positive correlation between all PGE and S. The silicate-related PGE has Pt/Pd ratios of 1.2-1.3 and a strong depletion in IPGE. We suggest that the Sulfide-Zone is formed by a major event of segregation of an immiscible sulfide liquid in the magma chamber, while the silicate-related PGE mineralizations result from direct crystallization of platinum group minerals from a PGE-enriched magma.

1 Introduction

Most of the platinum-group elements (PGE) deposits are hosted by a small number of layered intrusions (Cawthorn et al. 2005 and references therein). These deposits can generally be subdivided into sulfide- and chromite-related, as exemplified by the world-class Merensky Reef and UG2 PGE deposits in the Bushveld Complex (e.g., Barnes and Maier 2002; Cawthorn et al. 2005; Naldrett et al. 2012). The magmatic processes that lead to PGE concentration within sulfide-related and chromite-related deposits should be highly efficient, such that magmas with PGE contents of few ppb may form layers with economic grade (e.g., Finnigan et al. 2008; Mungall and Naldrett 2008).

The systematic characterization of the PGE deposit of the Luanga Complex (142 Mt @ 1.24 g/t PGE+Au and 0.11% Ni; VALE internal reports), based on petrographic and geochemical data (Mansur 2017), indicates different styles of PGE mineralization within this layered intrusion. These results also indicate significant PGE mineralizations that don't fit into the sulfide-related and chromite-related deposit types, thus supporting a discussion about additional magmatic processes capable to concentrate PGE in mafic to ultramafic layered intrusions.

2 The Luanga Complex

The Luanga Complex is part of the Serra Leste Magmatic Suite, a cluster of Neoarchean PGE-mineralized mafic-ultramafic intrusions located in the northeastern portion of the Carajás Mineral Province (Ferreira Filho et al. 2007; Teixeira et al. 2015). The Luanga Complex is a 6 km long and up to 3.5 km wide layered intrusion (Fig. 1), consisting of, from base to top, ultramafic cumulates (Ultramafic Zone), an intercalation of ultramafic and mafic cumulates (Transition Zone) and mafic cumulates (Mafic Zone) (Fig. 1a). geological sections defined by drilling indicate that the Ultramafic Zone overlies the Transition Zone, which overlies the Mafic Zone, suggesting thus that the layered sequence is tectonically overturned (Fig. 1b). The Ultramafic Zone, up to 800 m-thick, comprises a sequence of peridotite with few meters thick orthopyroxenite lenses within the upper portions. The Transition Zone, up to 800 m-thick, consists of a sequence of interlayered ultramafic and mafic cumulate rocks (mainly orthopyroxenite, harzburgite and norite). The Mafic Zone, up to 2000 m-thick, consists of a monotonous sequence of noritic rocks with minor interlayered orthopyroxenite. Chromitite layers of variable thickness (up to 60 cm-thick) and textures occur mainly in the upper portions of the Transition Zone and the lowermost portion of the Mafic Zone (Mansur 2017). The contact of the Ultramafic and Transition zones is marked by a stratabound horizon of disseminated (~ 1-3 vol.% ) sulfides, referred as the Sulfide Zone. Several other intervals with distinct types of PGE mineralizations also occur within the Transition Zone.

3 PGE mineralizations

Three distinct types of PGE mineralization occur in the Luanga Complex: i) sulfide-related PGE, ii) silicate-related PGE, iii) chromite-related PGE. Due to their economic importance, in this study we focused on the first two types (Fig. 1b).

The sulfide-related PGE mineralization corresponds to the stratigraphic horizon referred as the Sulfide Zone and...
hosts the bulk of PGE resources of the Luanga Complex. The Sulfide Zone (Mansur and Ferreira Filho 2016) consists of a 10-50 m thick interval with disseminated sulfides located along the contact of the Ultramafic and Transition Zones (Fig. 1b). The precise location of the Sulfide Zone along the contact zone is variable, such that sulfides may be hosted just by the lowermost orthopyroxenite of the Transition Zone, or straddles the orthopyroxenite and the underlying peridotite of the Ultramafic Zone (Fig. 1b). The mineralogy of the Sulfide Zone does not show major variation through the deposit and consists of a sulfide assemblage of pentlandite > pyrrhotite >>> chalcopyrite. The occurrence of sulfides is not restricted to the Sulfide Zone. Minor sulfide dissemination and/or sulfide-rich veinlets also occur in thin (up to 8 m-thick) discontinuous shear zones located along the Luanga Complex. However, sulfides in these zones have distinct texture and mineralogy than those described within the Sulfide Zone, and are composed predominantly of chalcopyrite hosted in amphibole-rich sheared rocks. These occurrences are ascribed as remobilized sulfides along discrete cross-cutting shear zones.

The term silicate-related PGE mineralization is used to indicate PGE-mineralized rocks devoid of base metal sulfides and/or chromite. The silicate-related PGE mineralization of the Luanga Complex consists of 2-10 m thick stratabound zones across the Transition Zone. These zones occur above the Sulfide Zone and do not show extensive lateral continuity between different cross-sections (Fig. 1a). Silicate-related PGE mineralization commonly occurs at the contact between layers of distinct cumulate rocks in the Transition Zone, but its occurrence

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**Figure 1.** a Geological map of the Luanga Complex (modified from unpublished report of VALE). Note the location of drill holes used in this study. b Geological section on the central portion of the layered complex. PGE mineralized intervals are indicated (modified from Mansur and Ferreira Filho 2016).
within one single layer is also observed (e.g., norite layer intersected by drill hole LUFD-077; Fig. 1b). The hosting rocks, mainly harzburgite and orthopyroxenite, do not show any distinctive texture or change in modal composition that characterizes the PGE enrichment. In this way, the PGE enriched intervals were not identified during core logging or routine petrographic studies, being identified by their anomalous Pt-Pd contents. A remarkable feature is the occurrence of anomalously Ni-rich olivines (up to 7400 ppm Ni; Mansur and Ferreira Filho 2016) in harzburgites closely associated with silicate-related PGE mineralization. The plot of S versus PGE contents for unweathered samples with PGE contents higher than 500 ppb and/or S contents higher than 0.05 wt.% is shown in Figure 2a. The correlation of these PGE-enriched (> 500 ppb) and/or sulfide-bearing (> 0.05 wt.%) indicates three geochemically distinct groups: i) sulfide-related PGE, ii) silicate-related PGE and iii) remobilized sulfides (Fig. 2a). The sulfide-related PGE group comprises samples with high PGE and S contents (i.e., up to 7000 ppb and 1 wt.%, respectively). These samples correspond to orthopyroxenite and peridotite with interstitial base metal sulfides from the Sulfide Zone (Fig. 1b). The silicate-related PGE group comprises samples with high PGE (i.e., up to 2000 ppb) and very low S contents (< 0.1 wt.%). These samples correspond to orthopyroxenites and harzburgite from the Transition Zone (Fig. 1b). The group referred as remobilized sulfides corresponds to samples with high S (up to 0.7 wt.%) and low PGE contents (< 300 ppb). The latter correspond to sheared rocks with abundant amphibole and chalcopyrite. As these rocks do not show magmatic textures and have low PGE contents, they are not detailed on the present study.

Sulfide-bearing rocks from the Sulfide Zone contain 1-3 vol.% of sulfides with pentlandite > pyrrhotite >>> chalcopyrite. The modal proportion of base metal sulfides in these rocks is consistent with their high Ni tenors (16-18 wt.%), low Cu tenors (1.3-1.4 wt.%) and, consequently, high Ni/Cu ratios (10-12). These samples have strong positive correlation between PGE and consistent Pt/Pd ratios (~ 0.55). Pt values systematically lower than Pd is a characteristic feature of the Sulfide Zone, with Pt/Pd ratios consistently lower than 1 along the entire extension of the ore zone. Mantle-normalized patterns (Fig. 2b) for samples from the Sulfide Zone show high to moderate PGE enrichment (10-1000 times) and depleted Ni, Cu and Co contents. The PGE patterns are enriched in PPG relative to IPGE, with Ir and Os contents below their detection limits, 5 and 3 ppb, respectively. PGE patterns indicate a progressive increase from incompatible IPGE toward compatible PPG, as well as a distinct negative anomaly for Au (Fig. 2b). The low contents of base metals are compatible with rare base metal sulfides and very low S contents in this interval (Fig. 2a).

Figure 2. Geochemical data of different types of PGE mineralization. a Plot of PGE versus S contents for samples with S and PGE values higher than 500 ppb and 0.01 wt.% respectively. b Primitive mantle-normalized chalcophile element profiles for representative samples from the sulfide-related PGE and silicate-related PGE. Primitive mantle normalization values are from Sun and McDonough (1989).

4 Discussion and conclusion

Our results indicate that two highly different styles of magmatic PGE mineralization occur in the Luanga Complex. These are referred to as sulfide- and silicate-related PGE mineralizations (Fig. 2a).

The sulfide-related PGE, comprising the Sulfide Zone, consists of PGE associated with interstitial base metal sulfides and is similar to typical PGE deposits originated from sulfide liquids segregated from mafic–ultramafic magmas (e.g., Campbell et al. 1983; Barnes and Lightfoot 2005). The silicate-related PGE mineralization, on the other hand, occurs in rocks with no base metal sulfides. Host rocks of silicate-related PGE mineralization have no distinctive feature compared to adjacent unmineralized
rocks. Sulfide-related and silicate-related PGE mineralization have distinct mantle-normalized PGE profiles (Fig. 2b) and Pt/Pd ratios, typically 0.5-0.6 and 1.2-1.3, respectively. The differences between both mineralization styles, together with its different stratigraphic positions, suggest that they formed by distinct processes. Because these different styles of PGE mineralization are closely associated with the Transition Zone, a genetic model for their origin should be consistent with the magmatic evolution of this stratigraphic interval.

The crystallization of olivine cumulates in the Ultramafic Zone without the crystallization of sulfide minerals progressively upgrades the S content of the residual magma. The Transition Zone marks an abrupt change in the dynamics of the magmatic chamber, caused by several magma inputs characterized by cyclic units (Mansur and Ferreira Filho 2016). Hence, these periodic inputs of primitive magma are considered responsible to trigger the S saturation of the magma and consequently the segregation of a sulfide liquid at the contact of the Ultramafic and Transition Zones. Due to the high partition coefficients, PGE and base metals segregated into this sulfide liquid (Barnes and Lightfoot 2005) to form the Sulfide Zone.

The silicate-related PGE mineralization occurs above the Sulfide Zone (Fig. 1b). The Transition Zone originated from several magmatic pulses, such that a depleted resident magma that may have originated following the segregation of the Sulfide Zone may recover the original PGE content. Thus, if this magma does not reach the S saturation, the resident magma should become progressively enriched in PGE. Ni contents in olivine in cumulate rocks of the Transition Zone (up to 7,500 ppm) stand among the highest values reported in layered intrusions globally (Mansur and Ferreira Filho 2016). High Ni contents in olivine are associated with zones of silicate-related PGE mineralization, indicating that Ni and PGE anomalies in the Transition Zone are connected. This connection led to the interpretation that the PGE- and Ni-rich parental magma of the Luanga Complex result from the “cannibalization” of previously formed sulfides (Mansur and Ferreira Filho 2016), following the model proposed by Kerr and Leitch (2005). We suggest now that silicate-related PGE zones result from PGE saturation in an unusually Ni- and PGE-rich magma, leading to concomitant crystallization of silicates and Platinum Group Minerals (PGM). The accumulation of PGE apart from chromite- and/or sulfide-bearing rocks has been documented in few other layered intrusions (e.g., Ferreira Filho et al. 2007; Knight et al. 2011). Although experimental results and/or models suggesting a direct crystallization of PGM from magmas have been proposed (e.g., Hiemstra 1979; Brenan and Andrews 2001), there is no agreement about the processes that originate these chromite- and/or sulfide-free PGE mineralized cumulates. The investigation of PGM is currently being developed to further constrain the processes leading to PGE enrichment in silicate-related PGE mineralization.

In summary, we suggest that the Sulfide Zone marks a significant event of sulfide immiscibility and segregation in the Luanga Complex, while the silicate-related PGE mineralization marks successive events of PGE saturation of a Ni- and PGE-rich parental magma.

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Orthomagmatic Ni-Cu-PGE mineralization in the Eastern Alps? Evidence from Haidbach, Tauern Window, Austria

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Abstract. The Haidbach Cu-Ni mineralization, situated in the Felber valley close to Mittersill (Salzburg, Austria), hosts precious metal minerals associated with pyrrhotite, chalcocyprite, pentlandite, pyrite, sphalerite, Ni-Co-Fe sulpharsenides and rarely included in silicate matrix (amphibole, chlorite). Most abundant are Ni-Pd tellurides of the melonite-merenskyite series (ca. 45% of the grains), followed by hessite (22%), sperrylite (16%) and electrum (12 %; 25-35 atomic percent Ag). Less common are michenerite, irarsite, petzite and Pb selenide. Rhenium sulphides included in pyrite and chalcocyprite comprise a more common euhedral phase of (Re,Cu)S2 stoichiometry and a Re-Pb sulphide forming small platelet-like crystals similar to molybdenite, which was also encountered in the ore. The mineralization is hosted by hornblende-nitite, chlorite-epidote schist and chlorite-epidote gneiss of the Paleozoic Habach Series in the Subpenninic nappe system of the Tauern Window, Eastern Alps that underwent greenschist- to amphibolite-facies polymetamorphic overprint. Total Pt+Pd+Au range from 0.4 to 2.9 ppm, at Cu and Ni concentrations up to 4 and 1.5 weight percent, respectively. Relict textures of sulphide droplets, relict chromian spinel and Ni-Co-Fe sulpharsenide compositions point to a pre-metamorphic origin of the ore, most probably from magmatic Fe-Cu-Ni sulphide melt segregated from silicate melt in a mafic-ultramafic vein or small intrusion in an ophiolitic environment.

1 Introduction

Platinum-group minerals (PGM) are rarely documented from the European Alps. Elevated Pt (up to 0.6 ppm) and Pd concentrations (up to 0.22 ppm) were recorded from Ni-Cu sulphide samples collected at the Haidbach locality in Salzburg, Austria (Weber et al. 1997). The mineralization is located in the steep western slopes of the Felber valley 3.4 km SSW of Mittersill, Salzburg, Austria, at 1400 m above sea level. It is hosted by chlorite-epidote schist, chlorite-epidote gneiss and minor amphibolite. Exploration between the first and second world wars opened 545 metres of mine adits. Several tons of manually pre-enriched ore were processed by Krupp in Germany. Results were promising, but the remoteness and difficult access prevented further activities and the works were abandoned after 1939. Ore reserves have been estimated to 10,000-15,000 tonnes of ore grading 0.76 % Cu, 0.86 % Ni and 0.15% Co (Aigner 1938), but appear overestimated considering the actual exposures. The mineralization was never described in detail and the mineralogical composition is unknown. Therefore, the old mine adits were mapped and samples were taken for geochemical and mineralogical investigation (Schwabl et al. 2015; Schwabl 2016). Microscopic work revealed a large number of precious metal-bearing phases including sulphides, sulpharsenides, arsenides, tellurides and bismutotellurides as well as Sb-rich phases. Most notable is the presence of discrete Re-rich sulphides. Heavy mineral concentrates from the most massive ore type were produced using the hydroseparation method in order to find larger grains more suitable for electron microprobe studies. Here we report on the chemical and mineralogical composition of ore and host rock, and on the unusual precious metal paragenesis.

2 Samples and analytical methods

Mine adits were mapped and systematically sampled. Rocks and minerals were investigated in thin and polished sections using transmitted and reflected light microscopy and scanning electron microanalysis (SEM) using a ZEISS EVO 10 equipped with a tungsten filament and a Bruker XFlash EDX detector. In special cases, compositional data were acquired by wavelength-dispersive spectrometry using a JEOL JXA 8200 electron microprobe (E.F. Stumpfl electron microprobe laboratory) and a FEG-JEOL JXA 8530-F microprobe at the Naturhistorisches Museum, Vienna. Heavy minerals from two size fractions (<30 μm and 30-50 μm) from a well-mineralized sample (P12; m = 670 g) were concentrated using the hydroseparation (HS) technique (www.hslab-barcelona.com) following conventional grinding and sieving. Subsequently monolayer polished sections were prepared at Barcelona as outlined by Aiglsperger et al. (2015). BSE images and EDX spectra were taken for quality analysis using a FEG E-SEM Quanta 200.

Whole-rock chemical analysis was performed using XRF and ICP-MS methods at the Institute of General and Analytical Chemistry, Leoben. The concentrations of trace elements were determined using Agilent 7500cx and Agilent 8800 mass spectrometers after dissolution of 0.1 g sample powder in Na2O2. Major and trace elements in sulphide-rich ore were also analysed in seven samples at Activation Laboratories, Canada using packages 1C-EXP2 und Ultratrrace 6 (www.actlabs.com). PGE and gold were analysed by ICP-MS after nickel sulphide fire assay collection, following the method described by Chan and Finch (2001).
3 Geological background

The Haidbach mineralization occurs in pre-Variscan rocks of the metavolcanic and metasedimentary “Habach Series” that is part of the Tux-Granatspitze nappe of the central Tauern Window, central Eastern Alps, Salzburg, Austria (Schmid et al. 2013). Chlorite-epidote schist and chlorite-epidote-albite gneiss are the dominant lithologies in the immediate vicinity of the mine site. They are composed of chlorite, albite, epidote, ilmenite and quartz. Amphibole-chlorite schist composed of calcic amphibole (hornblende, pargasite, edenite, tremolite), chlorite, biotite, ilmenite, titanite, apatite, monazite and calcite is the major host of the sulphide-mineralized zone. Rarely, relic chromian spinel was encountered. In the wider area surrounding the mine site, amphibolites of variable grain size and texture, including metagabbroic rocks, are exposed. Foliation planes in the mine indicate a large antiformal fold with a fold axis B trending at 260/20. Sulphide mineralization occurs in several layers or seams that can be followed for several decametres along strike. Maximum thickness of the mineralized zone is 3 metres, but mostly comprises cm-wide veinlets in a zone 1-2 m thick. Ores that are more massive occur at several locations, but they are highly deformed by folding and shearing. In some parts of the mine, disseminated sulphide mineralization mainly composed of pyrite is encountered. Crosscutting rock types within the sequence comprise tourmalinite veins, massive quartz veins, and carbonate veins.

4 Results

4.1 Geochemistry

The Fe-rich (15-30 wt.% Fe) sulphide ores (> 8 wt.% S) have Cu contents ranging from 0.2-4 wt.%, Ni from 0.2-1.4 wt.% and Co from 0.05-0.13 wt.%. The ore is also enriched in Cr (317-682 ppm), As (122-875 ppm), Se (41-79 ppm), but depleted in Zn (57-250 ppm) and Pb (2-14 ppm). Precious metal contents are in the range of: 2-23 ppm Ag, 149-1010 ppb Pt, 166-1110 ppb Pd, 59-356 ppb Au and 75-270 ppb Re. Total Pt+Pd+Au range from 0.4 to 79 ppm). Precious metal contents are in the range of: 2-23 ppm Ag, 149-1010 ppb Pt, 166-1110 ppb Pd, 59-356 ppb Au and 75-270 ppb Re. Total Pt+Pd+Au range from 0.4 to 79 ppm. With the exception of Te (up to 8 ppm), rare metals and semimetals associated with the precious metals have rather low contents (e.g., Bi <2 ppm and Sb <2 ppm). Molybdenum ranges up to 5 ppm, whereas W contents are well below 1 ppm.

Correlation analysis indicates that Cu controls the enrichment in Ag, Au, Zn, Cd and to a certain degree in W. Nickel shows a weak, positive correlation with Pd, whereas a negative correlation with Sb and Pb is evident. Cobalt reveals significant positive correlations with As and Sb. Among the trace elements, positive correlations are observed for Zn with Cd (sphalerite controlled), Pd with Te (telluride association), and Ag with Au (electrum controlled). Positive correlations of Cr, Mg and V indicate an ultramafic-mafic component.

4.2 Mineralogy of the ore

The mineral assemblage of the Haidbach Ni-Cu sulphide mineralization, despite being highly deformed, is quite constant throughout the mine. Therefore, we only distinguish a more massive from a disseminated ore type. However, some of the accessory minerals may vary considerably in abundance. Pyrrhotite, pyrite, chalcopyrite and pentlandite are the major sulphide minerals. Whereas pyrite, pyrrhotite and chalcopyrite usually appear fresh in polished sections, pentlandite is commonly altered to violarite. Globular blebs composed of pyrrhotite, chalcopyrite and pentlandite lamellae are observed as inclusions in pyrite. Rocks at the mine entrance and also along some of the mine stopes are intensely altered to a colourfull assemblage of Ni-Co-Cu arsenates, sulphates and others (e.g., erythrine-annabergite, calcanthite, gypsum). The mineralization is free of Fe-oxides or hydroxides, but carries rare chromian spinel. Associated silicates, mainly amphibole and chlorite, are rich in Cr and Ni. Rarely, barite was encountered in vugs of altered ore close to the mine entrance, suggesting formation during weathering.

The list of accessory minerals identified in unoxidized sulphide ores comprises 20 confirmed and three additional (unconfirmed) species. Most abundant are Ni-Co-Fe sulphasenides of the gersdorffite-cobaltite-arsenopyrite solid solution series forming grains up to >100 μm in size, commonly euhedral and associated with other accessory phases such as hessite and Pd-melonite. Subordinate sphalerite occurs as small inclusions associated with chalcopyrite. Iron contents are 5-8 wt.%, and substantial Cd (>1 wt.%) is detected. The mineralization is poor in Pb, explaining the rare occurrence of galena and Pb selenides. In several mineralized samples, molybdenite flakes up to 20 μm in size were encountered, mostly intergrown with pyrite. Scheelite is a rare accessory phase, which was detected in polished blocks of ore samples as well as in HS concentrates. However, it is not directly associated with sulphide phases.

4.3 Precious metal mineralization

The most common precious metal-bearing phases are Ni-Pd tellurides of the melonite – merenskyte solid solution series [(Ni,Pd)Te2] and hessite [Ag2Te] (Fig. 1). Hessite grains reach up to 80 μm in size and are occasionally intergrown with Pd-bearing minerals (Fig. 2) and sphalerite, often occurring along pyrite/pyrrhotite or pyrite/chalcopyrite interfaces. Silver-rich gold alloy with 25-35 atomic percent (at.%) Ag was mainly detected in the HS concentrates; the electrum grains are usually monomineralic, anhedral, inclusion-free and up to 80 μm in size.

Palladian melonite is the most common Pd phase, occurring as euhedral, anhedral or subhedral grains usually
of 5-20 μm, occasionally up to 90 μm in size. It is hosted by pyrite and chalcopyrite and intergrown with gersdorffite and hessite. Palladium contents average to 10 ± 2 wt.%, and the Ni/Pd ratio (in at.%) averages to 0.33 ± 0.8 (n = 60). Ni-rich melonite is rare, whereas merenskyite (Pd>Ni and Te/(Te+Bi+Sb) > 0.8) is a more common phase. Both Pd-melonite and merenskyite carry up to 6 wt.% Sb and Bi, and <3 wt.% Pt.

Palladium tellurides, bismutotellurides and Sb-rich bismutotellurides form small grains (commonly <20 μm) usually included in hessite and Pd-melonite (Fig. 2). However, in HS concentrates larger grains up to 55 μm in size are observed. Michenerite [PdBi(Te,Sb)] is characterized by Ni/(Pd+Ni) <0.1 and Te/(Te+Bi+Sb) ~0.5, commonly with Bi > Sb, and with significant (10-50%) proportion of testibiopalladite [PdSbTe] component. Sudburyite [PdSb] is rare and either associated with petzite [Ag3AuTe2] and Pd-melonite, or occurs as late-stage crack-filling phase in Fe and Cu sulphides.

Figure 1. Distribution, by number of grains, of precious metal-bearing minerals in sulphide concentrates prepared by hydroseparation from sample P12, <30 and 30-50 μm size fractions.

Figure 2. Hessite with euhedral, zoned inclusion of michenerite. The brighter rim is due to higher concentrations of Bi. Dark phase at upper left is Pd-poor melonite (3.3 wt.% Pd). HS concentrate (30-50 μm fraction), BSE image, FEG-EMPA NHM Vienna.

Figure 3. Rhenium sulphide – probably rheniite (white) enclosed by pyrite (dark grey). Brighter grey areas are Re-enriched (4-5 wt.%) Fe sulphides close to pyrrhotite inclusions. Sample P9, BSE image, FEG-EMPA NHM Vienna.

5 Discussion

The Haidbach Cu-Ni-Co-precious metal mineralization is unique in several features: (1) it is the only known of its kind in the pre-Alpine, sub-Penninic rock sequences of the Habach Series in the Tauern Window; (2) it contains discrete precious metal phases of Ag, Pd, Re, Ir, Pt and Au; (3) these minerals are associated with Te, Bi, Sb and As; Sperrylite is the only Pt-rich phase encountered, occurring both included in sulphides and in the silicate matrix. It is chemically rather homogeneous (Sb and Pd up to 1 wt.%), commonly forming euhedral and solitary grains in the range of <5 to 90 μm size. Only few grains of Ir-Pt-Rh sulpharsenide grains (irarsite) were encountered, enclosed in pyrite or in silicate matrix. Electrum is the most common Au-bearing phase, and its composition ranges from Au66Ag34 to Au76Ag24. Palladium contents are below detection limit, whereas Cu reaches up to 3 wt.% A few grains of petzite were identified in the HS concentrates, intergrown with electrum, sudburyite, hessite and Pd-melonite.

Rhenium-rich sulphides have been encountered in a few samples. At least two phases can be distinguished: (1) euhedral single grains of (Re,Cu,Fe)S2 included in pyrite, commonly <5 μm in size, but ranging up to 8 x 5 μm – probably rheniite (Fig. 3); they are associated with Fe sulphide carrying 4-5 wt.% Re and 1 wt.% Cu (Fig. 3). (2) Platy Re-Pb sulphides forming deformed laths similar in appearance to molybdenite. This phase usually occurs as inclusions in chalcopyrite or associated with its rims. Its stoichiometry is close to (Re,Pb,Cu,Fe)2S4.

Although bulk ore samples carry appreciable Se, selenides are rare, comprising small grains of Pb selenide (clausthalite?) that are associated with pyrrhotite and chalcopyrite.
Haidbach is the first documented occurrence of Re-associations commonly referred to as “orthomagmatic-ultramafic/mafic” (Ni-Cu-PGE) and “acidic-granitic” (Mo-W-Re).

Chemical analysis of host rocks including amphibolite, prasinite and chlorite schist indicates a MORB basaltic affinity of most rocks, and an intermediate basaltic andesitic to trachyandesitic character of the more leucocratic rock types. Chondrite-normalized rare earth element (REE) patterns reveal more fractionated patterns for the amphibolites typically indicating island arc volcanic suites (Höck 1993). In contrast, the immediate host rocks of the mineralization have mantle-like unfractonated REE patterns at 2-6 x CI with negative Eu anomalies. Due to regional metamorphism and widespread alteration near sulphide ore, the original character of the anomalies is difficult to resolve. However, the REE patterns along with low SiO₂ but high Mg and Cr concentrations argue for an ultramafic-mafic precursor, probably pyroxenite that was later transformed into hornblendite. It is unclear if the pyroxenite intruded into a basaltic to andesitic volcanic arc sequence, or represents a cumulate of a small mafic-ultramafic intrusion. In either case, the occurrence of serpentinitized ultramafic rocks including pyroxenite and harzburgite associated with metagabbro within the Habach Series are strong arguments in favour of a magmatic history in an oceanic environment of an ophiolite complex (Höck 1993; Melcher et al. 2002).

The Cu-Ni-Co-precious metal mineralization is hosted by altered ultramafic-mafic rocks, now metamorphosed to chlorite schist and hornblendeite. The mineral association with major pyrrhotite, chalcopyrite, pentlandite and pyrite represents a metamorphically equilibrated magmatic assemblage. Locally preserved polyphase sulphide droplets consisting of pyrrhotite, pentlandite and chalcopyrite enclosed by pyrite are strong arguments for an orthomagmatic origin. Precious metals that were originally present in monosulphide solid solution (mss) were redistributed during cooling and probably metamorphic re-heating to form discrete inclusion assemblages of mainly low-temperature minerals. However, intermediate compositions of Ni-Co-Fe sulpharsenides point to crystallization temperatures higher than the Alpine metamorphic grade (~400-450°C). Likewise, the presence of euhedral sperrylite and other minerals suggests higher temperatures. Similar to metamorphosed PGM assemblages found elsewhere, e.g. in the Las Aguilas intrusion, Argentina (Mogessie et al. 2000) and the Eastern Desert, Egypt (Helmy 2005), the Haidbach mineralization may be interpreted as a result of remobilization, redistribution and recrystallization of magmatic PGE-bearing base metal sulphide.

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References


Solving the enigma of UG1 chromitite emplacement in the Bushveld Complex, South Africa

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Abstract. In this work we present remarkable outcrop scale features of the UG-1 chromitite, along with geochemical data (bulk rock and chromite mineral chemistry) of the rocks in UG-1 stratigraphy. The main UG-1 chromitite usually occurs as a 1 metre thick massive layer that is underlain by anorthosite enclosing numerous thin chromitite layers (10's of cm-mm scale). Geochemical data suggests that the top and bottom massive UG-1 layers, separated by an orthopyroxenite layer, formed from individual large pulses of chromite-saturated melt on the chamber floor that experienced closed-system fractionation. Field features of thin chromitite layers in the footwall, such as matching boundaries of anorthosite autoliths enclosed within chromitite, with adjacent anorthosite layer, parallel disposition of bifurcating chromite branches, and chromitite protrusions into anorthosite that transgress layering in the latter, suggest however, that these were probably emplaced as sills into the anorthosite. Furthermore, undulating contact between anorthosite-chromitite layers implies magmatic erosion was at play, which may have facilitated the intrusion process. Thus, two modes of emplacement appear to have been involved in the origin of the UG-1 chromitite - the main layer formed from basal flows of melts directly on the chamber floor, whereas the thin ones within anorthosite were produced as sills.

1 Introduction

The UG-1 chromitite occurs in the 2.06 Ga old Bushveld Complex in South Africa, which is the largest layered intrusion in the world (> 90,000 sq. km; Finn et al. 2015). The UG-1 chromitite has been a subject of intrigue to petrologists because of the remarkable layering (10s of cm’s to mm-scale) that it displays with anorthosite, and because of its bifurcation, where the chromitite layer is found to split into branches with their total thickness being always equal to that of the unbranched chromitite layer (e.g., Nex 2004). All these features can be spectacularly traced for nearly 400 kms across the entire length and breadth of the Bushveld Complex.

Here we present certain key outcrop scale features of the UG-1 chromitite, as well as geochemical data (bulk rock- major element, trace element and platinum group element- PGE; mineral chemistry of chromite by EPMA), which help us to comprehend the emplacement of the UG-1 chromitite in the Bushveld Complex.

2 Geology of the Bushveld Complex

The Bushveld Complex is exposed as an arcuate-shaped body constituted by discontinuous lobes that occur in the western, eastern, northern and far western parts (Eales and Cawthorn 1996; Cawthorn 2015). An 8 km thick package of layered ultramafic-mafic rocks, known as the Rustenburg Layered Suite (RLS) comprise the complex (Maier et al. 2013), which intrude into the Paleoproterozoic sedimentary rocks of the Transvaal Group and the Archean basement (Eales and Cawthorn 1996; Cawthorn 2015). The RLS is overlain by felsic rocks of the Lebowa Granite and the Rashoop Granophyre Suites (Cawthorn 2015). The RLS is divided into five stratigraphic zones namely- the Marginal, Lower, Critical, Upper and Main Zones. The Critical Zone is significant for hosting economic mineralizations of chromite and PGE (Lee 1996). The UG-1 chromitite, which is the focus of this study, is hosted within the Upper Critical Zone of the RLS. This chromitite layer is not economically important for PGE unlike the UG-2 chromitite and the Merensky Reef, which occur higher up in the stratigraphy within the Upper Critical Zone, and are being extensively mined.

3 Geology of the UG-1 chromitite

The UG-1 chromitite consists of a metre-thick massive layer that is overlain by orthopyroxenite (4 – 9 m thick) in the hanging wall, and is underlain by anorthosite in the footwall (1.5 – 2.0 m thick), which is strongly interleaved with numerous thin layers of UG-1 chromitite (mm to 10s of cm thick). The chromitite-bearing anorthosite is further underlain by mottled anorthosite, which is devoid of chromitites. Sometimes, the massive UG-1 chromitite may enclose orthopyroxenite partings (40 – 50 cm thick) that occur at no specific horizon of the chromitite layer. The thickness of the orthopyroxenite parting is variable along the strike length of the chromitite layer, and is found to increase northwards along the western limb of the Bushveld Complex.

4 Field observations

The most significant field features that are distinct and diagnostic of the emplacement mechanism for the UG-1 chromitite in the Bushveld Complex, were observed during field work in underground mine workings (e.g. Anglo Platinum School of Mines, Impala Platinum and Union Platinum mines in the Western Bushveld), and in surface outcrops (e.g., Dwars River, Eastern Bushveld). The field
features are as follows: (1) the presence of anorthosite autoliths enclosed within the UG-1 chromitite interlayered with anorthosite- the autoliths show matching boundaries with the adjacent anorthosite layer (Fig. 1) (2) parallel disposition of bifurcating branches (mm scale) that are at an high angle to the main chromitite layer (a few cm’s thick) (Fig. 2) (3) the random direction of bifurcations, where the thickness of the bifurcating branches add up to the thickness of the undivided chromitite layer (4) chromitite offshoots branching out of pothole margins, where the pothole is filled by massive UG-1 chromitite that cuts down into the footwall anorthosite (Fig. 3a, b) (5) chromitite protrusions into anorthosite (6) the dimpled and irregular contacts between the UG-1 chromitite and the anorthosite (Fig. 4) and (7) the presence of thin remnant anorthosite lenses with high aspect ratios within the massive UG-1 layer, as well as in the chromitite layers occurring within the anorthosite.

**Figure 1.** Matching boundary of anorthosite autolith with adjacent anorthosite layer.

**Figure 2.** Parallel disposition of bifurcating chromitite branches.

**Figure 3a.** UG-1 chromitite offshoot branching out of pothole margin.

**Figure 3b.** Close-up of offshoot truncating layering in footwall anorthosite.

**Figure 4.** Dimpled contact observed between anorthosite and the UG-1 chromitite.

### 5 Methodologies for geochemical analysis

Bulk rock geochemical analysis of major elements, trace elements and PGE were analyzed from Intertek laboratory
(Australia) for the massive UG-1 chromitite, as well as those interlayered with anorthosite, from a drill core located in the eastern Bushveld Complex (HEX 107- Two River Platinum Mine). The drill core consists of an approximately 2 meter thick UG-1 chromitite that encloses a 40 cm thick orthopyroxenite layer towards the bottom. The footwall anorthosite shows two thinner UG-1 chromitite layers that have thicknesses of 10 cm and 40 cm respectively. Major elements were analyzed by lithium borate fusion methods using the XRF. Precision is better than 0.1 wt% for the major elements. The trace elements were analyzed using ICP-MS after four-acid digestion treatment of the rock samples. Nickel sulfide fire assay treatment followed by quantitative analysis by ICPMS was used to measure PGEs in the rocks. Detection limits are 0.1 ppm for the trace elements and 1 ppb for the PGEs. Chromite was analyzed using the SX 100 and SX 5 electron probe microanalyzer (EPMA), housed at the University of Johannesburg and the University of the Witwatersrand, respectively. The compositions of chromite are recalculated to cation proportions using the Fe$^{3+}$ calculation scheme of Droop (1987).

6 Geochemical results

The bulk rock major elements, trace elements and PGE show variable distribution in the otherwise uniform massive UG-1 chromitite layer, which is about 2 meters thick (Figs. 5, 6). The chemical composition of the chromitite layers interlayered with anorthosite vary within a very narrow range compared to the massive chromitite layer (Figs. 5, 6). The PGE shows slightly more variation than what is observed for the same rock (e.g., bottom-most chromitite layer) in terms of their bulk rock major and trace elements (Figs. 5, 6). The chromite chemistry also shows progressive changes across each chromitite layer (Fig. 5).

Geochemical data from the drill core indicates that the 2 metre thick massive UG-1 chromitite layer is actually constituted by two layers (separated by the orthopyroxenite layer), each of which shows fractionation trends that is understood by increasing concentrations of whole-rock Al$_2$O$_3$, and decreasing concentrations of whole-rock Cr$_2$O$_3$, V and PGEs towards the top of the layers (Figs. 5, 6). Decreasing concentrations of TiO$_2$ and Mg#$^#$ in chromites towards the top of each chromitite layer also support fractional crystallization trends (Fig. 5). Any deviation from this trend may be explained by the involvement of interstitial plagioclase, orthopyroxenes and PGE alloys. Similar observation is also seen for the bottom-most chromitite layer in the footwall anorthosite, and its narrow range of composition compared to the massive chromitite layer indicates similar composition of the parental melt for these chromitite layers.

The field observations that are discussed in this study are quite remarkable. For example, matching boundary of the anorthosite autolith enclosed within chromitite, with the adjacent anorthosite layer (Fig. 1), indicates that it was perhaps a part of the latter from which it was separated by an intruding chromite-saturated melt. The surprising parallel distribution of a few bifurcating chromitite branches indicates probable fracture and shear controlled emplacement of the UG-1 chromitite within the anorthosite (Fig. 2). UG-1 chromitite offshoots occurring within anorthosite, where they clearly truncate layering defined by pyroxene-oikocrysts in the latter, attest to the sill-like emplacement of the chromitite within the anorthosite layer (Fig. 3a, b). The undulating lower contact of the anorthosite layer with the UG-1 chromitite (Fig. 4), along with the presence of numerous thin and discontinuous anorthosite lenses, with high aspect ratios within the chromitite layer, indicate that magmatic erosion was responsible for forming these features.

Therefore, to summarize, our study suggests that the top and bottom massive UG-1 layer formed from two
separate large pulses of hot and dense melts that entered the chamber as basal flows and subsequently experienced closed-system fractional crystallization to form each of the chromitite layers. There was an intermediate period where formation of the bottom-most massive UG-1 layer was followed by the entry of an orthopyroxene-saturated melt in the chamber that formed the orthopyroxenite layer, following which chromite-saturated melt again entered the chamber as basal flows and experienced fractional crystallization to form the top-most massive UG-1 chromitite layer. The chromitite layers within anorthosite indicate a separate event, where some of them formed by sill-like emplacement of the melt that intruded into the anorthosite. Magmatic erosion played a key role in the intrusion process, further implying that the melt had to be superheated (Latypov et al. 2015). The superheated melt chemically dissolved the anorthosite and utilized inherent fractures in the latter, all of which facilitated the intrusion process.

8 Conclusion

The emplacement mechanisms for the UG-1 chromitite have been discussed in this study, using remarkable field observations and geochemical data. Geochemical data helps to distinguish that the 2 metre thick massive UG-1 can be divided into two layers, which are separated by an orthopyroxenite layer. Each of the chromitite layers formed from large pulses of chromite-saturated melts on the chamber floor. The chromitite layers formed by closed-system fractional crystallization and slow cooling of the melt in the chamber. The above interpretation was based on the variable distributions of bulk rock major elements, trace elements and PGE, and chromite chemistry across the chromitite layers. Field features of thin chromitite layers in the footwall, on the other hand, suggest that these were likely emplaced as sills into the anorthosite. Furthermore, undulating contact between anorthosite-chromitite layers implies magmatic erosion was at play. Magmatic erosion requires the melt, parental to the chromitite, to be superheated, which subsequently facilitated the melt to chemically dissolve the anorthosite and flow through the latter during the intrusion process. Thus, in conclusion, two modes of emplacement appears to have been involved in the origin of the UG-1 chromitite - the main layer formed from basal flows of melts directly on the chamber floor, whereas the thin ones within anorthosite were produced as sills.

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References

The formation of vanadium deposits of the Archean Bell River Complex, Québec, Canada: Insights from Fe-Ti oxide chemistry

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Abstract. Cryptic trends in the trace element chemistry of Fe-Ti oxides have been used to examine the importance of open versus closed system magma chamber processes during the formation of the vanadium-rich magnetite layers in Bell River Complex layered intrusion, Québec, Canada. Broad upwards depletion trends in elements that are highly compatible in Fe-Ti oxides, such as Cr and V, across 300 m of layered oxide-rich mafic and ultramafic rocks are consistent with closed system fractionation of a single parent magma. Although minor cryptic reversals do not necessarily eliminate the possibility of intermediate stage magma additions during the emplacement of the intrusion, these may also be explained by convection driven processes occurring within the magma chamber. While the rocks of the Bell River Complex have been metamorphosed to amphibolite facies, resulting in the alteration of magnetite in some metagabbros, Cr and V appear to be immobile in Fe-Ti oxides during metamorphic re-equilibration, and therefore remain valid tracers of primary igneous processes.

1 Introduction

Vanadium deposits in layered mafic intrusions (LMI) occur as variably thick layers rich in Fe-Ti oxides such as magnetite and ilmenite, in which V is primarily concentrated as a minor to trace element in titaniferous magnetite. While layered intrusions are a relatively common feature on earth, not all contain economically significant concentrations of vanadium-rich oxide layers. Among those that do, multiple models have been proposed to explain the mechanisms responsible for the formation of layers enriched in V-rich magnetite. These models generally fall into one of two categories: those involving fractional crystallization of a single parent magma in a closed system (e.g. the Bushveld Complex, South Africa (Reynolds 1985; Tegner et al. 2006)), and those in which a magma chamber is open to multiple injections of more primitive magma (e.g. Panzhihua, China (Song et al. 2013)). Which model a LMI falls into is commonly inferred by examining cryptic trends – i.e. variations in mineral chemistry with stratigraphy – of trace elements that are compatible into Fe-Ti oxides, such as Cr and V. Progressive fractionation of a single parent magma should result in the earliest formed magnetite and ilmenite from the lowermost oxide-rich layers having the highest concentrations of these elements, followed by consistent upward depletion profiles (e.g. Barnes et al. 2004). Any prominent cryptic reversals may signify mixing with later injections of more primitive magma (Namur et al. 2010).

The Bell River Complex (BRC) is a 2.72 Ga LMI located near the town of Matagami in the northern Abitibi greenstone belt, Québec, Canada. Its upper layered series is host to the prospective “Iron-T” vanadium deposit, and displays geologic similarities to a number of world-class Fe-Ti-V deposits (Maier et al. 1996; Tane 1998), although it has been regionally metamorphosed at amphibolite facies conditions (Goutier 2005). Inferred mineral resource estimates for the Iron-T deposit total 14.38 Mt at 0.77% V2O5EQ (NI 43-101 Technical Report, SGS Canada 2011). The purpose of this study is to examine chemostratigraphic cryptic variations in the trace element chemistry of Fe-Ti oxides across the layered series of the BRC, in order to determine whether its V deposits are the product of fractional crystallization occurring in a magma chamber which was open or closed to successive magma injections during its emplacement and cooling. Additionally, due to the fact that many of the world’s most prolific Fe-Ti-V deposits occur in relatively unmetamorphosed geologic settings, studying the BRC provides an opportunity to examine the effects of metamorphism on Fe-Ti oxide chemistry in Archean greenstone belts.

2 Methodology

Large-scale cryptic variations in Fe-Ti oxide chemistry of the BRC were examined by analyzing coarse-grained (i.e. primary) magnetite and ilmenite from 54 samples, collected from drill cores and outcrops which cumulatively cover approximately 300 m of the oxide-rich stratigraphy. Concentrations of 25 trace elements were determined using the laser-ablation (LA)-ICP-MS systems at the University of Ottawa and Geological Survey of Canada, Ottawa, using the methods outlined in Dare et al. (2014). Both LA-ICP-MS systems comprise a Photon-Machines Analyte (193nm) Excimer laser system and a 7700 Agilent quadrupole ICP-MS. Grains were analyzed using single line rasters approximately 300 μm long, with a beam diameter of 30-52 μm. Consideration was made to incorporate representative amounts of exsolutions (ilmenite and/or spinel in magnetite; hematite in ilmenite) in the analyses in order to better represent the primary composition of the Fe-Ti oxide before subsolidus exsolution processes took place.

3 Chemostratigraphy

Cr and V are two of the most compatible trace elements in Fe-Ti oxides (Klemme et al. 2006; Dare et al. 2014), and therefore how their concentrations in magnetite and
ilmenite vary with stratigraphic depth in layered intrusions should reflect fractionation of the parent magma as these minerals were crystallizing. Taking into account only those samples in which Fe-Ti oxides constitute a major portion (>10%) of the modal mineralogy, Cr is clearly present in the highest amounts (>1 wt%) in the lowermost magnetite of the BRC (Fig. 1), followed by a decrease of more than an order of magnitude (~300 ppm) upon the first appearance of massive oxide layers at approximately 250 m depth. Its abundance then remains relatively low over the remainder of the profile (<1000 ppm Cr), although a number notable reversals in cryptic trends are evident, particularly at 75 m (~1500 ppm); however, local Cr concentrations at this level reach only one-tenth that of those observed at the base. In comparison, V remains relatively consistent across the 300 m profile analyzed, generally remaining between 0.5-1 wt%, although it mirrors the broad depletion and reversal trends exhibited by Cr, particularly in the lowermost 150 m.

In general, host rock composition appears to have little influence on the V and Cr contents of Fe-Ti oxides examined in this study. A notable exception are the metaleucogabbros in which oxides are only a minor constituent (<5%) of the modal mineralogy. In these cases

the only oxide typically present is ilmenite, as magnetite appears to have been preferentially replaced by silicates during metamorphism. Both ilmenite and rare relict magnetite in these samples are consistently enriched in Cr and V relative to oxide-rich lithologies at similar stratigraphic levels (e.g. Fig. 1, 250 m depth).

4 Effects of metamorphism

The mafic and ultramafic rocks of the BRC have been regionally metamorphosed to amphibolite facies (Goutier 2005). In order to assess the chemostratigraphic variations in Fe-Ti oxide chemistry in terms of igneous fractionation processes, it is important to consider whether or not the chemistry of Fe-Ti oxides has been modified during metamorphism. This is particularly important since the Fe-Ti oxides most enriched in Cr and V (i.e. in the metaleucogabbros) are also those in which magnetite is the most visibly altered, in many cases being completely replaced by hornblende and/or chlorite (=biotite, epidote). However, the base of one particular massive oxide band (located at ~250 m on Fig. 1), in sharp contact with underlying oxide-poor metagabbro, exhibits a textural alteration gradient over the lowermost centimeter of the oxide layer, in which magnetite becomes increasingly replaced by silicates towards the metagabbro (Fig. 2). If one assumes that both the altered oxides in direct contact with the underlying gabbro and the massive, unaltered oxides only centimeters above them had similar primary compositions, then any observed compositional differences should provide insight into the behaviour of various trace elements in Fe-Ti oxides during metamorphic alteration and re-equilibration with silicates.

Magnesium is noticeably lower in altered magnetite and co-existing ilmenite relative to their unaltered counterparts (Fig. 3a). This is expected, as it is common that Fe-Ti oxides

Figure 1. Chemostratigraphic profiles showing variations in the V and Cr contents of magnetite with depth across the layered mafic and ultramafic rocks of the Bell River Complex. Rock type is given as the inferred protolith based on the observed metamorphic silicate assemblages coexisting with Fe-Ti oxides. Data points represent the mean of up to six analyses within a given thin section; error bars, calculated as one standard deviation from the mean, represent the natural variation in magnetite compositions within the analyzed thin section.

Figure 2. Photomicrographs in a PPL and b RL of gradationally altered magnetite from the base of a massive layer in contact with underlying an underlying metagabbro. Magnetite (Mt) is being increased by a mixture of chlorite, hornblende, and biotite towards the underlying gabbro, leaving only relict ilmenite (ilm) exsolution lamellae. Coarse-grained ilmenite is not visibly altered. Sample is located at ~250 m in Fig. 1. Width of view = 2.5 mm.
become increasingly Mg-poor with increased re-equilibration with ferromagnesian silicates such as olivine and pyroxenes (Frost, 1991). However, there appears to be little difference in their Cr and V contents (Figs. 3b, c). This suggests that these elements remain immobile in Fe-Ti oxides during metamorphism. Therefore, their concentrations observed in samples from the BRC are reflective of their primary concentrations, and are valid tracers of igneous processes.

5 Discussion and conclusions

Broad upward depletion trends exhibited by Cr and V in Fe-Ti oxides over approximately 300 m of layered oxide-rich mafic and ultramafic rocks of the Bell River Complex are presumably consistent with fractional crystallization of a single parent magma occurring within a closed system. Cr becomes rapidly depleted in magnetite and ilmenite upon the first appearance of massive oxide layers, and although numerous reversals in cryptic trends are observed over the remainder of the overlying stratigraphy, the local maximums observed at these levels are relatively minor in comparison to the absolute maximum observed at the base of the profile (Fig. 1). While such reversals in cryptic trends do not necessarily eliminate the possibility of intermediate-stage magma additions during the emplacement of the intrusion, they may also be explained by internal, convection driven processes occurring within the residual parent magma as fractionation progressed (Tegner et al. 2006). The V content of magnetite roughly mirrors those trends exhibited by Cr, albeit notably less pronounced. This may be due to the lower overall partition coefficient of V than of Cr, as well as its dependence on the oxygen fugacity conditions of the source magma, which may vary locally as magnetite crystallizes (Snyder et al. 1993; Toplis and Corgne 2002).

In contrast to the large-scale depletion trends exhibited by the oxide-rich lithologies in the BRC, metaleucogabbros in which Fe-Ti oxides are only a minor component are often significantly enriched in both Cr and V. They also display the most obvious textural evidence of metamorphic alteration and re-equilibration, as magnetite is commonly partially-to-completely replaced by Fe-rich silicate minerals characteristic of amphibolite facies metabasites. However, metamorphism appears to neither enrich nor significantly deplete relict Fe-Ti oxides in either Cr or V, suggesting that their concentrations in magnetite and ilmenite, as determined in this study, are representative of their compositions prior to metamorphism. Their anomalous enrichment in Fe-Ti oxides of metaleucogabbros are therefore interpreted to be igneous in nature. They are, however, not considered to be reflective of large scale differentiation trends - that is, they do not represent periodic injections of V- or Cr-rich magma. Rather, these oxides may be an intercumulus phase that simply crystallized, in low abundance, from an enriched trapped liquid.

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Variable genetic models for country rock-hosted massive sulphides

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Abstract. Fe-Ni-Cu-(PGE) sulphides are commonly found within mafic and ultramafic intrusions. However, many massive sulphides occur in sedimentary rocks, far removed from the intrusions, and are relatively underexploited, despite some significant metal endowments. Because these mineral occurrences are relatively underutilized, informed genetic models are currently lacking. Massive sulphides near the Tamarack Intrusive Complex, the Eagle Intrusion, and the Duluth Complex consist primarily of pyrrhotite, pentlandite, and chalcopyrite in variable proportions, but massive sulphides below the Stillwater complex are primarily pyrrhotite and magnetite. Major and minor elements in sulphides (Ni, Co, and Se) show significant compositional differences based on locality. Samples from Stillwater and Duluth have much higher S/Se ratios than found in the mantle, whereas Tamarack and Eagle have S/Se values near mantle values. Ni/Co at Tamarack and Eagle far exceed mantle ranges, but can potentially be explained by coupled Ni and Co scavenging in olivine-crystallizing magmas. Mantle normalized PGE patterns at Eagle, Tamarack, and Duluth are nearly identical to PGE profiles in the associated igneous-hosted sulphides. At Stillwater, however, PGE patterns are quite different in the country rock-hosted massive sulphides compared to igneous-hosted sulphides.

1 Introduction

Ni-Cu-PGE deposits associated with mafic and ultramafic intrusions can be broadly classified into two types: 1) igneous-hosted sulphides consisting of disseminated, semi-massive, and massive sulphide ores, and 2) country rock-hosted sulphides, usually consisting of massive sulphides hosted in sedimentary or metasedimentary country rocks.

Igneous-hosted sulphides are commonly found within, and at the base of, intrusive and extrusive rocks of mafic to ultramafic compositions. Documentation of field relationships, coupled with theoretical and experimental work, demonstrate that these igneous-hosted sulphides formed by segregation of a sulphide liquid from a parental silicate magma (Naldrett 1989). That is not to suggest that all components of the igneous-hosted sulphides came from the original magmatic source, but often require significant input of components, like S and Os, by way of crustal contamination.

Although most known resources of Ni-Cu-PGE sulphides are in igneous rocks, a significant and increasing number of occurrences are being found entirely within sedimentary or metasedimentary country rocks, with no visible connection to sulphides in the igneous rocks. At Noril’sk, for example, the Karaelak intrusions are characterized as picritic to gabbroic sills hosting disseminated sulphides throughout, with massive sulphides at the base of the sills (Naldrett et al. 1996). However, many massive sulphide occurrences at Noril’sk are also hosted in Devonian country rocks, up to tens of meters away from the sills. At Noril’sk, reserves of country rock-hosted massive sulphides are reportedly substantial with regards to overall reserves. These types of massive sulphides may represent large, and previously unknown resources at other localities where magmatic sulphides have previously been exploited.

The geological and geochemical characteristics of these massive sulphides, however, are less constrained than igneous-hosted sulphides, and genetic and exploration models are less developed. Almost certainly, a single model does not seem to explain the origins of all country-rock hosted massive sulphides.

2 Models of massive sulphide formation

Although one principal genetic model has not yet been used to describe the occurrence of all sediment-hosted massive sulphides, there are four primary models, which have been invoked in their formation:

1) Leaking of magmatic sulphides;
2) Sedimentary sulphides;
3) Partial melting of sedimentary sulphides; and
4) Hydrothermal sulphides

The most commonly prescribed model is that sulphides simply leaked out of the magmas and into country rocks via gravitational settling through faults and fracture networks. Although this model seems reasonable, it must also be noted that although many country rock-hosted massive sulphides occur below the intrusions with which they are associated, many are also documented laterally away from the intrusions, or even above them.

3 Characteristics of country rock-hosted massive sulphides

Samples of sediment-hosted massive sulphides were collected from metasedimentary rocks near the Tamarack Intrusive Complex, Minnesota; the Eagle intrusion, Michigan; the Duluth Complex, Minnesota; and the
Stillwater Complex, Montana.

The bulk of the mineralization at Tamarack and Eagle is Ni-rich (Cu ± PGE) disseminated, semi-massive, and massive sulphides within the intrusions (Taranovic et al. 2016; Ding et al. 2010). Both are conduit-style magmatic deposits derived from a picritic parental magma (Klewin and Berg 1988).

The Duluth Complex is characterized by Cu-rich (Ni ± PGE) disseminated sulphide mineralization hosted in the base of intrusions (Ripley 2014). Parental magmas are high-aluminum olivine tholeiites (Lee and Ripley 1996).

The Stillwater Complex is a layered mafic intrusion, most known for the occurrence of the JM Reef, which hosts disseminated sulphides and platinum group elements at an average grade of 18 ppm Pt+Pd (Zientek et al. 2002). There are other noted PGE occurrences, such as the Picket Pin area, and massive Ni-Cu sulphides at the basal, ultramafic portion of the complex.

3.1 Petrographic characteristics

Samples were examined using reflected and transmitted light microscopy to document the sulphide mineralogy and any potential alteration in the country rocks.

At the Tamarack and Eagle deposits, massive sulphides are characterized by pyrrhotite, pentlandite, and chalcopyrite, with lamellar pentlandite exsolution in pyrrhotite. Minor magnetite is also present, but rarely makes up more than ~2% of the massive sulphides. The contacts between massive sulphides and the host rocks display lobate/cuspatte pods of sulphide projecting into the country rocks. Another feature at both Eagle and Tamarack is the gradational boundary from pure massive sulphide, to silicate-bearing sulphide, to intermixed sulphide and silicate, and finally to silicate country rocks. The sedimentary rocks along the contact are variably altered to biotite and cordierite, but the alteration commonly extends no more than 2 cm into the country rocks.

At the Duluth Complex, the massive sulphides in the country rocks are primarily pyrrhotite and chalcopyrite with minor amounts of pentlandite, including pentlandite lamellae in pyrrhotite, and trace amounts of magnetite. Minor bornite is present in the sulphides, and is commonly concentrated nearer to the contacts. Sulphide textures at the contacts are similar to those at Tamarack and Eagle, including the lobate features and the change in sulphide morphology and abundance with proximity to the contact. The country rocks also show a narrow selvage of cordierite, orthopyroxene, and biotite near the contact.

Massive sulphides below the Stillwater Complex are composed of pyrrhotite and magnetite, with only trace amounts of chalcopyrite and pentlandite. Most of the massive sulphides at Stillwater are hosted within a cordierite-orthopyroxene hornfels, which is in contact with the base of the complex and extends for roughly 100 to 200 meters below the base. The contact between massive sulphides and cordierite-pyroxene hornfels display larger grain sizes of both cordierite and orthopyroxene at the contacts and have round blobs of sulphide in the silicate.

3.2 Trace element geochemistry

S/Se ratios may be used to assess the source of sulphur in sulphides that do not show strong evidence of S remobilization due to subsequent metamorphism, supergene, or hydrothermal activity (Queffurus and Barnes 2015). Mantle rocks have average S/Se ratios of ~3,300 (McDonough and Sun 1995). Conversely, crustal rocks are relatively depleted in Se compared to mantle-derived rocks, and they will usually have higher S/Se ratios (up to 100,000) (Yamamoto 1976).

At Tamarack, the average S/Se ratio in massive sulphides is 1,918 (Fig. 1), and ranges from 1,302 to 2,688, slightly lower than the mantle. At Eagle, the average S/Se ratio is slightly higher at 3,826, with a range from 3,195 to 4,925.

Ni/Co ratios at Eagle and Tamarack are higher than in the Duluth Complex, but Ni/Co ratios of mantle-derived sulphides can easily be elevated by early sulphide segregation in olivine-crystallizing magmas. To illustrate, a simple model of Ni/Co ratios in a first formed sulphide liquid have been plotted as a function of percent of fractional crystallization in high Fe picrite (Fig. 2). If S addition may occur at any time to induce sulphide saturation, Ni/Co ratios in the first formed sulphide start out at ~230 if no crystallization has occurred. By ~15% crystallization, Ni/Co ratios of the initial sulphide are ~75, with ~8 weight percent Ni.

At Duluth, S/Se ratios range from 3,293 to 10,078, significantly higher than mantle values. However, it is clear from published data that both S/Se and Ni/Co ratios of the massive sulphides at Duluth are quite similar to sulphide-bearing troctolites and norites (Co-rich and Se-poor) (Theriault et al. 1997).

At Stillwater, S/Se ratios of the massive sulphides are between 4,787 and 9,598, and are relatively more S-rich than the mantle. Ni/Co ratios are well constrained between 12.6 and 18.8. Possibly of more importance is that S/Se ratios of the JM Reef are relatively constant at around 1,882 (Godel and Barnes 2008), with highly variable Ni/Co ratios from 8 to 56.

Sulphur isotope ratios were measured at all four localities. At Tamarack, δ34S values range from 0.3 to 3.5 ‰ with an average value of 1.53 ‰; at Eagle, values go from 2 to 4 ‰ with an average of 3.03‰; at Duluth, values are 9.9 to 19.3 ‰ with an average of 13.4 ‰; and at Stillwater values range from -1.5 to 4 ‰. Multiple sulphur isotope analyses show Δ34S values for Tamarack, Eagle, and Duluth that are anomalous Δ34S values that range up to 0.22 ‰.
SY02 – Magmatic sulfide and oxide ore deposits in mafic and ultramafic rocks
A symposium in memoriam of the work and life of Prof. Hazel Pritchard

3.3 PGE geochemistry

At the Tamarack and Eagle deposits, mantle-normalized PGE trends of the massive sulphides have nearly identical patterns to the igneous-hosted sulphides. The trends of the PPGE rich massive sulphides at Tamarack are more like the PPGE enriched patterns observed in disseminated sulphides, whereas the IPGE enriched massive sulphides are more similar to those in the semi-massive sulphides (Taranovic et al. 2016). At Eagle, the massive sulphides in the country rocks and in the intrusions also have two distinct, matching trends: PPGE enriched and IPGE enriched (Ding et al. 2012).

PGE trends in massive sulphides below the Duluth Complex have a positive slope from Ni to Cu, but have major depletions in Pt and variable depletions and enrichments in Rh, Pd, and Au. Sulphide-bearing troctolites and norites in the Duluth Complex have PGE trends that display a steady positive slope from Ni to Cu, with variable enrichments and depletions in Rh, Pt, Pd, and Au, which were previously attributed to post-magmatic hydrothermal alteration (Ripley 1990).

PGE normalization of massive sulphides from the Stillwater Complex are trough-shaped (Fig. 3), indicating PGE depletion relative to Ni and Cu. Godel and Barnes (2008) demonstrated that the JM reef, the hanging wall, and the footwall rocks at Stillwater have an overall arch-shaped PGE profile, indicating PGE enrichment relative to Ni and Cu.

4 Conclusions

Mantle $^{34}$S and S/Se ratios are relatively well-constrained around 0 ‰ and 3,250, respectively, and both have a narrow range of variation. Ni/Co ratios are more variable due to different degrees of partial melting, crystallization sequence, percent crystallization, largely due to different partitioning of Ni and Co into silicates and sulphides.

At Eagle and Tamarack, S isotope ratios in the massive sulphides are in exactly the same range as their corresponding igneous-hosted sulphides, and S/Se ratios are very near mantle ratios. Taranovic et al. (2015) and Ding et al. (2012) suggest that isotopic evidence for crustal contamination at Tamarack and Eagle may be from isotopic exchange in the conduits. It is not unreasonable that such a process could also lead to S and Se exchange in the conduit, potentially masking the original S/Se ratios. Because the massive sulphides at Tamarack and Eagle have considerable similarities to their corresponding igneous-hosted sulphides in terms of mineralogy, sulphur isotopes, trace elements, and PGE distributions, we suggest those country rock-hosted massive sulphides were formed by leaking of igneous sulphides.

Higher S/Se ratios, such as those at the Duluth and Stillwater Complexes are commonly observed in crustal rocks. It has previously been shown isotopically that the Duluth Complex sulphides formed by crustal contamination from the Proterozoic Virginia formation. Elevated S/Se ratios in the sulphides (up to 10,000) are also a result of this process, given the narrow range of mantle S/Se ratios. The range of S/Se (and Ni/Co) ratios from the massive sulphides below the Duluth Complex are nearly identical to those seen in the igneous hosted sulphides, indicating that massive sulphides at Duluth were leaked from the intrusions into the country rocks. The overall trend of PGEs at Duluth is similar to that seen in the Duluth troctolites and norites, although depletions and enrichments of PPGEs are more variable. The range of $^{34}$S values (9.9 – 19 ‰) are slightly wider and higher than the range in the igneous rocks (6 – 13 ‰) (Ripley and Al-
Jassar 1987), and suggests partial melting of sediments may have also contributed to the formation of country rock-hosted massive sulphides.

Massive sulphides at the Stillwater Complex appear to be unrelated to sulphides in the intrusion. It has previously been suggested that the massive sulphides leaked from the base of the Stillwater intrusion; however, a PGE depleted magma carrying sulphides cannot create a PGE enriched magma. Because PGE plots of massive sulphides at Stillwater are PGE depleted relative to Ni and Cu, they could not be related to the PGE enriched igneous rocks. Additionally, S/Se ratios in the massive sulphides range from ~5,000 up to 10,000, whereas S/Se ratios in the JM Reef average about 1,800. Multiple sulphur isotope data also shows anomalous $\delta^{34}$S values, which are only observed in Archean sedimentary rocks. The lack of hydrous alteration assemblages around the sulphides precludes their formation from a hydrothermal fluid. Rounded sulphide blebs indicate the massive sulphides were originally sedimentary sulphides that were metamorphosed or partially melted during intrusion of the Stillwater Complex.

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**References**


Magnetite as an indicator mineral for magmatic sulphide mineralisation: a case study from Munali, Zambia

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Abstract. Magnetite is a common accessory mineral across magmatic, metamorphic and hydrothermal deposits. Recent advances in LA-ICP-MS have shown the trace element chemistry of magnetite to be indicative of modes of formation and has the potential to be used as a tracer for magmatic sulphide mineralisation. The Munali Ni deposit in southern Zambia is a magnetite rich, conduit hosted deposit and an ideal natural testing ground to assess the use of magnetite as a geochemical indicator. The Munali Intrusive Complex (MIC) is the result of multiple magmatic events, with multiple magnetite generations. Four magnetite styles are recognised: 1. Igneous phase magnetite 2. Sulphide associated magnetite, 3. Carbonate associated magnetite and 4. Reaction rim magnetite. Trace element chemistry, determined by LA-ICP-MS is used to establish discrimination criteria for each generation. Plots of Cr/V vs Ni are successful in discriminating between magnetite-hosting lithologies as well as those associated with mineralisation. Samples of magnetite collected from soil above regional magnetic targets thought to be possible Munali analogues are analysed as unknowns to test the possibility magnetite can be used as a geochemical indicator mineral.

1 Introduction

Magmatic Ni-Cu-PGE deposits are the world’s most important source of Ni and PGEs, accounting for ~60% of global Ni production (Schulz et al. 2010). Ore formation in these systems is the result of the segregation between immiscible sulphide droplets and silicate melt, formed when partial mantle melts reach sulphide saturation; the fundamental ore-forming process.

Iron oxides are common accessory minerals across a variety of magmatic, metamorphic and hydrothermal mineral deposits. Magnetite in mafic-ultramafic systems can form via a number of processes: directly as a product from fractional crystallisation in a silicate magma; secondary hydrothermal processes; or from the fractionating sulphide liquid itself. Magnetite has the ability to record the fractionation history of not only the silicate melt, but also that of a fractionating sulphide liquid (Boutry et al. 2014; Dare et al. 2014).

Trace element, and to a lesser extent, major element, chemistry recorded in magnetite is governed by the geological processes active during formation and as such demonstrates differences in geochemistry between occurrences (Naldrett, 1969; Fonseca et al. 2008; Boutory et al. 2014). It is this compositional variety between generations that make magnetite an effective tool in individually fingerprinting different magmatic and mineralising episodes.

Recent advances in Laser Ablation-ICP-MS (LA-ICP-MS) analysis of magnetite (Dupuis et al. 2011; Boutry et al. 2014; Dare et al. 2014) highlight the use of magnetite as a petrogenic indicator in determining source conditions, fractionation histories and chemistry. Similar to Cu/Pd ratios, the base metal concentrations in magnetite have been shown to yield the potential to indicate evidence of sulphide saturation within a magma. As such, magnetite has been suggested as a potential vectoring tool in the exploration for sulphide mineralisation, though this has never been tested fully in an exploration setting for Ni-Cu-PGE deposits.

Here, through textural classification and laser ablation-ICP-MS analysis, we use a case study from southern Zambia to test whether magnetite can be used in exploration as an effective indicator mineral for magmatic sulphide mineralisation.

2 Case study area

2.1 Introduction to the Munali Ni deposit

Situated in the Zambezi Supercrustal Sequence, the Munali Ni-sulphide deposit is located in southern Zambia, 65 km southwest from the capital, Lusaka. The Munali Intrusive Complex (MIC) comprises a mafic-ultramafic intrusion, emplaced close to the southern Congo craton margin. Munali is a conduit hosted system intruded into upper crustal basin sediments and is used as a case study due to the high abundance of magnetite from multiple origins.

The MIC comprises an unmineralised Central Gabbro Unit (CGU) and a mineralised Marginal Ultramafic-mafic Breccia Unit (MUBU), intruded ~1.55 Ma after the CGU (Holwell et al. 2017). The main mafic magnetite-bearing rocks at Munali include poikilitic gabbrro, microgabbros and dolerite dykes. Ultramafic lithologies include olivinites, olivine-magnetite cumulates and phoscorites (olivine-magnetite-apatite rocks). In addition, the massive sulphides that form the orebody within the MUBU also contain magnetite as an essential component of the ore...
Sufficient surface exposure, drillcore and accessible underground faces, coupled with the abundance of magnetite at Munali make for an excellent natural testing ground to assess magnetite’s potential as an indicator mineral. To achieve this, we implemented the following methodology: (1) texturally classify magnetite styles in the dominant lithologies; (2) classify the trace element geochemistry of each style through Laser Ablation-ICP-MS; (3) determine discrimination criteria for each generation of magnetite, including those associated with sulphide mineralisation; (4) analyse samples of magnetite from soil above regional magnetic targets thought to be possible Munali analogues to identify mineralisation signatures and test the possibility magnetite can be used as a geochemical indicator mineral.

Textural classifications are based on field observations (underground mapping and core logging) alongside EDX mapping using Carl Zeiss Microscopy’s automated petrological analyser, Mineralogic. Laser Ablation-ICP-MS was conducted at the University of Leicester.

3 Classification of magnetite

3.1 Textural classification of magnetite

The MIC is the result of multiple magmatic events, with subsequently, multiple generations of magnetite. Based on textural observations, four different generations of magnetite are recognised:

1. Igneous mafic/ultramafic magnetite (Fig. 1)
2. Sulphide associated magnetite (Fig. 2)
3. Carbonate associated magnetite
4. Reaction rind magnetite (Fig. 3)

Igneous mafic/ultramafic magnetite is classified as that which has formed via normal magmatic processes from a fractionating silicate liquid. As such, magnetite here is considered a normal rock forming constituent and is present in both the mafic and ultramafic units where primarily, magnetite is interstitial to silicate minerals (plagioclase, or olivine; Fig. 2; respectively). Within the poikilitic gabbro, magnetite is present as large oikocrysts (<1.6 cm) with plagioclase chadacrysts. It is important to note however that the mafic and ultramafic rocks are the product of two separate melts, not a single evolved melt. This was confirmed with high precision U-Pb dating on zircons whereby the poikilitic gabbro gave ages of 862.39 ± 0.84 Ma. and 857.9 ± 1.9 Ma. for the ultramafics (Holwell et al. 2017).

The sulphide associated category comprises magnetite that is at least spatially associated with massive sulphide (po>>pn>cpy) and thus encompasses magnetite that has formed via the fractionation and cooling of a sulphide liquid. However, the complex, brecciated nature of the ore body means magnetite clasts that are texturally associated with sulphide may in fact be the xenocrysts from the mafic-ultramafic rocks disaggregated during brecciation. Sulphide associated magnetite typically comprises rounded to sub-angular blebs, often with ilmenite bands at the magnetite-sulphide interface (Fig. 3).

Carbonate-associated magnetite is classified simply based on occurrences with carbonate material. This category exhibits spectacular textures, with magnetite often forming as rounded blebs marginal to sulphide (Blanks et al., 2017).

Perhaps the most complicated of classifications, identified through underground mapping, is the reaction rind texture. Reaction rind magnetite can be divided further into two categories based on its neighbouring material. 1) Silicate-silicate reaction rind (Fig. 3), often seen between mafic lithologies e.g. the poikilitic gabbro and dolerite; and 2) Silicate-sulphide, often seen around the margins of clasts of mafic or ultramafic rocks in contact with massive sulphide.

4 Magnetite geochemistry

Whilst there are many varying factors which control the trace element chemistry of magnetite, magnetite grains which are derived from environments that experience similar chemical behaviours should be reflected by sharing a similar composition (Boutroy et al. 2014; Dare et al. 2014). Magnetite grains which are derived from differing environmental conditions should subsequently show varying geochemical signatures (Dupuis and Beudoin 2011; Dare et al. 2014; Nadoll et al. 2014).

4.1 Trace element chemistry of magnetite

Representative samples from the dominant magnetite styles were selected for LA-ICP-MS analysis. From preliminary results, trace element characteristics for all magnetite generations show variable enrichment in Si, Al, Ge, Sc, Ga, Mg, Ti, Zn, Co, V, Ni and Cr. Chromium, an element commonly enriched in magmatic sulphide deposits is notably depleted within the MIC. No chromite was identified during Mineralogic mapping and ppm Cr levels in magnetite grains are significantly lower than that reported for other mafic-ultramafic systems. Yttrium, Pb, Zr, Hf, W, Ta, Nb, Cu, Mo and Sn are present although generally in lower abundances given their relative incompatibility into magnetite.

It is important to consider that anomalous patterns and subsequent variation in abundances of elements may result from element competition with co-crystallising minerals, notably with ilmenite or perhaps with co-crystallising sulphide. Chromium, V, Ga, Ni and Co are controlled primarily by magnetite fractionation. Titanium, Mn, Mg, Al, Y, Nb, Pb, Sc, Ca, Ta, Cu, W and Zn are controlled by the fractionation of ilmenite and as such, differences in the abundances of these elements are proportional to the amount of ilmenite incorporated into the analysis. From initial results, Cr, V and Ni contents, even with the internal variability within single samples, discriminate well between the different magnetite generations. Magnetite compositions in ultramafic and
**Figure 1.** Ultramafic phoscorite (a) ZEISS Mineralogic map and photomicrograph visualised using ZEISS Atlas correlative software showing large magnetite grains co-existing with sulphide (po>>pn). (b) BSE image highlighting ilmenite blebs and exsolutions in magnetite. (c) XPL photomicrograph showing magnetite and silicate relationships.

**Figure 2.** Massive sulphide (po>>pn>>cpy) with magnetite clasts (a) ZEISS Mineralogic map showing magnetite clasts within a matrix of massive sulphide with vein textured pn. (b) Secondary pyrite vein with magnetite rims (c) BSE image of magnetite with ilmenite rims at magnetite-sulphide interface. (d) Veined pn with magnetite within po.
Figure. 3. Core photograph depicting the magnetite reaction rind between poikilitic gabbro and dolerite.

Mafic lithologies are well defined, though Cr alone is ineffective in separating mineralised from non-mineralised lithologies, but in combination with Ni and V, provide useful distinctions.

4.2 Discriminant diagrams

Plots of Cr/V vs Ni appear to be effective in differentiating between both the composition of lithologies (e.g. mafic/ultramafic) and also those associated with mineralisation (Fig. 4).

Figure. 4. Discriminant diagram showing LA-ICP-MS data of magnetite in mineralised and barren fields. Normalised to bulk continental crust (Rudnick and Gao 2003).

5 Application to exploration

5.1 Blind test

Detrital magnetite fragments have been collected from over the Munali deposit, as well as from local exploration targets. As all major magnetite styles at Munali have an established trace element chemistry, these detrital unknowns provide a blind test in which the comparative geochemistry between ‘Munali’ type signatures and unknowns can be established.

Mineralising fields are defined based on Ni concentrations whereas lithological (magmatic phase) variations are identified using Cr/V ratios.

Based on the division of discriminant diagrams with known mineralised and non-mineralised signatures, we show whether detrital grains can be mapped on to these fields to identify: (a) the potential source origin of the magnetite (be that mafic or ultramafic) and (b) assess the fertility of the source and if it appears to show evidence of sulphide mineralisation and therefore, be used as an exploration vector towards sulphide mineralisation.

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References


P-rich patches and bands in P-poor olivine from the Baima layered intrusion (SW China) reveal disequilibrium textures and complicated magma chamber processes

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Abstract In this paper we report for the first time complex P zoning patterns recorded by high-resolution X-ray mapping of P in olivine from the Baima mafic layered intrusion in SW China. It shows that olivine grains have distinctly irregular P-rich patches/bands that are crosscut and interlocked by P-poor olivine sections. The P-rich patches/bands contain 250 to 612 ppm P, up to four times higher than those for P-poor olivine section (123 to 230 ppm). Under EBSD maps, P-rich patches/bands within a single olivine have the same crystallographic orientation, indicating that they were originally the same grain. Fe-rich melt inclusions and rounded magnetite are enclosed in the P-poor olivine sections. These textures thus clearly record a two-stage growth process of olivine. Followed by a secondary stage of dissolution and re-precipitation, P-rich olivine crystals formed in the first stage were dissolved by a disequilibrium Fe-rich ambient melt to form P-poor olivine section in the same grain, and were only preserved as P-rich patches/bands due to the slow diffusion of P.

1 Introduction

Olivine is a common phase in mafic-ultramafic intrusions, but it rarely shows growth zoning in major and some minor elements, e.g., Fe, Mg and Ni, due to the fast diffusion of these elements at high temperatures. Chemical compositions of olivine are thus thought not to be useful to decipher complex magma chamber processes, such as magma convection, multiple injection and mixing.

Growth of olivine at different cooling rates and degrees of undercooling may result in diverse crystal habits (Jambon et al. 1992; Faure et al. 2003). Olivine growth is experimentally proven to be diffusion-controlled on fast cooling and forms skeletal or dendritic morphology (Faure et al. 2003, 2007; Faure and Shiano 2004). This is consistent with that dendritic growth prevails for olivine phenocrysts in volcanic rocks regardless of their habits (Milman-Barris et al., 2008; Welsch et al., 2013, 2014). The dendritic skeleton of olivine is attributed to initial fast growth followed by slow ripening of hollow crystal on cooling (Welsch et al. 2014). On the other hand, olivine growth on slow cooling commonly develops polyhedral-shaped crystal and the olivine is assumed to grow in an interface-controlled, spiral or tree-ring growth model (Faure and Schiano 2005). However, concerning fast element diffusion and post-crystallization processes, e.g., trapped liquid shift effect and sub-solidus re-equilibrium of cumulus minerals in magma chamber, this experimental model has not yet been proven by natural olivine in deep-seated magma chamber where fast cooling is unlikely. It is thus worth to examine the growth process of olivine in igneous cumulates.

P has an extremely low diffusion rate among other major and minor elements in olivine (Watson et al. 2015), which may preserve the primary information of magmas during the crystallization of olivine. In this study, high-resolution X-ray mapping reveals complex P zoning patterns of olivine in net-textured Fe-Ti oxide ores from the Baima layered intrusion in SW China. These complex P zoning patterns recorded an unusual two-stage growth process of a single olivine and have important implications for the magma process of layered intrusion hosting giant Fe-Ti oxide deposit.

2 The Baima layered intrusion

The Baima mafic layered intrusion in the central part of the Emeishan large igneous province (SW China) hosts a giant Fe-Ti oxide deposit. The intrusion is divided into the lower and upper zones (Liu et al. 2014). The lower zone varies in thickness from 150 to 300 m and mainly composed of troctolite and olivine gabbro with <20 vol.% Fe-Ti oxides. The upper zone is up to 1500 m in thickness and composed of isotropic olivine gabbro, gabbro andapatite-bearing gabbro with <10 vol.% Fe-Ti oxides (Liu et al. 2014).

The major Fe-Ti oxide ore layers occur in the lower zone. They are mainly composed of net-textured ores with a total thickness of over 100 m. The net-textured ores are composed of 40-60 vol.% Fe-Ti oxides (titanomagnetite and ilmenite), 20-30 vol.% olivine, <10 vol.% plagioclase and clinopyroxene as well as small amounts of sulfide. Fe-Ti oxides occur as interstitial phases filling the space between silicate minerals (Fig. 1a).

Olivine in the net-textured ores is commonly rounded in 2-D sections and varies in diameter from 0.02 to 2 mm, and is enclosed in the interconnected matrix composed of Fe-Ti oxides and minor sulfides (Fig. 1a). Rounded titanomagnetite (<200 μm in diameter) and melt inclusions are occasionally enclosed within the olivine (Fig. 1b). Previous 3-D X-ray CT scanning reveals that the titanomagnetite in the olivine is spherical-shaped (Liu et al., 2014). Melt inclusions are mainly composed of...
titanomagnetite, ilmenite, spinel and phlogopite with sporadic apatite, amphibole and sulphide (Fig. 1c). Chlorite rim commonly occurs between olivine and Fe-Ti oxides (Fig. 1b). In local places, olivine relics are surrounded by serpentine, which is in turn enclosed by chlorite in the outermost rim.

3 Phosphorus zoning patterns in olivine of the net-textured Fe-Ti oxide ore

Phosphorus X-ray intensity mapping displays complex P zoning patterns in olivine of the net-textured Fe-Ti oxide ores. One common pattern shows that concentric P-rich bands are truncated by P-poor olivine section. The P-rich bands vary from ~30 to 200 μm in width and have sharp boundaries with P-poor olivine sections (Fig. 2b). The other common pattern shows that irregular P-rich patches that are either interlinked with each other in P-poor olivine section or form discrete domains that are completely isolated by P-poor olivine section (Fig. 2b). The boundary between the P-rich patches and P-poor olivine section is usually transitional. In addition, some olivine grains show uniform P distribution with thin P-poor rim in local places. The rounded titanomagnetite and melt inclusion are actually completely trapped in P-poor olivine section.

4 Phosphorus concentrations in olivine of the net-textured Fe-Ti oxide ore

Rounded olivine grains in the net-textured Fe-Ti oxide ores have Fo contents ranging from 71 to 75 mol.% without significant Fo variations within a single grain. In contrast, within one olivine crystal, the P-rich bands and patches have P concentration two to four times higher than those for P-poor olivine section against relatively restricted Fo contents of the grain. Overall, the P-rich bands and patches in the olivine have P concentrations vary from 250 to 612 ppm, whereas P-poor olivine sections have 123 to 230 ppm P, much lower than those of P bands and patches (Fig. 2c).

5 Crystallographic orientation of olivine

In the color-coded electron backscatter diffraction (EBSD) orientation map of olivine, olivine in the net-textured Fe-Ti oxide ores has one dominant crystallographic orientation with the degree variation less than 10°. The isolated P-rich bands and patches in a single olivine share the same crystallographic orientation with the P-poor olivine section.

6 A two-stage growth model of olivine in the net-textured Fe-Ti oxide ore

Olivine in volcanic rocks shows diverse P zoning patterns,
such as banded, concentric, feathery or dendritic (Milman-Barris et al. 2008; Welsch et al. 2013, 2014). Linear, continuous P-rich band and typical P-rich dendrite along the crystal faces of olivine are assumed to be primary skeleton that may have formed during initial diffusion-controlled rapid growth of olivine (Welsch et al. 2014).

The complex P zoning patterns in olivine of the net-textured Fe-Ti oxide ores from the Baima intrusion are distinctly different from the P-rich dendrite in olivine of volcanic rocks and igneous cumulates. Of particular significance are the embayment and curved borders of P-rich patches in the complex P zoning patterns. All these features indicate disequilibrium textures and could be interpreted as the resorption of P-rich bands/patches by P-poor olivine section (cf., Milman-Barris et al. 2008).

Given the isolated P-rich bands and patches in the same olivine grain have identical crystallographic orientation in the EBSD maps, it is likely that they were originally parts of the same grain. We thus consider that the P-rich bands and patches are the relics of primary skeleton that was probably dissolved by ambient melt due to chemical disequilibrium, whereas the P-poor olivine section could be the crystallization counterpart of the ambient melt.

The disequilibrium textures shown by the complex P zoning patterns in this study indicate that a single olivine grain may have experienced a two-stage growth process, rather than a simple fractional crystallization process as we usually thought. The first stage began with rapid crystallization of primary crystal skeleton from the parental magma to develop polyhedral olivine. The second stage involved the dissolution of primary olivine crystal and re-precipitation from ambient melt.

Although there is no way to constrain exact compositions of the ambient melt, a couple of evidence favors that it is likely very Fe- and H2O-rich. Firstly, olivine in the net-textured Fe-Ti oxide ores has low Fo contents ranging from 71 to 75 mol.% and the parental magma of the Baima intrusion was considered to be an evolved high-Ti basaltic magma (Shellnutt et al. 2009). Secondly, Fe-rich melt inclusions are commonly enclosed within P-poor olivine section, they are thus likely representative of the ambient melt. Thirdly, presence of phlogopite in the melt inclusions and prevalent chlorite rime between Fe-Ti oxides and olivine indicate that the ambient melt is likely H2O-rich. We thus assume that the ambient melt is likely more volatile-rich and Fe-rich than the parental magma of the Baima intrusion. One possibility to develop such an Fe-rich ambient melt is silicate liquid immiscibility of interstitial liquid in the Baima magma chamber (Liu et al. 2014b).

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Petrological insights into Ni-Cu-PGE-bearing mineralization mafic-ultramafic rocks of the Mangabal Complexes, Goiás, Brazil

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Abstract. The Goiás Magmatic Arc comprises around 15 small intrusions of mafic-ultramafic rocks. The regional geology implies that the intrusions were emplaced in a synorogenic context, favourable to the formation of many small mineralized bodies. The North and South Mangabal Complexes are two of such bodies, located 3 kilometres apart. Both are stratiform and metamorphic and host Ni-Cu-Platinum Group Elements (PGE) mineralization. The regional metamorphism affected these rocks reaches amphibolite facies. The mafic-ultramafic units of the complex have yielded PGE values of academic to economic significance. Amphibolite is the rock type that hosts most of the mineralization. The base metal sulphides associated with the PGE minerals consist of pyrrhotite, pentlandite, chalcopyrite and pyrite. The complexes are very similar in the terms of the mineralogy, petrology, geochemistry and mineralization, suggesting the same magmatic origin for both complexes.

1 Introduction
The intrusions of mafic-ultramafic rocks in the Goiás Magmatic Arc are poorly studied; despite the fact that some of these intrusions contain interesting Ni-Cu-PGE mineralization. This study provide new information about two of these intrusions: North Mangabal and South Mangabal. Geology and petrology of these complexes have been investigated using petrography, mineral chemistry and whole-rock geochemistry. The purpose is to obtain a better understanding about the geology of the intrusions and the factors controlling sulphide mineralization.

2 Geological setting
The area of study is located in the center of Brazil, in Goiás State. The Brasília belt is one of three orogenic belts formed from the collision of three major continental blocks: the Amazonian to the west, the São Francisco/Congo to the east and the Paranapanema to the south, this latter covered by sediments of the Paraná Basin (Pimentel et al. 2000).

The evolution of the Brasília orogen occurred over a long period (900 – 600 Ma) involving subduction, magmatism and terrain accretion. (Pimentel 2016). North Mangabal and South Mangabal are two of fifteen mafic-ultramafic small intrusions located within the Goiás Magmatic Arc, more specifically in the Arenópolis Arc. The Goiás Magmatic Arc is located in the Brasília Belt and represents a composite arc terrain, formed by the accretion of older (ca. 0.9 – 0.8 Ga) intraoceanic island arc(s), followed by more evolved continental arcs (Pimentel 2016). Goiás Magmatic arc comprises two main parts: Mara Rosa arc at the north and Arenópolis arc at the south (Pimentel et al 2000). The former is well known because the gold exploration in Chapada; the latter is very poorly studied and the details of its formation are unknown.

2.1 South Mangabal
South Mangabal is an medium-small intrusion, measuring
around 8.5 km in length and 5.5 km in width. The basal portion of the intrusion is represented by an intercalation of feldspathic-harzburgite and orthopyroxenite.

The feldspathic-harzburgite is fine-to-medium-grained, with cumulate texture. It consists of 35-60% subhedral to euhedral olivine (Fo79 to Fo84) grains. Bronzite (En64 to En83) is present 5-15% as anhedral grains. Olivine crystals included in bronzite oikocrysts show corrosion features, possibly indicating a peritectic reaction of cumulus olivine and intercumulus liquid. Plagioclase is the principal intercumulate material. Between olivine and plagioclase coronas of pyroxene and pargasitic amphibole are present. The contacts between orthopyroxene and olivine are smooth, whereas the amphibole and plagioclase is irregular (figure 2-A).

Orthopyroxenite (figure 2-D) medium-to-coarse grained. Orthopyroxene (En68 to En81) is the main cumulus phase, showing euhedral grains in ad-to-orthocumulatic texture, consisting of 30-50 vol%. Plagioclase and clinopyroxene are intercumulate phases. Anhedral clinopyroxene includes orthopyroxenes grains.

The upper portion is composed of norite, with grain size ranging from fine to coarse. It essentially consist of euhedral prismatic bronzite accounting for 20-40 vol%. Plagioclase occur as euhedral grains about 30-50 vol%. Plagioclase and bronzite shows a slight orientation of the prisms and laths in some portions. Both minerals are enclosed of anhedral oikocrysts of clinopyroxene; these oikocrysts can reach 2 cm of length. The margins of the minerals are altered to amphibole in some places. Plagioclase can also occur as an intercumulus phase.

Throughout all stratigraphy, many biotite-quartz-felspathic pegmatites cross the lithologies and on these portions, the rocks are intensely altered. The rocks with higher degrees of alteration are amphibolite composed of magnesium-hornblende, plagioclase and phlogopite (figure 2-C), some amphibolite presents as accessory minerals titanite, rutile, talc, chlorite, apatite and kyanite.

Sulphides occur disseminated throughout the stratigraphy (1-15 %vol). Some portions contain massif sulphide. The mineral assemblages consists essentially of chalcopyrite, pyrrhotite, pentlandite and pyrite. The sulphides occur interstitial to a cumulus framework of silicates. The amphibolite, transformed from orthopyroxenite, contains the largest amount of sulphides. The Ni-Cu-PGE mineralization are directly associated with metamorphic rocks.

2.2 North Mangabal

North Mangabal is a small intrusion, measuring around 7 km². The complex is composed by mafic-ultramafic rocks and the metamorphic equivalent rocks.

The basal portion is a fine-to-medium grained peridotite. Olivine (Fo81 to Fo83) is the most abundant mineral ranging from 40 to 65 vol%, in a meso to adcumulate texture. Chrome-spinel can also occur as an accessory (not exceed more than 2 vol%). The intercumulate phase is mainly clinopyroxene (ranging from 15 to 30 vol%), plagioclase (5-10 vol%) and orthopyroxene (5-10 vol%).

Norite and orthopyroxenite (such as those described in South Mangabal), interlayering in different scales (from a few centimetres up to meters) is above the peridotite. There is a small amount of chlorite-serpentinite (as alteration product of harzburgite), in a 2 m thick layer.

Discordant fractures and pegmatites cross the complex and the contact with this hydrate the original rocks, modifying the original mineralogy in different degrees. The higher degrees of alteration results in the formation of amphibolite, composed by magnesium-hornblende, plagioclase and phlogopite.

Sulphide mineralization occurs on a lesser scale than the one noticed on South Mangabal and is restricted to the orthopyroxenite portions, occupying intercumulate interstices. The mineral assemblages consists of chalcopyrite, pyrrhotite and pentlandite. The PGE
enrichment (pt + pd > 1.0 ppm) occurs associated with copper and niel sulphides contents, but not within the sulphides.

Figure 3. Photomicrographs of major rocks from Mangabal Norte. a Peditotite. Meso-cumulatic olivine, involved by clinopyroxene as intercumulus phase. b Bronzite cumulus, involved by clinopyroxene partially transformed in amphibole. Plagioclase occurs as intercumulus phase.

2.3 Metamorphism

South and North Mangabal presents a wide range of degrees of alteration. Even with many igneous relicts and preserved primary textures, metamorphic rocks of the ones described above are common. Amphibolite represents the most altered rocks of the complexes and are commonly associated with fractures and veins that cut the rocks. The further away the rocks are from these veins, more preserved they are.

This indicates that hydrothermalism affected the rocks, hydrating the igneous minerals. Another line of evidence, which corroborates with this alteration of the rocks, is present on the PGE mineralization in the rocks, where the PGM are hosted within the metamorphic silicates, as amphiboles.

3 Discussion

South Mangabal and North Mangabal are located 3 kilometres apart, intruded in the same set of sialic basement and the same regional context. Besides that, the mineralogy, mineral chemistry and the arrangement of the complexes indicates more similarities than the previous studies have shown. The simplified stratigraphic columns of both complexes (figure 04) can show the differences and similarities of Mangabal Norte and Mangabal Sul. The subdivision of Mangabal Complexes, in three different zones, is based on cumulatic phases and the whole-rock chemical behaviour of the rocks.

North Mangabal is divided into two zones: An Ultramafic Zone and a Transition Zone. The ultramafic zone is expressed by peridotite, composed by olivine as unique principal cumulus phase. The Transition zone is composed by interlayering of feldspathic harzburgite, norite, orthopyroxenite and chloride-serpentinite. Transition zone is expressed by the appearance of orthopyroxenite as a cumulus phase.

Figure 4. Simplified stratigraphic column of North Mangabal and South Mangabal.
South Mangabal has two zones: Transition Zone and Mafic Zone. The Transition zone is similar to the transition zone of North Mangabal, an interlayering of feldspathic harzburgite, norite and orthopyroxenite. The Mafic Zone has a sequence of monotonous noritic rocks.

Both complexes show an interlayering of harzburgite, orthopyroxenite and norite. In South Mangabal it occurs in the basal portion, in Mangabal North the layering occurs in the upper portion. The microprobe mineral analysis show that the composition of the minerals of these portions are very similar, the forsterite, enstatite and anortite content are the same. The whole-rock chemistry also shows a similar behaviour in the Transition Zone, in both complexes. It is in this Zone that the Ni-Cu-PGE mineralization occurs on both complexes. The nickel, copper, sulphides and platinum group minerals are concentrated in the same layers, namely the metamorphic rocks of these zone. The hydrothermalism that affected the rocks concentrated the PGM in phases within the silicates minerals in both cases.

Based on the comparison with classical layered intrusion stratigraphy and considering the regional geologic evidence it is suggested that both complexes have the same origin and are derivate from a unique chamber. Therefore, North Mangabal represents the basal portion of this chamber and South Mangabal represents a more evolved magma, the upper portion of the magmatic chamber. The regional geology shows a deformed terrain and the bodies are aligned with regional structural which makes this model possible.

4 Conclusion

Despite the previously studies, the new analysis of the Mangabal Complexes indicates that the two bodies are more related than previously thought. This implies a new vision about the small mafic-ultramafic intrusions of the Goiás Magmatic arc, which may change the method of prospecting for Ni-Cu-PGE in the area. Before it was believed that all bodies were completely isolated and had different evolutions. From now on, it is possible to study this relation among these bodies and to define new prospects on the area.

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Chalcophile element concentrations in magmatic nickel sulphide deposits

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Abstract. The advent of new and more efficient analytical methods is beginning to provide results for a variety of chalcophile elements that have not previously been considered in detail when considering the processes forming magmatic Ni sulphide deposits. It is a challenge to understand the significance of the distribution of these elements and whether they can be used in exploration strategies. Presentation of the data on mantle normalized plots helps to separate some of the processes that occurred.

1 Introduction

Until recently most work on magmatic nickel sulphide deposits has focussed on the concentrations of valuable metals in the ore, Ni, Co, Cu, and the platinum-group elements (PGE). However, in addition to collecting these elements the base metal sulphide (BMS) liquid will have concentrated other chalcophile elements and the behaviour of these elements is not yet well documented and understood. With the advent of cheaper and more accurate whole rock analysis it is now possible to more closely consider the distribution of the various chalcophile elements and in particular to consider Te, As, Bi, Sb and Sn (TABS). These elements are particularly important in the formation of platinum-group minerals. In addition to TABS elements such as Mo, Pb and Bi may also be important in tracing crustal contamination of primary magmas.

2 The distribution of chalcophile elements in major reservoirs

The chalcophile elements here are defined as those that have partition coefficients between a mafic magma and a BMS liquid of greater than one. They can be divided into slightly chalcophile (Dsul/sil 1-20), moderately chalcophile to strongly chalcophile, (Dsul/sil 20-1000), and highly chalcophile (Dsul/sil >1000) (Fig. 1). Some of these elements; PGE, Au, and Re are commonly referred to as highly siderophile, however this definition is based on their behaviour at low fO2. Under crustal conditions they behave as highly chalcophile elements.

In order to consider all of the chalcophile elements a method presenting the data is needed. Lesher and Keays (2002) in presenting data from komatiite ores suggested an order based on decreasing mantle normalized values in the Kambalda ores. However this order is the product of the processes leading the formation of a particular deposit and may obscure the factors leading to the genesis of an ore. Following the tradition of lithophile geochemistry the elements can be plotted in order of their incompatibility with an MORB source (Fig. 2). If the MORB order were strictly preserved Ni would be placed between Pt and Rh, but this does not take into account the fact that MORB is generally saturated in a BMS liquid and thus the PGE are strongly depleted in MORB. In order to keep all of the PGE together the elements are plotted in order of compatibility with picrite/komatiitic basalt which gives essentially the same order apart from Ni and Co.

Figure 1. Partition coefficients between mafic magma and sulphide liquid; I indicates range of values from experiments conducted at fO2 between -2FMQ and +2FMQ; — indicates partition coefficients between MORB and sulphide droplet; arrows indicate minimum partition coefficients. Modified after Barnes (2016).

Figure 2. Comparison of mantle normalized concentrations of chalcophile elements in picrite/basaltic komatiite, MORB, upper continental crust and black shales. Modified after Barnes (2016).
3 The distribution of chalcophile elements during contamination of a mafic magma

In order to bring about saturation of a mafic magma with a BMS liquid and form a magmatic Ni-sulphide deposit it is commonly argued that the magma must become contaminated with crustal rock (Lesher and Burnham 2001). Whereas contamination with the average upper continental crust (pink line Fig. 2) could bring about saturation in a BMS liquid and would markedly enrich the magma in slightly to moderately chalcophile elements As, Sb, Pb and Bi, it would dilute it in Ni and PGE and is therefore not the ideal contaminant.

Black shales are a particularly appropriate contaminant due to their high S content and their ability to reduce Fe2O3 both of which would lead to BMS liquid saturation. Contamination with a black shale (blue line Fig. 2) would strongly enrich the magma in many elements from Sn to Te and although it would dilute the magma Ni content somewhat the effect would be much less than for average upper continental crust. At the Duluth Complex the lower unit contains disseminated sulphides and numerous black shale xenoliths. A mixture of 50 % picrite and 50% black shale (black line on Fig. 3) has similar element concentrations from Mo to Ag to the norites (green) with disseminated sulphides from the basal unit. However, from Cu to Co, the norites are richer in metals than a simple bulk mixture.

As pointed out by Lesher and Burnham (2001) this difference in behaviour between highly chalcophile elements and moderately to slightly chalcophile elements could be a result of the equilibration of the sedimentary sulphide with the mafic magma. The more the sedimentary derived sulphide liquid react with the magma the closer the composition approaches a purely magmatic sulphide. The reaction with the mafic magma estimated via the R-factor, the ratio of silicate liquid to sulphide liquid. Because of the high partition coefficient of the highly chalcophile elements into the sulphide liquid the effect of contamination is readily overprinted for these elements. For example, Pt concentrations increase by two orders magnitude from the sedimentary sulphide liquid to a sulphide liquid equilibrated at R=1000. At the same time the concentrations of the slightly chalcophile elements decreases (e.g. arsenic decreases by two orders of magnitude, Fig. 4). Most ore deposits require R-factors of 100 to1000 thus the effect of contamination on the concentrations of slightly to moderately chalcophile elements is not readily visible at in most ores.

4 The distribution of chalcophile elements during crystallization of sulphide liquids

If the sulphide liquid has the opportunity crystallize slowly fractional crystallization may occur and the chalcophile elements will be fractionated based on their compatibility with monosulphide solid solution (MSS). During fractional crystallization Cu behaves as an incompatible and concentrates in the fractionated liquid. Thus, in many cases

![Figure 3](image-url) Mantle normalized concentrations of chalcophile elements in Duluth Complex black shale and sulphide bearing norite compared with a mixture bulk mixture of 50:50 picrite plus black shale. Data from Samalens et al. (2017).

![Figure 4](image-url) Mantle normalized plot showing changes in chalcophile element patterns as the sedimentary sulphide liquid reacts with a mafic magma for changing ratios of silicate to sulphide liquids (R).

Ore bodies can be divided into MSS cumulate rocks, which are Cu-poor, and the products of fractional liquid crystallization, Cu-rich rocks. Classic examples of this type zonation occur in the world’s two largest magmatic Ni sulphide camps, Norilsk and Sudbury.

The Sudbury Complex is thought to be the product of flash melting of the crust by shock waves from a giant meteor (Dietz 1964). The chalcophile element pattern for sulphide liquid formed at R=5000 from this melt has been modelled on Fig. 5. The MSS cumulate formed from the melt would be enriched in Os, Ir, Ru, Rh, Re and Mo, but depleted in all other elements, as they are incompatible with MSS. The result is a chalcophile element pattern that is relatively flat, similar to the Cu-poor ore from Sudbury (red pattern on Fig. 5). Similarly, the fractionated liquid would be depleted in Os, Ir, Ru, Re and Mo and enriched in all other elements. The result is a pattern showing a steep increase from Os to Pt, then flattening out from Pt with negative Mo and Re anomalies similar to the Cu-rich ore from the McCreedy East deposit at Sudbury (green pattern on Fig. 5). Interestingly the Cu-rich ore appears to reflect a positive Pb and Bi anomaly observed in the initial model liquid.
Figure 5. Mantle normalized plot showing changes in sulphide patterns during fractional crystallization of model sulphide liquid formed from melting the average continental crust at R=5000 (pink line); Cu-poor sulphides (MSS cumulate) from the Creighton Mine, Sudbury and Cu-rich sulphides (fractionated liquid) from McCreedy East Mine Sudbury. Data from Dare et al. (2010, 2014).

5 Conclusions

The behaviour of the full range of chalcophile elements in magmatic nickel sulphide ores can be considered by using mantle normalized plots with elements in order of compatibility with a picritic source. Massive sulphides which are commonly MSS cumulates have essentially flat patterns. Copper-rich ores, which are thought to represent fractionated sulphide liquid, show strong depletion in Os, Ir, Ru and Rh relative to Pd, Pt, Au, Te and Cu. The Cu-rich patterns also have negative Re and Mo anomalies. The depletion in Os, Ir, Ru, Rh, Mo and Re occurs because these elements are compatible in MSS.

The effects of contamination of mafic magma with black shale, which is rich Te, As, Bi, Sb, Sn, Pb and Mo, can be seen on the mantle normalized patterns in sulphides with low R-factors <100. However, at the R-factors commonly required to form an ore deposit (100 to 10000) the sedimentary sulphides equilibrate with the magma and the effects is not obvious.

Acknowledgements

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Abstract. Small-scale podiform chromitites without economic significance occur in the Loma Caribe peridotite, Dominican Republic. These chromitites are heterogeneous in appearance, geochemistry and mineralogy. Nevertheless, all chromitites are PGE- and PGM-rich, with chromian spinel compositions showing high Cr# and high TiO2. An uvarovite-bearing chromitite sample from Loma Cumpié with a total PGE content of 6.5 ppm reveals chondrite-normalized PGE patterns with a positive Pt anomaly, which is absent in massive chromitites from the study area. The Pt anomaly is explained by the presence of Pt-Fe alloys included within veins of uvarovite cross-cutting the chromitite, hosting Ru and Os dominated primary PGM (e.g., laurite/erlichmanite). Our observations suggest that Pt was effectively mobilized by the low-temperature hydrothermal fluids that also precipitated uvarovite. This contribution provides direct evidence for low-temperature PGM formation at hydrothermal stages. Pt-Fe alloys formed at low-temperatures may represent the source for supergene formation of Pt-Ir-Fe-Ni alloys previously observed in the study area.

1 Introduction

Chromitites are monomineralic rocks almost made up of magnesiochromite (i.e., chromite s.l.), and can be divided into three main subtypes: (1) stratiform, associated with large-scale layered intrusions, (2) podiform, found in peridotites from ophiolite complexes, and (3) chromitites in concentrically zoned Ural-Alaska-Aldan-type complexes (CUAAC). Chromitites from layered intrusions and CUAAC are well-known to have relatively high contents of platinum-group elements (PGE: Os, Ir, Ru, Rh, Pt and Pd), sometimes reaching economic values. In contrast, chromitites associated with ophiolitic complexes contain in general relatively low, sub-economic PGE contents (Gonzalez-Jimenez et al. 2014 and references therein).

However, Tsoupas and Economou-Eliopoulos (2008) reported unusual high PGE contents of up to 25 ppm total PGE in small-scaled, podiform chromitites in Greece, which have been affected by post-magmatic events such as brittle deformation and metasomatic fluids. These authors observed platinum-group minerals (PGM) associated with Cr-bearing garnets (uvarovite?) and interpreted that PGM may have formed due to PGE mobilization during hydrothermal processes.

In this work, we provide new insights on the PGE geochemistry and mineralogy of uvarovite-bearing podiform chromitites in Loma Cumpié, Loma Caribe peridotite in the Dominican Republic. We report one of the few cases in which there is direct evidence of PGE mobility and PGM formation by low-temperature hydrothermal fluids.

2 Geological overview

Loma Caribe peridotites are one of the occurrences of the ophiolite-related ultramafic rocks along the northern margin of the Caribbean plate (Lewis et al. 2006). They are exposed in the Cordillera Central of the Dominican Republic as a NW-SE oriented Mesozoic belt that occupies a 95 km long and 4 to 5 km wide area. The belt is bounded by major faults and the peridotites mainly crop out as isolated dismembered bodies in tectonic belts. The major faults within the body strike parallel to the northwest trend of the massif and to the foliation (Haldermann et al. 1979).

The Falcondo Ni-laterite mining area is located in the central part of the Dominican Republic and developed on the so-called Loma Caribe peridotite (Fig. 1). The weathering profile is structured from bottom to top into: (i) serpentinized protolith (harzburgite>dunite>lherzolite), (ii) saprolite with hydrous Mg silicate-dominated mineralogy, and (iii) limonite with Fe-oxide(s)-dominated mineralogy (Lewis et al. 2006; Tauler et al. 2009; Villanova-de-Benavent et al. 2014, 2016; Aiglsperger et al. 2016b). Small chromitite occurrences without economic significance are scattered within the lateritic profile (Baurier-Aymat et al. 2015; Fig. 1). These chromitites appear either as massive pods in saprolite or as highly weathered “floating chromitites” within limonite (Proenza et al. 2007; Aiglsperger et al. 2016b, respectively). A general feature for all chromitites is that they reveal unusual high total PGE contents up to 17.5 ppm and rather unusual positive Pt trends are occasionally observed in chondrite-normalized patterns (Aiglsperger et al. 2016b). Platinum enrichment within “floating chromitites” is
explained by most likely biogenic mediated supergene formation of Pt-rich alloys close to the surface (Aiglsperger et al. 2016b). However, Pt-bearing minerals in unweathered chromitites are rare and hence the source of Pt for supergene formation remained unclear.

**3 Methods**

Whole-rock PGE contents were obtained at Genalysis Ltd., Maddington, Western Australia, by ICP-MS after nickel sulphide fire assay collection, following the method described by Chan and Finch (2001). Detection limits are 1 ppb for Rh, and 2 ppb for Os, Ir, Ru, Pt and Pd. Polished thin sections were prepared from one uvarovite-bearing chromitite sample from Loma Cumpié (Fig. 2) and subsequently investigated using a Quanta 200 FEI XTE 325/D8395, and a field-emission scanning-electron microscope (FE-SEM) Jeol JSM-7100 at the Serveis Científics i Tecnòlogics, University of Barcelona, Spain. Quantitative EMP analyses were obtained with a JEOL JXA-8230 electron probe microanalyser in the wavelength-dispersive spectroscopy (WDS) mode, operating with an accelerating voltage of 20 kV, a beam current of 10 nA and a beam diameter of 1 μm.

**4 Composition of chromian spinel and PGE geochemistry**

As reported from Baurier-Aymat et al. (2015) chromian spinels from the studied uvarovite-bearing chromitite sample reveal high average Cr# of 0.81 and heterogeneous TiO₂ contents, from 0.08 to 0.44 wt%. NiO contents are relatively high, reaching values ranging 0.14-0.41 wt%. Furthermore average concentrations of V₂O₃, MnO and ZnO are 0.19 wt%, 0.36 wt% and 0.13 wt%, respectively. Whole-rock PGE contents from uvarovite-bearing chromitites reach 6.5 ppm and are hence approximately three times higher than other massive chromitites from the study area (e.g., Loma Peguera; Proenza et al. 2007). The chromitite samples exhibit bulk-rock chondrite-normalized PGE patterns characterized by rather flat slopes from Os to Ru and subsequent negative slopes from Rh to Pd similar to other chromitites in ophiolites (Gonzalez-Jimenez et al. 2014), excepting a pronounced positive Pt anomaly similar to the one previously observed in highly altered chromitites from Loma Larga (Fig. 3).

**5 PGE mineralogy**

PGM are abundant in polished thin sections and range from 1 to 10 μm in diameter. In general PGM within the chromitite can be divided into two groups according to their form of appearance: (i) euhedral crystals of PGM included in chromian spinel and believed to be primary and crystallized from the parental melt of their host chromitite, and (ii) secondary PGM, derived from (trans)-formation of previous PGM during alteration processes (e.g.,
Euhedral crystals of primary PGM from the laurite-erlichmanite series are frequently observed and occur associated with pyroxene and attached Ir-bearing alloy (Fig. 4a). Secondary PGM are mostly Ru-Os-bearing alloys with associated Ir, showing a tendency of mobilization when affected by cross-cutting uvarovite veins (Fig. 4b). However, Pt-Fe alloys of variable grain size and irregular shapes are observed only within veins of uvarovite, hence suggesting significant Pt mobilization with subsequent PGM formation at low-temperatures (Fig. 4c).

6 Discussion

Uvarovite mineralizations in ophiolitic chromitites are usually considered as secondary mineral assemblages that formed during the post-magmatic infiltration of low-temperature hydrothermal fluids (Melcher et al. 1997; Proenza et al. 1999). Arai and Akizawa (2014) reported on chromite enclosed in zoned crystals of uvarovite in chromitites in the Oman ophiolite and suggested that chromitites can form during hydrothermal stages. However, uvarovite of this study is cross-cutting chromitites at Loma Cumpié, which are clearly magmatic in origin. These chromitites show intergrowths with interstitial clinochlore formed after chromite alteration. Our observations suggest that uvarovite has precipitated from a hydrothermal fluid penetrating through a network of brittle fractures. The close association of uvarovite with clinochlore and ferrian chromite in the Loma Cumpié chromitite points to alteration temperatures of the hydrothermal process close to 200–300ºC (Proenza et al. 1999).

In a recent review about PGM O’Driscoll and González-Jiménez (2016) write: “The Pt-Pd-Rh ± base-metal alloys (23%), isoferroplatinum (12%), sperrylite (9%), and Pt-oxides (derived from the alteration of Pt-sulfides such as malanite) are the most abundant PGM in the altered zones of the chromitite.”. However, primary Pt-rich PGM have yet not been observed within chromitites in the Loma Cumpié chromitites and a secondary reconcentration of Pt by hydrothermal fluids may explain the positive Pt anomaly in chondrite-normalized PGE patterns for uvarovite-bearing chromitites (Fig. 3). The representative examples of PGM shown in figure 4 provide a good example how primary PGM are affected by hydrothermal solutions causing formation of secondary Ru-Os alloy and coeval mobilization of PGE (Fig. 4b). Furthermore, the exclusive association of Pt-rich PGM with uvarovite (Fig. 4c) is a strong argument for their formation during the hydrothermal alteration of the chromitite.

Pt-rich alloys formed by such processes are believed to represent the source for recently observed Pt-Ir-Fe-Ni alloy formation under supergene conditions (Aiglsperger et al. 2016b).

Figure 4. BSE images of typical PGM found in the studied sample: A) euhedral crystal of primary laurite/erlichmanite associated with pyroxene and an iridium alloy. B) Desulphurization of primary PGM by hydrothermal fluids leading to formation of secondary PGM (i.e., Ru-Os alloy) and significant PGE mobilization (e.g., Ir enters the uvarovite vein); C) Pt-Fe alloys included in uvarovite believed to have formed after PGE mobilization (neoformation).

7 Concluding remarks

PGE-rich chromitites in the Loma Caribe peridotite are characterized by a rather heterogeneous geochemistry and a diverse mineralogy, which is quite unusual when compared with other podiform chromitites around the world.
In this work we presented evidence that clearly shows that hydrothermal activity affecting chromitites of the Loma Caribe peridotite result in: (1) formation of secondary PGM, (2) a significant PGE mobilization changing the whole-rock PGE budget, and (3) low-temperature formation of Pt-Fe alloys within uvarovite-veins in chromitites.

Such alteration processes have to be considered in geochemical investigations related to PGE/PGM (e.g., chondrite-normalized patterns; Re/Os; etc.).

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Changes in mineralogy and precious metals content in the Morrison deposit, Sudbury

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Abstract. Ore samples from the footwall type, Cu-Ni-PGE Morrison deposit were analysed. MD3 domain contains mainly chalcopyrite, pentlandite cubanite, mackinawite, pyrrhotite. In MD5 domain chalcopyrite, pentlandite and millerite dominate. The majority of the platinum is present in moncheite which often forms composite grains with hessite. Michenerite is the dominant Pd-phase. Gold is found near large moncheite-hessite grains, in Ni-sulphides and in the secondary magnetite. The platinum to palladium ratio increases almost linearly with depth, which can be a result of collecting palladium by base metal sulphides (mainly pentlandite) which makes Pd concentration in residual sulphide melt less efficient in comparison to Pt. Alternatively, it could be a result of later alteration of the orebody as Pd is more likely to be mobilized by hydrothermal fluids than Pt.

1 Introduction

One of the largest Ni-Cu-PGE resources in the world are hosted by the 1.85 Ga Sudbury impact structure. The contact type deposits, rich in nickel, has been widely recognized as a result of segregation of immiscible sulphide melts that accumulated along the base and embayments of the Sudbury Igneous Complex (SIC) during cooling of the impact melt sheet (Ames and Farrow 2007). Origin of footwall type deposits, which exhibit a spectrum of different mineralization styles, is not so clear. Sharp-walled deposits seems to represent a magmatic ISS-MSS-HzSS (intermediate solid solution - monosulfide solid-solution - heazlewoodite solid solution) cumulates crystallized from a residual sulfide liquid which migrated from the contact (Mungall 2007). Other studies emphasize the role of hydrothermal fluids in ore formation, especially regarding low-sulphide mineralization (Farrow et al. 2005; Penteš et al. 2008; Tuba et al. 2010).

Limited number of experimental works focused on the partitioning behaviour of metals and semimetals between the residual sulphide liquid and ISS/HzSS as well as complicated history involving magmatic, hydrothermal and metamorphic events are one of the reasons why some details of the mineralization processes in the footwall are not fully understood.

2 Geological setting

The Levack-Morrison system is located on the north range of the SIC, and consist of a contact type orebody (Levack) and the Cu-Ni-PGE-rich footwall mineralization (the Morrison deposit). Ore in the latter is divided into three types by Ames and Kjarsgaard (2013): transition ore in the former Rob’s zone (with Ni:Cu=1); sharp-walled veins (Cu>Ni, PGE); and low-S, high-PGE disseminated ore.

The deposit is comprised of a steeply dipping, chalcopyrite dominated veins containing lesser pentlandite, cubanite, bornite, pyrrhotite and millerite. Nelles (2012) concluded that most of the mineralogical and textural features observed in the ore can be explained by fractional and equilibrium crystallization of a sulfide melt (crystallization and subsolidus breakdown of MSS in upper domain and probably Hz-ISS in lower domain) with additional interaction between fractionated sulphide and wallrock to explain problematic presence of bornite and millerite in peripheral parts of the veins.

3 Analysis and results

Based on depth, the Morrison deposit is divided vertically into several parts. From the top to the bottom: MD1 (close to the SIC contact, former Rob’s zone), MD2, MD3, MD4, MD5 (away from the SIC contact). Ore samples from different levels of the Morrison deposit were collected. One continuous vein transecting almost whole MD3 domain (F vein, thickness 0.5-3 m) was chosen and sampled at different levels: 3690 (ft) at the top of the vein, then 4030 (ft), 4340 (ft) and 4520 (ft) at the peripheral part of the vein (4520 belongs to MD4 domain). Additional specimens were collected in the MD5 part (level 4860 ft and from 3 boreholes).

3.1 Ore mineralogy

The major mineral in the F vein is chalcopyrite, often containing mackinawite and cubanite laths; pyrrhotite patches and exsolutions are common. The main nickel mineral is pentlandite which occur in three forms: 1) rounded grains with mackinawite exsolution, 2) grains with small pyrrhotite lamellas, 3) a mass containing structurally oriented chalcopyrite laths (probably result of pentlandite replacement by chalcopyrite).

Massive pyrrhotite grains were rare and observed only in one sample close to the vein contact with the footwall rocks. Minor components are sphalerite (often with chalcopyrite exsolution) and magneteite, the latter present in four forms: as a non-altered grains, similar but altered grains, thin straight veins (Fig. 1a) and as an irregular patches containing sulphide inclusions (Fig. 1b). Peripheral part of the vein consists of chalcopyrite matrix (without cubanite, pyrrhotite and mackinawite but with numerous small holes) and irregular blebs of millerite.

Samples from the MD5 domain present a slightly
different mineral assemblage than MD3 domain. Chalcopyrite remains the dominant mineral but it doesn’t contain cubanite, mackinawite and pyrrhotite. Pyrite, absent in MD3, begins to appear in the samples although in small quantities. The dominant nickel mineral is millerite, whose veins are often accompanied by pentlandite or pentlandite-pyrite-carbonate assemblage. Magnetite in form of a primary, non-altered grains, sphalerite and galena are a minor component of the ore.

![Figure 1.](image1)

**Figure 1.** a Primary magnetite crystal in chalcopyrite with secondary magnetite vein. b Secondary magnetite with sulphide inclusions. c Composite grain of moncheite and hessite with native gold (left top). d Native gold in the magnetite.

### 3.2 Precious metals

The main carrier of platinum in both domains is moncheite (PtTe₂), which usually forms composite grains with hessite (Ag₃Te) (Fig. 1c) and sometimes with altaite (PbTe). Sperrylite (PtAs₂) and maslovite (PtBiTe) are rarely present. The most common palladium mineral is michenerite (PdBiTe), small crystals (5 μm) of paolvite (Pd₂Sn) was found in one sample. PGM grains usually has straight-sided or rounded boundary (indicating textural equilibrium), irregular and cuspatte boundaries with smaller satellite grains (indicating textural disequilibrium) are rare. Majority of the PGMs are hosted by chalcopyrite, but some michenerite are present in millerite. Some of the tellurides and bismutellurides show extensive Pd-Pt and Bi-Te substitutions.

Gold was present in MD3 domain inside secondary magnetite with sulphide inclusions and in magnetite at the border of sulphide vein (Fig. 1d). Native gold and electrum are found in 3 assemblages in MD5 domain: with composite PGM moncheite-hessite grains (Fig 1c), inside and at the border of millerite grains and in pentlandite. The average content of precious metals at different levels is shown on figure 2.

![Figure 2.](image2)

**Figure 2.** Average content of Ni, Cu, Pt, Pd and Au in hand grabbed samples collected from different levels of the F vein.

### 3.3 Gangue minerals

As noted by Nelles (2012), although there are problems with hydrothermal fluids generating the Morrison deposit, orebody was definitely modified by them. Minerals which can be attributed to hydrothermal activity: authigenic quartz containing small inclusions of sulphides (Fig. 3), epidote, carbonates, actinolites as well as magnetite forming veins and irregular mass with sulphide inclusions (Fig 1b).

### 4 Discussion

Differences in mineralogy of the F vein and in general, between MD3 and MD5 domains, might be an expression of changes and evolution of the sulphide melt which became progressively depleted in iron further away from the SIC contact. Crystallization of MSS and ISS poorer in Fe could produce lower part of F vein where pentlandite and chalcopyrite don’t exsolve mackinavite and cubanite. The same reason causes the absence of pyrrhotite, mackinavite and cubanite in the MD5 domain. There is a general trend observed in the deposit: from the uppermost part (domain MD1) composed of pyrrhotite with lesser pentlandite and chalcopyrite, MD2-MD3 containing chalcopyrite with lesser cubanite, pentlandite, pyrrhotite millerite and bornite and to the MD4-MD5 domains where chalcopyrite, millerite, bornite and pentlandite are present. It could reflect an increase in melt S/Si with depth.

Alternatively, this changes in mineralogical composition might be a result of interaction with the footwall rocks and hydrothermal fluids, because formation of alteration minerals (epidote, actinolite, magnetite) at the vein borders would consume iron. Uppermost and lowermost parts of the F vein are significantly thinner than rather uniform middle part so the Fe-loss had more impact there (bigger amount of melt in the thicker part acted as a buffer). It could explain why instead of Fe-richer phases (cubanite, pentlandite with mackinawite and pyrrhotite) only pentlandite and chalcopyrite are observed in the 3690 level. In the lowermost part, stronger interaction at the vein periphery would cause bigger loss of Fe in comparison to 3690 level and is responsible for presence of chalcopyrite, millerite and bornite. These two models are not mutually exclusive.
Figure 3. Simplified sequence of events playing role in the formation of the Morrison deposit.

Stage 1 – Sulfide droplets are collected in the embayment at the base of SIC.

Stage 2 – Contact deposit in the embayment is formed.

Stage 3 – Contact deposit consists mainly of MSS cumulates (3a). Part of the sulfide liquid, rich in Cu, escapes into the footwall along Sudbury Breccia zones. Orebody shows zonation: mineral assemblage in upper part of the deposit (MD3) is Fe-rich (3b: pentlandite with mackinawite exsolutions, 3c: cubanite and pyrrhotite exsolution in chalcopyrite, pentlandite) while lower part (MD5) is Fe-depleted (3d: millerite veins with pentlandite and chalcopyrite, 3e: millerite, pentlandite and pyrite).

Stage 4 – PGMs crystallize from residual melt left between ISS grains (A; 4a: composite grains of moncheite and hessite in reflected light, 4b: SEM image of moncheite and hessite grain) or as a result of hydrothermal activity (B; 4c: maslovite in the magnetite). Hydrothermal fluids modified some primary PGM grains (4d: cusped and irregular moncheite-hessite grain).

Stage 5 – hydrothermal activity is responsible for presence of alteration minerals postdating sulfides e.g. authigenic quartz (5a), actinolite, epidote, carbonates and secondary magnetite (5b).
The most striking feature in the figure 2 is a decrease in Ni, Cu and Pd grade and increase in Au and Pt content in the 4520 level. One explanation for “decoupling” of Pt and Pd might be a different behaviour of these metals in the melt and distinctive partitioning between MSS/ISS/residual liquid. Experimental studies in the S-poor Fe–Ni–Cu–S system (Peregoedova and Ohnenstetter 2002) indicate that Pt generally behave incompatibly with MSS, ISS and HzSS and form its own discrete phases. Palladium on the other hand, could be incorporated into base metal sulphides and its behaviour is controlled by variations in $f_{S_2}$ (amount of dissolved Pd increase with $f_{S_2}$). Nickel content of the crystallizing sulfides also play a role, Pd became more compatible with heazlewoodite–intermediate solid solution (HzSS–ISS) and MSS when their Ni content increases (but it does behave incompatibly with Fe-MSS and Cu-rich ISS).

As a result, observed increase in $f_{S_2}$ and Ni content with depth in the Morrison deposit would allow Pd to partially partition and enter Hz-ISS and/or MSS solid solution. Therefore, Pt would steadily concentrate in residual melt and form discrete Pt minerals, while Pd concentration would be less effective because crystallization of Hz-ISS and/or Ni-rich MSS scavenge part of the Pd (pentlandite often contain significant amount of palladium and very small amount of platinum, Barnes and Ripley 2016). This would allow Pd levels in the residual sulfide liquid to exceed those of Pd and increase ratio Pt/Pt+Pd with depth, as can be seen in the figure 4.

Figure 4. Pt/(Pt+Pd) ratio display almost linear increase with depth, available data for domains MD3-5.

Another process which might be responsible for this pattern is a hydrothermal modification of the ore. Replacement of pentlandite by millerite-pyrite-carbonates would release, mobilize and transport palladium to the adjacent footwall or to the other parts of the orebody. There is a possibility that hydrothermal fluids remobilized and redistributed also gold, and to lesser degree, platinum (indicated by presence of maslovite, native gold and electrum as a vein filling in magnetite). However, the distances across which the precious metals were mobilized are uncertain; the overall effects on the grade of the deposit needs further research.

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The mafic-ultramafic Jacurici Complex (NE Brazil): a chromite-hosted mineral inclusions study

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Abstract. The Monte Alegre Sul is a segment of the mafic-ultramafic intrusion Jacurici Complex and hosts an up to 8 m-thick chromitite layer. Chromite-hosted inclusions are abundant along the entire chromitite layer. Inclusions are usually 10-20 μm in size, normally randomly distributed and composed of a single mineral phase that comprises olivine, ortho- and clino.pyroxene, amphibole, phlogopite, magnetite and pentlandite. Chromite-hosted hydrated silicate inclusions indicate that the magma in which chromite crystallized contained early formed hydrous minerals or became hydrated. The chromitite massive layer interval occurs at a stratigraphic level where significant petrological changes occur. We suggest in this study that crustal contamination releasing fluids into the magma during magma ascent through conduits could have played an important role in the extensive chromite crystallization and formation of the thick chromitite layer.

1 Introduction

Solid inclusions within chromite grains have been described in disseminated and massive chromitites both in ophiolitic and stratiform tectonic environments. The association of solid inclusions in chromite has been recognised as being related to the factors controlling the formation of chromitites since the 1960s (McDonald 1965). Since then, several attempts have been made to understand the mechanisms of entrapment and the relationship of the chromite-hosted solid inclusions and the origin of massive chromitites (e.g. Irvine 1975; Peng et al. 1995; Li et al. 2005; Spandler et al. 2005). Although the Jacurici Complex hosts one of the thickest chromitite layer in the world and represents the Brazilian largest chromium deposit, no attempt has been made so far to investigate its origin in the light of chromite-hosted solid inclusions. This study aimed to better constraint magma conditions at the time of chromite crystallization and shed some light on chromitite formation.

2 Geological setting

The Jacurici Complex, located in the São Francisco Craton, Northeastern Brazil, is composed by several mafic-ultramafic bodies, many of them mineralized with chromite. The bodies are believed to be disrupted segments of a single intrusion (Marques et al. 2017, in press). The Complex intrudes gneisses of the Mesoarchean Santa Luz Complex (Silveira et al. 2015) and presents a general N-S orientation cropping out parallel to the Paleoproterozoic Itiuba Syenite (Fig. 1) and extending along a belt of at least 70 km long. The bodies are thin (up to 300 m) and host massive chromitite layers of variable thickness, ranging up to 8 m thick in some segments. The Monte Alegre Sul (MAS) segment occurs in the central part of the Complex and was mined in the 1970’s in open pit by the FERBASA Group. The mineralized layer has an average thickness of 5 m and is found between 50 and 150 m deep (Marinho et al. 1986).
3 Sampling and analytical procedures

The drill core MAS-105-65° of the Monte Alegre Sul segment was selected and carefully described. Representative silicate samples and regularly close spaced massive chromitite samples were collected. Polished thin sections of chromitite were analysed using a scanning electron microscope (SEM), JEOL 6610-LV, equipped with an energy dispersive spectrometer (EDS), Bruker Nano XFlash Detector 5030, at the Laboratório de Geologia Isotópica from the Universidade Federal do Rio Grande do Sul. The aim was to identify chromite-hosted mineral inclusions. The SEM was operated with 15 kV acceleration potential and 14 mm working distance. The standard ZAF calibration method was applied. Complementary analyses for major and minor elements of selected inclusions were performed using an electron microprobe, JEOL JXA-8230 at Universidade de Brasilia. The equipment was operated with 15 kV acceleration potential and a 20 nA beam current, using natural mineral standards and standard ZAF matrix corrections. Care was taken to avoid fractures and interference with the host chromite.

4 Results

4.1 Stratigraphy of the Monte Alegre Sul

The MAS-105-65° borehole intercepts 55 m of a mafic-ultramafic intrusion hosting an almost 8 m thick massive chromitite layer. The stratigraphy of the Monte Alegre Sul (Fig. 2) fits in the division proposed by Marques & Ferreira-Filho (2003) for the Ipueira and Medrado areas, located about 30 km to the south, and can be divided into a Mafic Zone and an Ultramafic Zone. The Mafic Zone is only represented by an interval of about 6 m thick and is constituted by an altered gabbro in tectonic contact with basement rocks. The Ultramafic Zone can be subdivided into an Upper Ultramafic Unit, a Main Chromitite Layer (MCL) and a Lower Ultramafic Unit. The Upper Ultramafic Unit is 35 m thick and is represented by the predominance of pyroxenite with lenses of lherzolite. The MCL will be detailed in the next section. The Lower Ultramafic Unit has only its upper part recovered and is represented by serpentinite.

4.2 Main Chromitite Layer

The contacts between the MCL and the host rocks are faulted though it is possible to observe a banding at the basal contact, marked by interlayered centimetre-tick silicate lamina and millimetre-tick chromitite lamina (Fig. 3a), followed by an upward increasing in chromite content. Most of the MCL is represented by massive chromitite containing 90 vol% or more of chromite (Fig. 3b), showing interstitial pyroxene, amphibole and serpentine. Chromite grains are mainly subhedral, well preserved and very fine-grained, ranging 0.25 mm and, in a few cases, up to 1 mm.

Figure 2. Stratigraphy of the MAS-105-65° drill core. The Lower Ultramafic Unit is not completed once the drilling stopped after achieving the MCL.

Figure 3. General aspect of a banded chromitite close to the basal contact and b fine-grained massive ore.

4.3 Chromite-hosted solid inclusions

Along the entire MCL interval inclusions within chromite grains are abundant, though they are less frequent near the layer’s core. Most of the chromite grains host at least one inclusion, but the number of inclusions is variable. In a single thin section inclusion-free chromite grains can occur side by side with inclusion-bearing grains (Fig. 4a). In
inclusion-rich chromite, the inclusions can account for as much as 15% of the host grain surface (Fig. 4b). Most of the inclusions are randomly distributed, though in some cases they can form an internal corona, following the chromite crystallography (Fig. 4c). Inclusions can reach the size of 50 μm, the majority ranging around 10-20 μm. Spherical and anhedral inclusions are common (Fig. 4a and b), however several show subhedral prismatic habit (Fig. 4c) or show outlines that appear to follow chromite symmetry (Fig. 4d); tiny hexagonal euhedral inclusions are rare. Most of the inclusions consist of a single silicate phase, among which phlogopite (Fig. 4e), olivine, clinopyroxene, orthopyroxene and amphibole (Fig. 4f) were identified so far; inclusions of magnetite are frequent; inclusions of pentlandite are rare; one semi-included zircon was found. It is not unusual that a single chromite grain hosts inclusions of almost all the cited minerals (Fig. 4f).

![Figure 4. a-c Photomicrographs with reflected light and d-f back-scattered SEM images of mineral inclusions within chromite grains. Phl: phlogopite; Opx: orthopyroxene; Cpx: clinopyroxene; Am: amphibole; Ol: olivine. See main text for explanations.](image)

5 Discussion

The subhedral and euhedral inclusions, along with the single phase character point to entrapment of early crystallized minerals by chromite rather than entrapment of melt in which chromite was forming. Even anhedral and spherical inclusions are composed of one homogeneous phase and do not resemble trapped melt.

The observed internal coronas formed by the mineral inclusions seem to indicate (1) a period of interruption in chromite crystallization allowing precipitation of other minerals around chromite grain boundary followed by a new chromite grow event or (2) that some moments in the chromite formation history are more suitable for mineral entrapment. If the second hypothesis is true and the bulk of chromite is inclusion-bearing, the factors controlling chromite crystallization can be related to those favouring mineral entrapment.

One important feature regarding inclusions composition is the hydrated nature of some of them (phlogopite and amphibole). These minerals indicate that the primitive magma from which chromite crystallized was initially hydrous or that it became hydrated by the time of chromite crystallization. The presence of hydrous minerals as inclusions in chromite has been reported from various important stratiform chromitite deposits – Bushveld Complex (McDonald 1965; Li et al. 2005), Stillwater Complex (Page 1971; Spandler et al. 2005), Muskox Intrusion (Irvine 1975), Bird River Sill (Talkington et al. 1983) – as well as in ophiolitic chromitites – Oman Ophiolite (Lorand & Ceuleneer 1989; Borisova et al. 2012), Hongguleleng Ophiolite (Peng et al. 1995) and many other minor ophiolites (Talkington et al. 1984). Several authors interpret the presence of these hydrous silicate inclusions as a result of reaction between primitive magmas and fluids, either in a magma chamber context (Peng et al. 1995; Borisova et al. 2012) or in a localized context within inclusions (Li et al. 2005).

Previous workers from the Jacurici Complex have recorded important changes in the magmatic system occurring exactly in the MCL interval. Marques et al. (2003) performed Os and Nd isotopic studies on the Ipueira and Medrado segments and suggest that crustal contamination occurred in MCL interval. Ferreira Filho & Araujo (2009) assumed crustal contamination as a trigger for the MCL formation in the Ipueira and Medrado areas; they suggest increase in oxygen fugacity of the magma, caused by assimilation of carbonate-rich wall rocks. Marques and Ferreira Filho (2003) and Marques et al. (2017, in press) propose that the Jacurici Complex represents remnants of a feeder dike of a large igneous continental province; they consider that huge volumes of primitive magma would be required to explain the anomalously thick chromitite layer in thin mafic-ultramafic intrusions.

In a combined model of chromite formation inside a conduit emplaced in metasedimentary rocks (Marques et al. 2003, Ferreira Filho e Araujo 2009, Marques et al. 2017, in press) argue that primitive magma-wall rock interaction could be expected and crustal contamination involving hydration becomes a possible scenario. The presence of water in the magmatic system is known to widen the stability field of chromite (Ford et al. 2002; Feig et al. 2006), thus favoring extensive chromite crystallization. Fast growth rate is assumed to be required for entrapment of large amounts of small melt inclusion in chromite of komatiites (Barnes 1985; Godel et al. 2013). Considering wall rock assimilation, crustal fluids released
into the magma could contribute to fast chromite growth rate, explaining the abundance of trapped minerals. Chromite-hosted mineral inclusions were already observed in chromitites of other segments in the Jacurici Complex. Detailed work should thus be extended to tentatively map possible stratigraphic and/or geographic variations in the textures and compositions of these inclusions.

6 Conclusions

The presence of hydrous silicate mineral inclusions in chromite suggests that the parental magma was initially hydrous or became hydrated during formation of the Jacurici Complex massive chromitite. Although magma hydration and even the role of hydrated fluids remains debatable, it is believed that magma-wall rock interaction accompanied by addition of fluids could have played an important role in chromitite formation. Furthermore, hydrated primitive magmas seem to be a significant feature in chromitite deposits worldwide, so an interaction between fluids and primitive magmas appears to contribute to chromitite formation.

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Magmatic sulfide mineralization in orogenic belts

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Abstract. World-class magmatic Ni-Cu-(PGE) deposits have been extensively studied and were thought to primarily occur in extensional intraplate settings. However, mafic-ultramafic intrusions in orogenic belts, such as the Central Asian Orogenic Belt, Appalachian Orogen, and Variscan Orogenic Belt, have been reported to contain significant Ni-Cu resources. Preliminary studies about magmatic sulfide deposits in orogenic belts suggest that these deposits have features different from those in intraplate settings. They have formed from siliceous high magnesium basaltic (SHMB) magma, different from high magnesium basalt in cratonic settings. The SHMB-like magma was produced by hydrous melting of the mantle source under temperature relatively lower than that in cratonic settings. These SHMB-like magmas have undergone selective crustal contamination during emplacement. The intrusions in orogenic belts were generally formed by multiple magma injections with very different compositions, which is rare in mafic-ultramafic intrusion in cratonic settings. By comparison of deposits in both environments, we believe that the difference between magmatic sulfide deposits in orogenic belts and cratonic settings are due to the different mantle source and evolution of magma evolution histories.

1 Introduction

Magmatic sulfide deposits associated with mafic-ultramafic intrusions are important resources of Cu, Ni and platinum-group elements (PGE). Most world-class magmatic sulfide deposits, including those at Thompson and Vosey’s Bay (Canada), Noril’sk and Pechenga (Russia), Jinchuan (China), Bushveld (South Africa), and Eagle and Duluth (USA), are thought to occur in intraplate or cratonic marginal settings (Naldrett 2009; Begg et al. 2010). Sulfide deposits in orogenic belts were generally considered to be small and noneconomic (Naldrett 2009). However, a few magmatic sulfide deposits have been discovered in orogenic belts recently, such as the Tati and Selebi-Phikwe intrusions in Tati-Limpopo belt, Botswana (Maier et al. 2008), Kotalahti and Vammala intrusions in the Syecofennian orogenic belt, Finland (Barnes et al. 2009), the Sally Malay in the Halls Creek Orogen, Australia (Sproule et al. 1999), the Porneuf-Mauricie intrusion in the Greenville Orogen, Canada (Sappin et al. 2011), the Bruvann intrusion in the Caledonian orogenic belt, Norway (Boyd and Mathiesen 1979), the Aguablanca intrusion in the Variscan orogenic belt, Spain (Pina et al. 2010), Alaskan-type intrusions and intrusions in the Appalachian Orogen, USA and Canada (Paktunc 1990; Thakurta et al. 2008), and the Kalatongke, Huangshandong, Huangshanxi, Xiangshan, Hongqiling and Baishiquan intrusions in the south margin of the Central Asian Orogenic Belt (CAOB), China. These sulfide-bearing mafic-ultramafic intrusions in orogenic belts have several unique characteristics: 1) they have rocks rich in orthopyroxene; 2) they are linearly distributed along faults; and 3) they are generally funnel-shaped. These features are different from those in cratonic environments, which may suggest a unique origin for these orogenic magmatic sulfide deposits.

Although these deposits do not have reserves similar to those in cratonic settings, they have been an important source of Cu and Ni in some countries. On the other hand, there are a large amount of mafic-ultramafic rocks in orogenic belts, but only few of them contain sulfide mineralization. Therefore, how and why these mineralized intrusions reached sulfide saturation and formed sulfide deposits are still unclear but very important for understanding the metallogenesis of and exploration for sulfide deposits in orogenic belts.

2 Comparison of orogenic sulfide mineralization with those in intraplate settings

2.1 Composition of parental magmas

Because of the lack of chilled margins, the compositions of the parental magmas for intrusions along the southern margin of the CAOB are difficult to estimate. However, rocks from such intrusions contain variable amounts of orthopyroxene, indicating a siliceous basaltic composition for the parental magma (Gao and Zhou 2013a).

Fe/Mg distribution between olivine and silicate melts is nearly constant (Kd=(FeO/MgO)O/ (FeO/MgO)L = 0.3±0.03) (Roeder and Emslie, 1970), so olivine compositions can be used to constrain the composition of parental magmas. Olivines in mafic-ultramafic intrusions in the orogenic belts have variable Fo contents (78-91): the Aguablanca intrusion has olivine with the highest Fo contents (up to 91) (Pina et al. 2006), while the Kalatongke intrusion contains olivine with the lowest Fo contents (up to 80) (Zhang et al. 2009; Gao et al. 2012b). Assuming the olivine with highest Fo value has equilibrated with the most primitive melts, the parental magmas would have MgO/FeO ratios from 1.1 to 3.0. Calculations using the MELTS program (Ghiorso and Sack, 1995) under conditions of a pressure of 0.5-2 kb and fO2 = FMQ, yield more than 10 wt.% MgO for the equilibrated melts of most intrusions except Kalatongke (~8.5%). Although olivines from Kalatongke have low Fo contents, nearly constant Ni/Fe ratio of olivines suggest that they have re-equilibrated with sulfide liquids. Moreover, the Kalatongke intrusion has chrome spinels.
with high Fe$^{3+}$ contents and Fe/Mg ratios, indicative of crystallization from evolved magma (Gao et al. 2012b). Thus, the parental magma of Kalatongke may have previously undergone fractional crystallization of olivine. The non-cumulate norite is better to represent the parental magma composition under such conditions. The Kalatongke magma may have MgO higher than 11% as Zhang et al. (2009) calculated using whole-rock compositions. Therefore, parental magmas of all these intrusions should have MgO contents higher than 10%, consistent with high-Mg compositions.

The Iridium-subgroup of PGEs (IPGE; Ir, Ru and Os) and Ni are more compatible in the mantle residue than the palladium-subgroup (PPGE; Rh, Pt and Pd) and Cu during partial melting of the mantle and fractional crystallization (Barnes et al. 1985). High degrees of partial melting that generate high-Mg magmas would produce magmas with low Pd/Ir and high Ni/Cu ratios. On the Pd/Ir versus Ni/Cu diagram, most of sulfide ores from intrusions in orogenic belts plot within or close to the field of high-Mg basalts and layered intrusions, indicating that the parental magmas were likely high-Mg basaltic in composition, consistent with the calculated results in terms of olivine composition. Although the parental magma of the Aguablanca intrusion was not well constrained, the Aguablanca intrusion is temporally related to an Andean-type continental magmatic arc as the product of the subduction of the South Portuguese zone beneath the Ossa-Morena zone during the Hercynian orogeny (Eguíluz et al., 2000). Rocks of the intrusion are characterized by strong enrichment in LILE, LREE and Pb with negative Nb and Ta anomalies (Pina et al. 2010), indicative of typical subduction-related magmas. These rocks contain large amounts of orthopyroxene, similar to those in the southern margin of CAOB. High contents of orthopyroxene indicates that the parental magmas of SI–Mg-rich (SHMB) (c.f. Wang et al. 2006).

### 2.2 Nature of mantle sources and parental magmas

Although the origin of these intrusions is still a matter of debate, these intrusions have mineral chemistry and whole-rock geochemistry different from those intrusions formed in cratonic settings.

Olivine is a common mineral in mafic-ultramafic intrusions and mantle residues. During the partial melting of the mantle, Mg has constant partition coefficient between the olivine and silicate melts, but the partition coefficient of Ni could be highly affected by the composition and temperature of silicate melts (Adam and Green, 2006). Thus, Ni contents in olivine could be used to represent the conditions during partial melting of mantle. Mafic-ultramafic intrusions in Aguablanca, southern margin of CAOB and Appalachian Orogen contain olivine with lower Ni than those from intrusions in Noril’sk, Voisey’s Bay and Emeishan province. The Jinchuan intrusion is an exception that has olivine with relatively low Ni because the olivine has reacted with sulfide melts to lower the Ni in olivine (Li et al. 2004). Similar Fo values of olivine suggest that mafic-ultramafic intrusions in both environments may have similar major elemental compositions, particularly the MgO contents. Hence, low-Ni olivine from intrusions in orogenic belts may indicate a different origin. Experiment results indicated decreasing melting temperature would increase the partition coefficient of Ni between olivine (mantle residuals) and melts (Adam and Green 2006). Thus, the SHMB-like magmas in orogenic belts might be produced by partial melting under temperature lower than that in cratonic environments.

Parental magmas of mafic-ultramafic intrusions in orogenic belts are SHMB-like with high MgO contents, which should be produced by either medium-high degrees of partial melting with crustal contamination or hydrous melting due to the addition of water can significantly lower the solidus temperature of the mantle.

Olivine grains at Kalatongke and Huangshandong also have low CaO contents (<0.11%), indicative of low-Ca (CaO<10%) magmas (Gao et al. 2012b; Gao and Zhou 2013a). Calcium behaves differently from Mg and Fe during partial melting and crystallization. During partial melting processes, CaO in the silicate melts would reach the highest when the degree of partial melting is 15-20%, whereas MgO and FeO in the melts will increase with increasing degrees of partial melting. Low Ca and high Mg contents of the Kalatongke and Huangshandong magmas are possibly produced by ~10% degrees of partial melting so that high MgO affinity of their parental magmas can not be the result of medium-high degrees of partial melting. On the other hand, all mafic-ultramafic intrusions in orogenic belts commonly contain primary hydrous minerals such as amphibole or phlogopite (or biotite), indicating that their parental magmas were water-rich. In addition, the lithospheric mantle under orogenic belts is likely to be hydrous due to previous subduction of oceanic crust (Mooney et al. 2012). Thus, SHMB-like magmatism derived by low degrees (~10%) of partial melting of hydrous mantle source might be a common feature in orogenic belts.

Mafic intrusions in the southern margin of CAOB, such as the Kalatongke, Huangshandong, Huangshanxi, Xiangshan, Baiqiquan and Hongqiling, have positive εNd values and low 87Sr/86Sr ratios (Figure 1). Some rocks may have experienced later alteration so that they have highly radiogenic whole-rock Sr isotopic compositions, e.g. high Sr isotope sample from Baiqiquan. The study of in situ Sr isotope shows that the fresh plagioclase grains from Kalatongke and Huangshandong have initial 87Sr/86Sr ratios lower than 0.7040, although whole-rock initial 87Sr/86Sr can be up to 0.7055 (Gao and Zhou, 2013a, b). Although the Aguablanca intrusion has negative εNd values (-7.5 to -5.2) and highly radiogenic Sr isotopes (0.7083 to 0.7100), Casquet et al. (2001) considered that the parental magmas were derived from a mantle source with isotopic compositions between those of bulk Earth and depleted mantle and that the enriched isotopic compositions were caused by contamination by ~2 Ga.
basement. Therefore, all these isotopic characteristics indicate that parental magmas of these intrusions were derived from depleted mantle source.

**2.3 Selective crustal contamination**

Crustal contamination is very common for basaltic magmas and is an important process in the formation of magmatic Ni-Cu-PGE sulfide deposits (Ripley et al. 1999; Keays and Lightfoot 2010). The addition of either silicate or sulfur to the magma can trigger the sulfide saturation (Naldrett 2009). Crustal contamination would increase SiO2 contents and thus show more enriched lithophile isotopes such as Sr, Nd and Pb, whereas the assimilation of sulfide would result in the magma with highly radiogenic Os isotopes (Yang et al. 2012).

Sr-Nd isotopes of the hosting rocks of typical magmatic sulfide deposits in intraplate setting and orogenic belts are summarized in Figure 1. The Noril’sk, Voisey’s Bay and Emeishan intrusions have widely varying Nd isotopes with εNd values from -13 to +8, indicating different mantle source and large degrees of crustal contamination. On the contrary, mafic intrusions in Aguablanca and the southern margin of CAOB generally have narrow variations of Nd and Sr isotope compositions, suggesting that parental magmas may have undergone less degrees of crustal contamination or assimilation of juvenile crustal materials.

The Kåltångke, Huangshandong, Huangshanxi and Hongqiling intrusions were emplaced into wall rocks with similar Nd-Sr isotopic compositions so that Nd-Sr isotopes can not well constrain the degrees of crustal contamination. The Baishiquan and Tianyu intrusions intrude the Proterozoic Xingxingxia and Kawabulak Groups that have Nd-Sr isotopic compositions significantly different from these two intrusions. Although the Baishiquan and Tianyu intrusions have relatively large variations in Nd and Sr isotopes, they have positive or slightly negative εNd values. Modeling using Sr-Nd isotopic compositions suggested that they have undergone small degrees of crustal contamination. Thus, mafic-ultramafic intrusions in orogenetic belts are likely to have been experienced low degrees assimilation of silicate wall rocks.

In comparison to lithospheric radiogenic isotope systems, the Re-Os system holds the greatest potential to trace the process of crustal contamination because Re is a moderately incompatible element, while Os is a strongly compatible element. Crustal rocks therefore have high Re and low Os when they separated from the mantle so that they have much higher radiogenic Os isotopic compositions (γOs values up to several thousand) than the mantle (Lambert et al. 1998). Lithophile elements (e.g. Sr, Nd) and chalcophile elements (e.g. Os) behave differently during the interaction between mantle-derived magmas and crustal rocks because chalcophile elements in the crust are mainly hosted in sulfides (Lambert et al. 1998; Ripley et al. 1999).

ε Nd and γOs values of mafic-ultramafic intrusions in intraplate environments and orogenic belts are summarized in Figure 2. The Noril’sk and Jinchuan intrusions have relative small variations in both Nd and Os isotopes, whereas the Voisey’s Bay is highly variable in both isotopes, indicating variable degrees of contamination and possibly multiple contaminants. Mafic-ultramafic intrusions along the southern margin of CAOB have relatively uniform εNd values but highly variable γOs values (Figure 2). Neodymium isotopes of these intrusions do not show strong assimilation of crustal materials, but significantly variable and high Os isotopes suggest different amounts of addition of crustal Os. Thus, the Re-Os system has decoupled from the Sm-Nd system in these intrusions.

During the crustal contamination processes, crustal silicate rocks could be completely digested by basaltic magmas or partial melted with restite as xenoliths (Lesher and Burnham 2001). The degree of assimilation silicate rocks might be a function of temperature of the magma and the composition of the xenolith. On the other hand, sulfides and other volatile minerals are much easier to be assimilated into the magmas than silicates due to low melting point (Lesher and Burnham 2001). Thus, it is possible that sulfide was easily assimilated into the magmas, but siliceous crustal materials may have been partially digested by mafic magmas (Ripley et al. 1999; Lesher and Burnham 2001). Osmium isotopic compositions of mantle-derived basaltic magma would be
2.4 Magma differentiation and sulfide saturation

Petrology, mineralogy and geochemistry of some magmatic sulfide deposit within orogenic belts suggest that these deposits formed by multiple magma injections with very different compositions. Although different pulses of magma may have evolved from the same magma, variable pre-emplacement evolution may have controlled the crystallization sequence and assemblages of minerals, resulting in different types of sulfide mineralization. For example, in Kalatongke, the two magma injections formed the massive and disseminated sulfide ores respectively (Gao et al. 2012b); the early magma of Huangshandong segregated PGE-depleted sulfide ores, while the later one formed PGE-undepleted sulfides (Gao et al., 2013); sulfide ores at Aguablanca are hosted in the later intrude breccia (Pina et al., 2010). Thus, multiple magma injections with different compositions may be a common feature of the orogenic magmatic sulfide deposits.

3 Conclusions

Parental magmas of mafic-ultramafic intrusions in orogenic belts were generally siliceous high magnesium basaltic (SHMB-like) produced by partial melting of hydrous mantle. In different orogens, the mantle sources have variable compositions from depleted to less depleted. Relatively lower melting temperature produced such SHMB-like magmas with relative low CaO and Ni.

Mafic-ultramafic intrusions in orogenic belts have decoupled Nd and Os isotopic compositions, indicating selective addition of more crustal sulfur and less silicate materials. Multiple injections with different compositions are also important for the formation of mafic-ultramafic intrusions in orogenic belts.

Acknowledgements

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Formation of magmatic Fe-Ti-V-P deposits within the Lac St. Jean anorthosite suite, Saguenay, Québec, Canada: Insights from trace element composition of Fe-Ti oxides

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Abstract. The (1170-1140 Ma) Lac St. Jean anorthosite suite located near Saguenay, Quebec is a voluminous massif-type anorthosite complex associated with anorogenic anorthosite-mangerite-charnockite-granite (AMCG) magmatism of the Grenvillian orogeny. This anorthosite complex hosts many magmatic Fe-Ti-V-P ore bodies along its margins. The ore bodies vary in texture from massive, semi-massive, to disseminated and the mineralogy varies with relative proportions of magnetite (source of V), ilmenite (Ti), and apatite (P). This project will study representative ore bodies along each margin of the complex to determine any pluton-scale variations in mineralogy and geochemistry. It will involve detailed petrography, electron microprobe analysis, and laser ablation (LA)-ICP-MS to obtain their respective mineralogy, and major and trace element chemistry of Fe-Ti oxide minerals (magnetite, ilmenite, and spinel). Since the geochemistry of Fe-Ti oxide minerals is sensitive to magma differentiation and oxygen fugacity (fO2), these results will be used to determine crystallization history of the ore and if the different deposits can be linked by differentiation of a common magma. Upon completion of this project, differences on both the deposit- and pluton-scale will be used to constrain a formation model for magmatic Fe-Ti-V-P deposits within the Lac St. Jean anorthosite suite.

1 Introduction

The Lac St. Jean anorthosite suite is located within the Mesoproterozoic Grenville Province, near Saguenay, Québec and is associated with geon-11 (1180-1110 Ma) anorthosite-mangerite-charnockite-granite (AMCG) magmatism. (Rivers et al. 2012). Along the margins of this complex are several magmatic Fe-Ti-V and Fe-Ti-P ore bodies hosted within the Lac St. Jean anorthosite which possibly formed from a residual ferrodiorite liquid (Longhi et al. 1999). In general, Fe-Ti oxide ore bodies associated with anorthosite complexes can display four mineralogical assemblages, 1) (gabbro-)noritic ilmenite ± apatite ± magnetite, 2) Ti-magnetite ± apatite, 3) nelsonite (~2/3 Fe-Ti oxide minerals, ~1/3 apatite), and 4) rutile-ilmenite ore (Charlier et al. 2015). Previous work by Hebert et al. (2005) on the Lac St. Jean anorthosite shows visible differences with respect to field relationships, ore mineral and silicate assemblages, and metal grades. Composition of the host anorthosite also effects the crystallizing Fe-Ti oxide phase, with hemo-ilmenite as the predominant Fe-Ti oxide mineral in andesine-type (An23-48) anorthosites and Ti-magnetite in labradorite-type (An45-63) anorthosites. Also, apatite-bearing ore bodies only occur within andesine anorthosite while remaining absent in labradorite anorthosite-hosted ore bodies (Hebert et al. 2005). Furthermore, Fe-Ti-V-P ore bodies associated with Proterozoic anorthosite suites can have four distinct morphologies, 1) massive, 2) stratiform, 3) massive to layered tabular bodies, and 4) lenticular ore bodies (Charlier et al. 2015). Some of these form discordant dykes/lenses of massive Fe-Ti-P ore, which continues to provoke questions about the origin of these ore bodies. A number of models are proposed to form Fe-Ti oxide and apatite deposits: 1) fractional crystallization, 2) magma mixing, 3) liquid immiscibility and, 4) solid-state remobilization (Charlier et al., 2015).

Variability in Fe-Ti oxide mineralization in a single anorthosite complex could be due to varying magma composition (e.g., Ti, P, and aSiO2 of the magma), oxygen fugacity, and/or mode of formation (Woodruff et al. 2013; Charlier et al. 2015). It is also important to consider any sub-solidus effects associated with cooling and deformation during high-pressure metamorphism associated with the Grenvillian orogeny (Rivers et al. 2012).

Considering the parameters affecting Fe-Ti-V-P mineralization within Proterozoic anorthosite suites, in-situ mineral chemistry of Fe-Ti oxides within these ore bodies should provide constraints on how these deposits formed. Applying this technique can constrain the relationship between Fe-Ti-V-P ore bodies and their host rocks on both the deposit-scale and throughout the Lac St. Jean anorthosite suite.

2 Fe-Ti-V-P mineralization of the Lac St. Jean anorthosite suite

Locations of the occurrences to be examined during this study are displayed in Figures 1 and 2 and details of their morphology, ore assemblages, grade and tonnage data are summarized in Table 1. Mineralized zones studied in this project will represent the northern (Lac à Paul, Lac Margane, and nearby Lac Houlière-Nord), eastern (Buttercup, Lac à l’Orignal), southern (St. Charles de
Bourget), and western (Lac Perron) margins of the Lac St. Jean anorthosite.

Fe-Ti-V deposits (Figure 2) appear more abundant than Fe-Ti-P deposits (Figure 1) and all of these ore bodies collect along the margins of the Lac St. Jean anorthosite suite. Apatite is abundant in the Lac à Paul, Lac à l’Original, and Lac Perron (even though marked as Fe-Ti-V) deposits, corresponding to elevated P$_2$O$_5$ values in Table 1. Lac Margane, Lac Houlière-Nord, and Buttercup are devoid of apatite. No hemo-ilmenite deposits have been noted in the Lac St. Jean anorthosite suite. The proportion of magnetite to ilmenite varies among the deposits: Lac à Paul ore is ilmenite-dominated while Buttercup and St Charles de Bourget are magnetite-dominated, which correlates with elevated vanadium contents (Table 1). Lac Margane, Lac Houlière-Nord, Lac à l’Original, and Lac Perron appear to have approximately equal portions of magnetite and ilmenite.

**3 Analytical methods**

Detailed petrography will be completed on polished thin sections to classify each sample based on modal percentages of Fe-Ti oxide minerals, available silicate minerals, and presence or absence of apatite.

Electron microprobe analysis will be performed using a JEOL JXA-8230 located at the University of Ottawa. Both oxide and corresponding silicate phases (if present) will be analysed for major and minor elements.

LA-ICP-MS analyses will determine concentrations of 25 trace elements in Fe-Ti oxide minerals using a Photon Machines Analyte (193nm) Excimer laser system and a 7700 Agilent quadropole ICP-MS at the University of Ottawa. Following the method outlined in Dare et al. (2014), the Fe-Ti oxides will be calibrated using GSE-1g and data quality will be monitored using secondary reference materials (GOR-128, GSD-1, and natural magnetite BC-28). Fe is used as the internal standard using Fe values from the microprobe.

**4 Summary**

There are many parameters controlling the formation of magmatic Fe-Ti-V-P deposits in Proterozoic anorthosite complexes. Variations among the Lac St. Jean anorthosite ore bodies, such as varying modal proportions of ilmenite relative to magnetite and presence or absence of apatite, exist not only at the deposit-scale, but also at the scale of the anorthosite complex. Our approach is to use trace element chemistry of Fe-Ti oxides themselves to provide important constraints on the formation of these enigmatic deposits (such as in Chartier et al. 2007, 2009, 2010; Dare et al. 2014; He et al. 2016).
### Acknowledgements

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**Table 1.** Location, morphology, ore assemblages, and grade and tonnage data of occurrences to be examined during this study. (Dashes indicate missing data, mt=magnetite, ilm=ilmenite, ap=apatite).

<table>
<thead>
<tr>
<th>Occurrence</th>
<th>Location</th>
<th>Morphology</th>
<th>Ore assemblage</th>
<th>Tonnage</th>
<th>FeO₃</th>
<th>TiO₂</th>
<th>V</th>
<th>P₂O₅</th>
<th>References</th>
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<tbody>
<tr>
<td>Lac à Paul</td>
<td>North</td>
<td>Intrusion-hosted</td>
<td>Ilm+ap (minor Mt)</td>
<td>702 Mt</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.16%</td>
<td>Ariane Phosphate (2015)</td>
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<td>Lac Margane</td>
<td>North</td>
<td>Layered Sequence within intrusion</td>
<td>Mt+Ilm</td>
<td>-</td>
<td>65%</td>
<td>25%</td>
<td>3200 ppm</td>
<td>-</td>
<td>Tremblay (2016)</td>
</tr>
<tr>
<td>Lac Houlière-Nord</td>
<td>North</td>
<td>Layered sequence within intrusion</td>
<td>Mt+Ilm</td>
<td>-</td>
<td>65%</td>
<td>25%</td>
<td>3200 ppm</td>
<td>-</td>
<td>Tremblay (2016)</td>
</tr>
<tr>
<td>Buttercup</td>
<td>East</td>
<td>Lense-shaped</td>
<td>Mt (trace Ilm)</td>
<td>3.2 Mt</td>
<td>49%</td>
<td>19%</td>
<td>0.67% V₂O₅</td>
<td>-</td>
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</tr>
<tr>
<td>Lac à l’Orignal</td>
<td>East</td>
<td>Intrusion-hosted</td>
<td>Mt+Ilm+ap</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.5%/45m</td>
<td>Laverdiere (2012)</td>
</tr>
<tr>
<td>Lac Perron</td>
<td>West</td>
<td>Lense-shaped</td>
<td>Mt+Ilm+ap</td>
<td>606 000 t</td>
<td>64.4%</td>
<td>25.8%</td>
<td>0.6% V₂O₅</td>
<td>6.6%</td>
<td>Tremblay (2014)</td>
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<tr>
<td>St. Charles de Bourget</td>
<td>South</td>
<td>Numerous lenses in anorthosite</td>
<td>Mt&gt;Ilm+ap</td>
<td>37 Mt</td>
<td>48%</td>
<td>20%</td>
<td>0.4% V₂O₅</td>
<td>5.7%</td>
<td>Girard and Barrette (2011)</td>
</tr>
</tbody>
</table>
Geochemical composition of the chromite from sulfide and graphite ores of the Beni Bousera ultramafic massif (north Morocco)

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Abstract. Magmatic S-G ores in the ultramafic massif of Beni Bousera (Internal Rif, Northern Morocco) are made up of sulfides (pyrrhotite, pentlandite, chalcopyrite), sulfoarsenides (cobaltite), arsenides (nickel, maucherite) and chromite ± graphite, associated with phlogopite, clinopyroxene and plagioclase. These ores are variably altered at lower temperature during serpentinization/weathering processes. During this alteration process, chromite mostly remains unaltered, either in terms of major or minor elements. However, the geochemical variation in chromite is obscured by local equilibrium with associated silicates during their crystallization.

1 Introduction

The chemical composition of chromite has been commonly used as an indicator of the composition of parental melt form which it crystallizes (e.g. Irvine 1965, 1967; Arai 1992; Barnes and Roeder 2001; Kamenetsky et al. 2001). Zn, Mn and Co content in chromite are considered as an indicator of Co–Ni–Zn–Cu sulfide mineralization or mineralizing environments associated with serpentinitized ultramafic rocks (e.g., Groves et al. 1977, 1983; Wylie et al. 1987; Gahlan and Arai, 2007). Altered chromite remains as zoned crystals with unaltered cores and ferrian chromite rims (e.g. Barnes 2000; González-Jiménez et al. 2009; Mukherjee et al. 2010); however, recent research show that chemical composition of chromite can be modified during metamorphism (Gervilla et al. 2012). This modification affects chromite rims, and chromite cores, considered previously as unaltered (Colas et al. 2014).

Unusual magmatic ore assemblages consisting of Fe-Ni-Cu sulfides and graphite ± chromite occur within the ultramafic massif of the alpine Betic-Rif chain (south Spain and north Morocco) (Gervilla and Leblanc 1990; Gervilla et al. 2002). Ores occurring in the south of Spain massifs preserve their primary mineralogy and texture but those from the Beni Bousera massif in north Morocco were affected by serpentinitisation/weathering process.

2 Geological setting

The ultramafic massif of Beni Bousera (Internal Rif, Morocco. Fig. 1) belongs to alpine peridotites group bordering the western Mediterranean Sea (Kornprobst 1974; Reuber et al. 1982). It is a portion of the upper mantle emplaced into the continental crust under compressional regime by lithospheric shear zones (Afiri et al. 2011; Frets et al. 2014). Leucogranite dyke were injected subsequently to the intra-crustal emplacement of peridotite (El Beghdadi 1993). Subsequently, serpentinitisation and weathering processes affected the Beni Bousera massif, especially along the NE fault contact of the massif with the overlying Ghomaride Unit (Fig. 1).

Two types of ores are present in the Beni Bousera massif: (1) the first one correspond to chrome and Ni-arsenide associated with orthopyroxene and cordierite, hosted in strongly serpentinitized area located close to the NE contact (Cr-Ni ores). (2) The second one includes a group of irregular, variably altered masses of magmatic Fe-Ni-Cu sulfides containing variable proportions of graphite and minor chromite (S-G ores). S-G ores are widespread in the massif, represented in four deposits (Fig. 1).

3 Alteration stages

The petrographic study of S-G ores in the Beni Bousera massif allows definition of two mineral assemblages generated as the consequence of different types and variable degree of alteration: 1) unaltered ores; 2) ores assemblage modified during serpentinization and weathering process. Some primary ores assemblages remain unaltered in Mina del Rio and Amasiden deposits; they consist of sulfides (pyrrhotite, pentlandite, and chalcopyrite) sulfoarsenide (cobaltite) and arsenides (mauchérite) ± chromite ± graphite, associated with phlogopite pyroxene, and plagioclase. The second ore assemblage is well represented in Amasiden Malikath and Islan deposits. In Amasiden, the occurrences are intersected by serpentinization fault (N160°E), inducing the amphibolitization of pyroxene followed by chloritization, sericitization of plagioclase. Chromite had a spongy appearance. In the Islan deposit, the occurrences are marked by the formation of sepiolite and dolomite associated with graphite; the serpentinitization does not affect chromite. In Malikath deposit, the ores are marked by the formation of iron oxides and hydroxide resulting from sulfide lixiviation. Thus, ores consist of chromite associated with graphite, included in a matrix of chlorite and Fe-vermiculite.
4 Chromite

4.1 Texture

Chromite texture in the S-G ores depends on the mineral assemblage. In ores constituted mainly of sulfides in the unaltered ores from Mina del Rio deposit and in ores associated with sepiolite from Islan deposit, chromite is disseminated among the massive sulfide grains; it has idiomorphic to subidiomorphic forms with average grain size of 200 μm. Disseminated chromite in graphite from the Malikath deposit is highly corroded. In ores constituted of sulfide and pyroxene/plagioclase-bearing ore altered into Mg-hornblende, chlorite, and zeolite, chromite has a spongy appearance with corroded edges.

4.2. Chemical composition

The chemical composition of chromite was obtained by electron-probe micro analysis (EPMA) at the Centro de Instrumentación Científica (CIC) of the University of Granada, using a CAMEBAX SX100 instrument with an excitation voltage of 20 kV and beam current of 20nA. Beam diameter was 5μm. Monitored spectral lines were: MgKα, FeKα, AlKα, CrKα, SiKα, TiKα, MnKα, NiKα, VKα, and CoKα. Standards used were MgO, Fe2O3, Al2O3, Cr2O3, SiO2, TiO2, MnTiO3, NiO and V2O3, ZnS, NiO, cobalt, STi2.

The chemical composition of chromite in the Amasiden deposit varies according to the mineral assemblage. Chromite from clinopyroxene-bearing ores (Cr=0.53-0.65 and Mg=0.17-0.25) is slightly richer in Al2O3 than that associated with plagioclase (Cr#=0.62-0.7, and Mg#=0.03-0.2) (Fig. 2a). These chromites have also some distinctive minor elements contents. In fact, chromite from clinopyroxene-bearing ores contains lower MnO (0.32-0.4 wt.% and slightly higher ZnO (0.74-1.1 wt.%) than that from plagioclase-bearing ores (MnO=0.39 to 0.7 wt.% and ZnO=0.59 to 1.0 wt.%) (Fig. 2 d & e).

In the Mina del Rio deposit, chromite is associated with sulfides, phlogopite and plagioclase. It is characterized by Cr# =0.55-0.61 and Mg# =0.18-0.24 (Fig. 2a), with V2O3=1.97-2.16 wt.% (Fig. 2c), MnO =0.35-0.47 wt.% (Fig. 2d), and ZnO=0.87-1.44 wt.% (Fig. 2e).
In the Malikath deposit, chromite is associated with vermiculite and graphite. In terms of major elements, it has Cr# (0.31-0.48) well below the chromite from the other S-G ores studied and comparable Mg# (0.19-0.34) (Fig. 2a). However, this chromite exhibits the highest V2O3 (1.44-2.63 wt.%; Fig. 2c) and ZnO (1.34 to 1.88 wt.%; Fig. 2e) contents. MnO varies from 0.23 to 0.49 wt.% (Fig. 2d).

Chromite from the Islan deposit occurs associated with graphite and sepiolite, and it is characterized by a Cr# and Mg# values ranging respectively from 0.62 to 0.67, and from 0.29 to 0.33 (Fig. 2a). V2O3 contents vary from 0.63 to 0.71 wt.% (Fig. 2c), MnO from 0.21 to 0.33 wt.% (Fig. 2d) and ZnO from 0.43 to 0.76 wt.% (Fig. 2e).

The chemical composition of the analyzed chromite from Beni Bousea mostly plots within the field of S-G ores from the Serranía de Ronda ultramafic massifs (Gervilla et al. 2002) and partly overlaps the fields of chromite from Stillwater and Fiskenaesset stratiform complexes (Fig. 2a). ZnO contents show positive correlation with Mg# values and negative correlation with Cr# values (Fig. 2e). MnO contents show an opposite trend to that of ZnO contents (Fig. 2d). Chromite from phlogopite-bearing ores and vermiculite bearing ores from both Mina del Rio and Malikath deposit shows higher V2O3 contents than in those associated with plagioclase, clinopyroxène and sepiolite from Amasiden and Islan deposit (Fig. 2c). This feature exists also in chromite from phlogopite-bearing Cr-Ni ores. NiO and CoO are respectively lower than 0.09 wt.% and vary from 0.06 and 0.14 wt.% (Fig. 2f). Although sulfides and Ni arsenides were leached out, in Malikath deposit, chromite was not rich in NiO or CoO (Fig. 2f).

Figure 2. Compositional variations of chromite grains from S-G mineralization in Beni Bousea massif, in terms of Cr/(Cr+Al) (Cr#), Mg/(Mg+Fe2+) (Mg#), and minor oxides (TiO2, V2O5, MnO, ZnO, NiO, CoO) in wt.%. Black square: clinopyroxene and plagioclase bearing ores. Blue triangle: phlogopite-bearing ores from the Mina del Rio deposit. Dark green circle: vermiculite-bearing ores from the Malikath deposit. Light green circle: ores from the Islan deposit. S & G: chromite from S-G mineralization in Serranía de Ronda massif (Gervilla et al. 2002); St: chromite from stratiform complex (Jackson 1968); F: Chromite from the Fiskenasset complex (Ghisler 1976).

5 Discussion

Major and minor element proportions in chromite show a significant variation depending on fluid re-crystallisation. No geochemical variation due to alteration process were identified. Cr# value and MnO content are higher in plagioclase-bearing S-G ores than in pyroxene or phlogopite bearing ores. Mg# value and V2O5, ZnO contents shows significantly higher contents in phlogopite-rich, sulfide-rich ores in Mina del Rio, and in vermiculite rich, sulfide-poor ores in Malikath deposit. Therefore, variations in chromite composition are the result of local equilibrium with associated silicates during their crystallization. Thus, the co-crystallization of chromite and plagioclase promotes preferential Al partitioning to plagioclase leading to the formation of Cr-rich chromite, as it is observed in Amasiden. Serpentization/weathering of S-G ores does not affect
the composition of chromite. At Islan, this type of alteration causes only formation of serpilolite at the expense of anhydrous silicates, coeval with the formation of carbonates. In Amasiden, these processes reveal a more complex alteration, starting with amphibilization of pyroxene and followed by chloritization and sericitization of plagioclase. This stage is better represented in Malikath where chromite occurs associated with graphite (up to 90%), iron oxides, and hydroxides, resulting from sulfides lixiviation. The latter are included in a matrix of vermiculite and Fe-rich vermiculite. This mineral assemblage reveals complete alteration of sulfides, giving rise to iron oxides and hydroxides, and replacement of primary silicates by hydrous phyllosilicates.

6 Conclusions

Chromite from S-G ores remains almost unaltered during serpentinisation/weathering process identified in the Beni Bousera massif. Chromite geochemical variation is only due magmatic differentiation, because these ores formed from a chromite- and sulfide-bearing sulfide melt, segregated after the crystallization of the parent arsenide melt of Cr-Ni ores.

Acknowledgements

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Use of chromite chemistry for correlation of PGE-bearing reefs within the Bushveld Igneous Complex

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Abstract. The Platreef and a massive chromitite seam below it have recently been proposed to be the lateral equivalents of the Merensky and UG-2 reefs, respectively. In addition, a recent study showed cryptic layering in the UG-2 chromitite, which was interpreted to result from sequential accumulation of discrete chromite seams, implying that chromitites may form by coalescence of discrete seams each with slightly different chemistry. This project aims to further assess the usefulness of chromite chemistry as a petrogenetic tool and to assist in the correlation between the Northern Limb and the rest of the Bushveld. In this context, chromitite samples from a UG-2 reference suite (from the Western limb) and the massive chromitite below the Platreef (currently considered as the UG-2 ‘equivalent’ and labelled as UG-2E) were analysed and compared. Preliminary results, based on EPMA and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), as well as EPMA data compiled from the literature show distinct and partially overlapping compositional fields: samples from the massive chromitite in the Northern Limb have slightly lower Cr# at the same Mg# than UG-2 suites. The results also show sharp variations in some trace elements (e.g. Mn, Ga) across the thickness of the seam, which is consistent with the formation by accumulation of discrete seams.

1 Introduction

The 2050 Ma old Bushveld Igneous Complex (Scoates and Friedman 2008) is the largest known mafic-ultramafic igneous complex on Earth and consists of four different igneous rock suites. The most studied being the Rustenburg Layered Suite (RLS), which contains the largest reserves of platinum group element (PGE) in the world (Maier et al. 2014). The RLS consists mainly of mafic-ultramafic cumulate rocks exposed at three limbs: the Eastern, Western, and Northern limbs. These limbs host PGE mineralization in layers referred to as ‘reefs’, namely: UG-2, Merensky Reef (MR), and Platreef. The Western and Eastern limbs host PGE ores within the UG-2 (massive chromite) and the Merensky Reef (chromite- and sulfide-bearing pyroxenite), whereas ores within the Northern Limb are associated to the Platreef (also chromite- and sulfide-bearing pyroxenites).

Although the MR and the Platreef are roughly at the same stratigraphic position, correlation is difficult for two reasons: first, in most places the Platreef has been affected by assimilation and interaction with country rocks; second, mineralization in the Platreef tends to be much thicker than in the MR. Deep drilling by Ivanhoe Mines intersected a massive chromitite seam (~ 120 cm thick) below the Platreef. Based on this and other lithological similarities, this seam has been interpreted as the stratigraphic equivalent of the UG-2 unit that is recognized in the Eastern and Western Bushveld (Grobler et al. 2016). Because chromite is an early cumulate mineral, a key mineral in all the reefs, and has relatively high closure temperatures, it likely preserves information about crystallization conditions in its crystal chemistry (e.g. Junge et al. 2014). The goal of this project is to establish whether chromite chemistry can be used to assist in the correlation of chromitite seams and also as a tool to infer crystallization conditions. Here we document preliminary results pertaining to major, minor and trace elements in chromite samples from a reference UG-2 chromitite seam from the Western Limb and a chromitite seam below the Platreef (the ‘UG-2 equivalent’ and henceforth labelled the UG-2E for clarity).

2 Samples and analytical methods

The UG-2E studied is a massive chromitite seam (roughly 120 cm in thickness) intersected below the Platreef in drillhole UMT-365. Half core of the chromitite seam was sampled and prepared to have a set of petrographic polished sections of the entire chromitite seam. The reference UG-2 chromitite consists of a suite of samples from a 60-cm thick chromitite seam sampled every 3 cm (the ‘Waterval Suite’ documented in Naldrett et al. 2012). Samples of both chromitite seams were characterized petrographically and analysed using Electron Probe Microanalysis (EMPMA) for major elements and using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) for minor and trace elements.

3 Results

Some similarities and differences were recognized petrographically and after mineral chemistry analyses. Main similarities: The majority of chromite grains occur as discrete crystals with euhedral to subhedral habit of non-uniform size. Association of rutile with chromite is common and the interstitial space is composed mostly of pyroxene and plagioclase. Chromite grains are homogenous in composition (no zoning was identified), and are occasionally annealed. Main differences: Sulfides are more abundant in the UG-2E below the Platreef (from roughly 1 % to up to 7 %) whereas the reference UG-2 chromitite contained very little sulfides (up to about 1% in some sections). Sulfides are mostly interstitial but sulfide inclusions inside chromite grains are also more abundant in the UG-2E. Modal proportions and grain size are also slightly different. The UG-2 reference suite is
predominantly massive (chromite proportions generally > 90 %) and with smaller crystals (from 0.001 mm to around 0.6 mm), whereas the UG-2E is more variable (chromite proportions ranging from 46 % to 83 %) and slightly larger chromite grains 0.001 mm to around 1.3 mm).

3.1 Chromite chemistry

Figure 1 shows the samples analysed in this study and data compiled from peer-reviewed literature pertaining Bushveld chromites (from different parts of the Bushveld Complex). In general, the data distribution shows decreasing Mg# with increasing Cr# (trend A from Naldrett et al. 2012), proposed to be characteristic of changing melt composition as a result of multiple injections of primitive magma during chromite crystallization, as observed in other chromites from layered igneous intrusions (Naldrett et al. 2012, Jones 2013). In general, MR chromites have the lowest Mg# and highest Cr#, the majority of data with Mg# > 0.4 corresponds to the UG-2 and the UG-2E and other samples from the Platreef. The UG-2 reference suite analysed in this study (blue dots) is consistent with other published data; the UG-2E suite (red squares) is consistent with other data from the Northern Limb. Generally, the suites from the Northern Limb define a trend that is parallel to that of the rest of the Bushveld but with lower Cr# at the same Mg#. In addition, samples from the UG-2E have the highest documented Mg#, only comparable with data in Jones (2013). The reasons for these differences are not clear at this point but may reflect multiple processes (e.g. degree of differentiation of the magma, degree of re-equilibration with intercumulus melt and surrounding silicates, etc.)

Figure 1. Mg# versus Cr# of Bushveld Complex chromites from this study (UG-2 in blue, UG-2E in red) and other studies. Other data shown include: Kruger & Marsh (1985): basal chromitite layer of the Merensky cyclic unit. Li et al. (2005): inclusion-bearing and inclusion-free chromites from basal chromitite seam of MR. Mitchell & Scoon (2007): upper and lower chromitite stringers and also from disseminated within PGE-mineralized pyroxenites. Vukmanovic et al. (2013): chromite grains from the upper and lower chromitite layer of the MR. Mathez & Mey (2005), Junge et al. (2014), and Veksler et al. (2015): massive UG-2 chromitite layers. Yudovskaya & Kinnaird (2010): massive and disseminated chromites from the Upper and Lower chromitite zones of the Platreef (different farms). Jones (2013): ‘massive’ chromitite from Overysel and Zwartfontein farms of the Platreef. Nodder (2015): massive chromites (also considered UG-2E, from drillhole UMT336D1). Mg# = Mg2+/(Mg2+ + Fe2+); Cr# = Cr3+/(Cr3+ + Al3+).

3.2 Cryptic variations in UG-2 and UG-2E

Figure 2 shows variations in chromite chemistry with height from the base to the top (top of chromitite seam is 0) of the two chromitite seams (top, in blue, for the UG-2 reference; bottom, in red, for the UG-2E, which is almost twice as thick). The two suites of samples were analysed using roughly the same analytical protocols. Error bars show 1-sigma uncertainties. The Mg# and Cr# are from EPMA data whereas Mn and Ga content is from LA-ICP-MS analyses. Although a large suite of trace elements was analyzed only Mn and Ga data are shown here because
they had the smallest relative uncertainty and also because Mn is expected to substitute for divalent cations and likely follows the relatively fast diffusion of the Mg²⁺-Fe²⁺ pair, whereas Ga is expected to substitute for the main trivalent cations (Al and Cr) and have relatively slower diffusion. In general, UG-2E unit chromites have larger uncertainties compared to UG-2 chromites, which may reflect larger heterogeneity in grain composition (although several analyses did not reveal any significant variation between core and rim composition). The scales are matched so that the two suites of samples can be compared in terms of their range and relative uncertainties. Both suites of samples show sharp variations, which are overall consistent with the variations documented by Junge et al. (2014), which they interpreted to indicate a succession of discrete chromitite layers that segregated sequentially on top of each other. However, the reference UG-2 chromitite has significant less variability than the UG-2E.

For the UG-2 reference, most of the variation seem to be recorded in the Cr#, although some significant changes (larger than 2-sigma) are documented in the Mn content. In contrast, for the UG-2E all the parameters (Mg#, Cr#, Mn and Ga content) show significant variations. The UG-2E chromitites have higher Mn and Ga contents, but also have relatively larger uncertainties compared to the UG-2 chromitite reference. It is significant to note that not all parameters vary systematically (e.g. the largest shift in Ga content is not matched by a shift in Cr#).

Figure 2. Comparison of the UG-2 and UG-2E ranges and variability in major elements (summarized by Mg# and Cr#) and some trace elements. Top panel: Mg#, Cr#, Mn and Ga contents through the 60-cm-thick UG-2 chromitite reference suite. Bottom panel: Mg#, Cr#, Mn and Ga contents through the 120-cm thick UG-2E chromitite. All data were collected using the same equipment and with the same analytical conditions.
4 Preliminary conclusions

The results show that the 'UG-2 equivalent' in the Northern Limb (the UG-2E) has lower Cr# and higher spread in Mg# than the reference UG-2 suite. Compilation of data from the Northern Limb and rest of the Bushveld indicates that this may be a consistent difference between the limbs. The results also confirm the sharp variations in Mg# and Cr# documented by Junge et al. (2014) and includes trace element data that also show such variations. Some of the trace elements (e.g. Mn, Ga) seem more useful than Mg# and Cr# because they have smaller relative uncertainties and the magnitude of the changes are relatively large.

As tool for correlation, the results, thus far, are inconclusive and not sufficient to support (or discard) the hypothesis that the UG-2E is truly the extension of the UG-2 in the Northern Limb. Although both chromitite seams have similarities there are some significant differences, which may be attributed to several variables (potentially including lateral variations, proximity to feeder dikes, etc.). Current work includes analysis of disseminated chromite in the sequence (above and below the UG-2E) and use of diffusion coefficients to estimate the temperature needed to equilibrate the composition of a chromite seam and potentially erase the documented shifts. Future work includes mineral chemistry of the surrounding silicates to assess the effect of re-equilibration with intercumulus melts.

In terms of using chromite chemistry to unravel petrogenetic processes, the results are partially consistent with those of Junge et al. (2014), meaning that the variations documented are consistent with cryptic layering and their ‘sequential segregation’ model. If this is the case, then models suggesting accumulation of chromites by other processes (e.g. slurries) would not be supported by the data because slurries should result in a random distribution of chromite grains with different chemistries. However, the fact that sharp variations in some trace elements (e.g. gallium) are not matched by variations in Cr# seem to indicate that the variations observed may have a different origin (i.e. ‘sequential segregation’ may not be the only possible explanation).

In general, this work highlights the potential of detailed and systematic trace element chemistry as a tool to understand the origin of massive chromitite seams.

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Strontium isotope stratigraphy of the Platreef: a tool for correlation with the rest of the Bushveld Igneous Complex

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Abstract. Strontium isotope stratigraphy throughout the Eastern and Western Limbs of the Bushveld Igneous Complex (BIC) shows a significant shift across the Merensky Reef near the top of the Critical Zone. However, in the Northern Limb, the strontium isotope stratigraphy is incomplete. Available data through the Main Zone of the Northern Limb show similar isotopic stages as the Eastern and Western Limbs, but there are no data through the Critical Zone. Such data are needed for correlation with the rest of the BIC, and in particular to assess whether the Platreef (which has been interpreted by some to be the stratigraphic equivalent of the Merensky Reef) also displays a large isotopic shift. The goal of this study is to expand the strontium isotopic profile of the Northern Limb by analysing a suite of samples collected through the transition between the Main Zone and the Critical Zone (including the Platreef). Anorthite content in plagioclase is a promising proxy as it shows a marked shift at the base of the Platreef.

1 The Bushveld Igneous Complex

The Bushveld Igneous Complex (BIC), South Africa, consists of three main units: (1) the Rooiberg rhyolite, a suite of cogenetic volcanic rocks preceding the intrusion phase of the BIC; (2) the Rustenburg Layered Suite (RLS), the layered mafic intrusion of the BIC; and (3) the Lebowa granite, the end phase of the BIC intrusive sequence. The 2.06 Ga intrusion extends over an area of 60,000 km² and is world renowned for its PGE, Cr and V deposits with additional Cu, Ni, Au, Sn, fluorite and Fe resources. The Rustenburg Layered Suite hosts many PGE-rich units (Merensky Reef, UG2 and Platreef) and multiple chromitite layers, which are the focus for mining throughout the BIC (e.g., Maier et al. 2013).

2 The Eastern and Western Limbs

2.1 Magmatic stratigraphy

There are 5 main stratigraphic zones in the Eastern and Western Limbs of the RLS: (1) the Marginal Zone, located at the contact between the magmatic sequence and the footwall; (2) the Lower Zone, dominated by interlayered harzburgites and dunites; (3) the Critical Zone, which is defined by the appearance of chromitite layers (e.g., Lower Group, Middle Group and Upper Group) and composed of norites, anorthosites, pyroxenites and some harzburgites; (4) the Main Zone, dominated by norites and gabbronorites with minor pyroxenites; and lastly, (5) the Upper Zone (predominantly norites, anorthosites and diorites but also hosting several magnetite layers). The Critical Zone is of special economic interest because it hosts PGE mineralization (Merensky Reef, UG2, Platreef) and sequences of large chromitite layers (e.g., Maier et al. 2013).

2.2 Strontium isotope stratigraphy

The strontium isotope profiles of the Eastern and Western Limbs of the BIC have been well documented by Kruger (1994). In a closed magmatic system, the initial strontium isotope ratio (i.e., 87Sr/86Sr) should not change; therefore, shifts in initial strontium isotope ratios have been interpreted to mainly document new pulses of magma (from different reservoirs) into the magmatic chamber or in-situ contamination via assimilation of wall rocks.

Using strontium isotopes, Kruger (1994) documented two main stages through the Rustenburg Layered Suite: an Integration Stage and a Differentiation Stage. The Integration Stage comprises part of the Lower Zone, all the Critical Zone and the lower part of the Main Zone. This stage is interpreted to record an active magmatic chamber with multiple pulses of magma entering the chamber causing sharp shifts, typically to lower strontium isotopic ratios. The more gradual shifts toward higher values are interpreted to be caused by rock assimilation during ascent or in-situ contamination. Although new magma pulses are typically related to a negative shift, some positive shifts may represent atypical isotopic compositions caused by assimilation of continental crust in intermediate magma chambers (thus increasing the strontium isotopic ratio before entering the final magma chamber).

The Differentiation Stage occurs from the Upper Main Zone upwards. The relatively constant initial strontium isotope ratio is interpreted to represent fractional crystallization in a closed system. The only documented shift occurs at the Main Zone-Upper Zone boundary, also known as the Pyroxenite Marker, where a large influx of new gabbroic magma is inferred to have entered the chamber (Kruger 1994).

2.3 The Merensky Reef shift

The largest shift in initial strontium isotope ratio in the Eastern and Western Limbs occurs through the Merensky Cyclic Unit (Kruger et al. 1982). There is a relatively sharp
increase in $^{87}$Sr/$^{86}$Sr, from 0.706 at the bottom of the Merensky Reef to 0.708 at the top of the cyclic unit (Seabrook et al. 2005). This shift is interpreted to be caused by a large pulse of gabbroic magma with atypical isotopic composition causing the large positive shift (Kruger 1994). This shift can be correlated from the Eastern to the Western Limb, which is over 250 km. The significance is if consistent across the Bushveld, it could provide an additional tool to correlate lithologies from the Northern Limb with the rest of the BIC.

3 The Northern Limb

3.1 Magmatic stratigraphy

In general, the magmatic stratigraphy of the Northern Limb is similar to the stratigraphy of the Eastern and Western Limb but with some major differences. The Upper Zone and Main Zone also occur in the Northern Limb but the Critical Zone and Lower Zone are different from the rest of the BIC and in many cases, only the topmost part of the Critical Zone is in direct contact with the Archean basement. Because of this, the terminology used in the Northern Limb for the mineralized horizons within the Critical Zone is either the Platreef (North of Mokopane) or the Grasvally Norite-Pyroxenite-Anorthosite (GNPA) member (South of Mokopane; Smith et al. 2014).

In general, the term Platreef is used where the Pt-Pd mineralization is in proximity to the footwall or within the assimilation zone. In this zone, most magmatic cyclic units are lost with relic layers still distinguishable and units present are varied-textured due to assimilation or proximity of xenoliths (Maier et al. 2008). The GNPA member is used where magmatic units are visible between and below Pt-Pd mineralization. The GNPA is represented by a sequence of gabbronorite, norite, pyroxenite and anorthosite with several chromitites, including multiple PGE-rich zones (McDonald et al. 2005).

Ivanplats has developed a stratigraphy dependent on magmatic cycles or units found on their farms (Grobler et al. 2016). The Turfspruit Cyclic Unit (TCU) can be applied on the Ivanplats’ farm (Turspruit) but cannot necessarily be applied throughout the Northern Limb. The inconsistent stratigraphy of the Northern Limb is related to two main reasons: (1) the mineralization of the Northern Limb is significantly thicker than the Pt-Pd mineralization of the Merensky Reef; and (2) the mineralization is in proximity of the footwall, which consequently destroyed magmatic cycles that typically occur with and below mineralization present in the Eastern and Western Limbs (Kinnaird et al. 2005; Ihlenfeld et al. 2011). Grobler et al. (2016) interpreted the Platreef to be the equivalent of the Merensky Reef due to less interaction with footwall rocks and appearance of magmatic cycles when drilling away from the contact farther down dip. Also identified were massive chromitite layers below the Platreef that were interpreted to be the equivalent of the UG2.

3.2 Strontium isotope stratigraphy

Despite the success of strontium isotope stratigraphy in the Eastern and Western Limbs, studies using strontium isotopes in the Northern Limb are scarce. To our knowledge, the only strontium isotope stratigraphic data from the Northern Limb is reported by Mangwegape et al. (2016). Although the section studied included a portion of the Platreef, the Sr isotope study focused only on parts of the Upper Zone and the Main Zone but excluded the Platreef (likely due to proximity of the footwall). The sample spacing in Mangwegape et al. (2016) was not as dense as in Kruger (1994) making correlation of macro-units difficult. However, two different stages, similar to the Integration and Differentiation stages in the Eastern and Western Limbs, can be identified.

The drill hole selected for this study is located farther down dip, to avoid interaction of the mineralized zone with the footwall and to increase the chance of identifying preserved magmatic stratigraphy, which other studies could not accomplish. The drill hole chosen is 1602 m deep, of which 1375 m is identifiable magmatic stratigraphy, followed by 29 m with disrupted magmatic layering due to assimilation and the following 198 m is footwall. Mineralization in this hole is 38 m thick. There is 112 m of magmatic stratigraphy below mineralization making this drill hole ideal to perform an isotopic stratigraphy study. A total of 47 samples were taken from 158 m above mineralization and through to the bottom of the magmatic stratigraphy focusing around major contacts between cyclic units. Thirty samples will initially be analysed by Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) for strontium isotopes and additional samples will be analysed based on preliminary results.

4 Preliminary results

4.1 Plagioclase composition

Figure 1 shows how the anorthite content of plagioclase changes through the stratigraphy of the Platreef and Main Zone. The results show a change from lower anorthite content in plagioclase to higher anorthite content at major contacts between cyclic units (e.g., the contact between the Platreef and the Footwall Cyclic Unit). This may be due to new pulses of magma entering the magmatic chamber and driving the composition of the resident magma to a more mafic composition, which is then reflected in the cumulates formed.
5 Future work

5.1 Strontium isotopes

Samples were collected through magmatic cyclic units from a drill hole on Ivanplats’ Turfspruit farm. The Lower Main Zone, through mineralization of the Platreef, and into cyclic units below mineralization were sampled for strontium isotopes. Sampling density increases around major unconformities, mainly around the unconformity occurring at the bottom of the Platreef. Whole-rock initial strontium and rubidium isotope ratios will be calculated using measured \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{87}\text{Rb}/^{86}\text{Sr}\) by MC-ICP-MS analyses. Shifts found through the stratigraphy will be compared to shifts that occur through the rest of the BIC. In-situ strontium isotope analyses of plagioclase will also be completed to compare with whole rock values and to identify different isotopic populations of plagioclase, if any, through the stratigraphy (Seabrook et al. 2005).

5.2 Lead isotopes

Lead isotope stratigraphy has scarcely been used in the BIC but could be a great addition to strontium isotopes. Lead isotopes have also been documented to record processes, such as contamination, in magmatic systems (Chutas et al. 2012). Lead isotope analyses could record different sources of contamination or record different processes that occurred in the magmatic chamber.

5.3 Mineral compositions

Mineral compositions have been documented to change gradually and sharply though the stratigraphy of the RLS. A comparison of the mineral compositions of plagioclase, orthopyroxene, clinopyroxene, olivine and chromite could help indicate, in combination with isotopes, the similarities of the Eastern and Western Limbs to the Northern Limb. Mineral compositions will also be used as a petrogenetic tool to help unravel the formation of the Platreef and development of the magmatic stratigraphy in the Northern Limb.

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Composition of iron oxides in Archean and Paleoproterozoic komatiite-hosted Ni-Cu-PGE deposits in Finland

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Abstract. Using electron probe microanalyzer (EPMA), we have analyzed Fe-oxide grains from Archean and Paleoproterozoic komatiite-hosted Ni-Cu-PGE deposits in Finland. The main research targets were the Ruossakero Ni-(Cu) deposit, Lomalampi PGE-(Ni-Cu) deposit, Tulppio dunite and related Ni-PGE mineralization, Hietaharju Ni-(Cu-PGE) deposit, Vaara Ni-(Cu-PGE) deposit, and Tainiovaara Ni-(Cu-PGE) deposit. In addition some samples from barren komatiite sequence (Kovero) has also been studied. Our results show that EPMA analysis of magnetite and Cr-magnetite can be used to discriminate magnetites that are magmatic or hydrothermal in origin and as indicators of potential Ni-Cu-PGE mineralization. We also found positive correlation between the Ni tenor of the deposit and Ni content of magnetites. This indicates that a high Ni content of magnetites can be due to post-magmatic oxidation of sulfides or a primary feature related to a high Ni content of magma from which these Fe-oxides crystallized.

1 Introduction

Several Archean and Paleoproterozoic komatiite-hosted Ni-Cu-PGE deposits are found in eastern and northern Finland. Most of them represent disseminated sulfide deposits, but massive and/or post-magmatically modified sulfide concentrations also occur. Some are significantly enriched in PGE and Cu, representing relatively rare group among the komatiite-hosted sulfide deposits globally (Konnunaho et al. 2013, 2015, 2016), while Lomalampi (Törmänen et al. 2016) in Central Lapland greenstone belt is the single Paleoproterozoic PGE-(Ni-Cu) deposit. In addition, we studied oxides in Archean non-mineralized komatiites from the Kovero area, eastern Finland (Konnunaho 1999).

The formation of primary magmatic oxide phases in sulfidic ores is possible if oxygen is present in the Fe-bearing sulfide liquid. An immiscible FeS-rich liquid (matte) can contain appreciable amounts of oxygen, which is depending on the conditions and metal contents of the liquid. Experimental studies have shown that the solubility of oxygen in sulfide-rich melt increases with increasing oxygen fugacity and iron content and decreases with increasing nickel and copper grade, with the role of Ni being more important than that of Cu in reducing the oxygen solubility (e.g., Lee 1999; Fonseca et al. 2008). This suggests that the potential of a Ni-rich sulfide melt to crystallize primary magnetite is lower than that of a low-Ni melt. Another factor that affects the oxide content of sulfide ore is the degree of post-magmatic hydrothermal oxidation process that sulfides may undergo after magmatic crystallization process. There are examples (e.g., the studied Vaara Ni-Cu-PGE deposit; Konnunaho et al. 2013) where the most part of the original sulfide assemblage has been altered to secondary hydrothermal magnetite and Ni-rich sulfide minerals, such as millerite and violarite. From the above discussion, it is evident that variations are expected to occur in the abundance and composition of oxide phases (magnetite, chromium magnetite, chrome spinel) that are associated with sulfide minerals in different komatiite-hosted Ni-Cu-PGE deposits. Finnish komatiite-related sulfide deposits represent various magmatic and post-magmatic histories, providing a good opportunity to study the characteristics of oxide phases formed under different conditions and possibly use their geochemistry for exploration.

2 Overview of research targets

Figure 1 shows a map of Archean and Paleoproterozoic greenstone belts and their Ni-Cu-PGE deposits in Finland. Of our research targets, Archean Ni-Cu-PGE deposits are represented by Ruossakero and Tulppio in northern Finland and Tainiovaara, Vaara, and Hietaharju in eastern Finland (Konnunaho et al. 2013, 2015, 2016), while Lomalampi (Törmänen et al. 2016) in Central Lapland greenstone belt is the single Paleoproterozoic PGE-(Ni-Cu) deposit. In addition, we studied oxides in Archean non-mineralized komatiites from the Kovero area, eastern Finland (Konnunaho 1999).

The komatiitic rocks associated with the studied mineralization are often completely metamorphosed with no magmatic silicate minerals preserved. Petrographic studies indicate that serpentine-(+chlorite-carbonate-talc-amphibole) rocks represent former olivine+pyroxene cumulates and amphibole-chlorite-(+serpentine-talc-carbonate) rocks were originally non-cumulates.

Sulfide minerals in the Lomalampi, Hietaharju and Tainiovaara deposits are typical magmatic sulfides, consisting of pyrrhotite, pentlandite, and chalcopyrite. In the Tainiovaara deposit, there is also some pyrite. The Vaara and Ruossakero deposits contain mainly Ni-rich sulfides, such as millerite and violarite, and also a significant amount of pyrite, which were generated during...
post-magmatic processes. The sulfide mineral assemblage in the Tulppio deposit is also typical for magmatic deposits, consisting of pyrrhotite and pentlandite.

Magnetite shows various modes of occurrence (Fig. 2). In all studied samples, it occurs as individual grains or grain aggregates together with silicates and as an alteration product of chrome spinel (i.e., zoned Cr-magnetites). In addition, it can be found within sulfides (Hietaharju, Tainio, Ruossakero, and Lomalampi) or as mobilized magnetite veins (Hietaharju, Vaara, Ruossakero, Lomalampi). The Vaara deposit is a special case as a substantial amount of magnetite has been generated via post-magmatic oxidation of sulfide minerals.

Figure 1. Komatiite-hosted Ni-Cu-PGE deposits in Finland and recently discovered Sakatti Cu-Ni-PGE deposit. GB = greenstone belt, CLGB = Central Lapland greenstone belt. Modified after Konnunaho et al. (2015).

3 Materials and methods

Selected representative polished thin sections were characterized with polarization- and ore microscopes, and oxides were analyzed at the Center of Microscopy and Nanotechnology, the University of Oulu, using a Jeol JXA 8200 Superprobe electron probe microanalyzer (EPMA). The analytical conditions were as follows: 10 μm beam size, 15 kV accelerating voltage, and 100 nA beam current, mimicking those employed by Dupuis and Beaudoin (2011) and Boytroy et al. (2014). The following 17 elements were analyzed: Fe, Ti, Cr, V, Ni, Cu, Co, Mg, Si, Zn, Mo, Mn, Pb, Pt, Rh, and Ga, with the detection limits falling approximately in the range of 50–400 ppm.

4 Results

Around one thousand Fe-oxide EPMA analyzes were performed from 36 thin sections. Figure 3 shows a summary of relevant major and minor concentrations in different deposits.

Chromium and titanium are high in the Tulppio and Kovero samples, in which the oxides constitute mostly secondary Cr-magnetites and magnetites after chrome spinel.

The Vaara and Ruossakero deposits show the highest Ni contents among the analyzed oxides, with the median Ni content being 0.16 wt.% at Vaara and 0.21 wt.% at Ruossakero. This is consistent with their high Ni tenors of ~18-38 and ~23 wt.%, respectively, and the presence of Ni-rich sulfides, such as millerite and violarite (Konnunaho et al. 2015). Also the Tainiovaara deposit has a relatively high Ni tenor, ~13-26 wt.% (Konnunaho et al. 2015), and moderately high Ni contents (median 0.10 wt.%) in magnetites. The Lomalampi and Hietaharju deposits show generally lower Ni tenors, ~6 wt.% and ~3 wt.%, respectively (Konnunaho et al. 2015), and their magnetites are also lower in Ni, falling generally below 0.10 wt.%. Analyzed Ni contents in Tulppio oxides were all below detection limit. Nickel tenor data are not available from Kovero or Tulppio at the moment.

In the Ti vs. Ni/Cr ratio discrimination diagram, most of the magnetite compositions from Hietaharju, Lomalampi, Tainiovaara, and Vaara plot in the magmatic field (Fig. 4). An interesting feature is that even though the Hietaharju deposit is the most intensively hydrothermally altered of the studied deposits, the sulfide and oxide compositions are still magmatic. The magnetite compositions from the Ruossakero deposit fall both into the magmatic and hydrothermal field. Instead, due to their high Ni content, most of the magnetite grains from the Vaara deposit plot in the hydrothermal field.

Figure 3. Log-scale box-and-whisker diagrams for relevant major and minor elements (wt.%) in Fe-oxides.

Figure 4. Ti vs. Ni/Cr ratio discrimination diagram for individual magnetite compositions. Magnetites from Tulppio were excluded because of their low Ni contents falling below the detection limit. The line separating the magmatic and hydrothermal fields taken from Dare et al. (2014).

Figure 5. Ni-Cr vs. Si+Mg discrimination diagram for mineralized samples. Cr-rich magnetites are filtered out by using compositions with Cr <1 wt.%. The field of Ni-Cu-PGE deposits is after Dupuis and Beaudoin (2011).
In the Ni-Cu-PGE discrimination diagram (Fig. 5), most of the magnetite compositions from Vaara and Tainiovaara and some from Ruossakero plot in the Ni-Cu-PGE field. This is also true for some magnetite grains from Lomalampi, and Hietaharju. Two groups of analyses from the Ruossakero deposit plot away from the Ni-Cu-PGE field and have high Si+Mg values. They are most likely secondary hydrothermal magnetites. Tulppio magnetites plot close to the right-hand border of the Ni-Cu-PGE field.

5 Conclusions

This is the first systematic study of iron oxide compositions in the most well-known komatiite-hosted Ni-Cu-PGE deposits of Finland. The new data allow us to draw the following conclusions:

1) By using the Ti vs. Ni/Cr diagram (Dare et al. 2014), we can discriminate between magmatic and hydrothermal magnetites (Fig. 4). Most of the Fe-oxide compositions from the Hietaharju, Lomalampi, Tainiovaara and Kovero deposits suggest a magmatic origin, whereas most of the Fe-oxide in the Vaara deposit are hydrothermal, originating from oxidation of sulfides in post-magmatic low-temperature hydrothermal processes (Konnunaho et al. 2013). Also, some Fe-oxide grains from the Ruossakero deposit plot in the hydrothermal field.

2) The Ni+Cr vs. Si+Mg diagram (Dupuis and Beaudoin 2011) can provide indications for potential Ni-Cu-PGE mineralization (Boutroy et al. 2014). Results of electron microprobe analyses are sufficiently robust for characterizing and discriminating oxide minerals and also provide an application for exploration when using the Ni+Cr vs. Si+Mg diagram (Dupuis and Beaudoin 2011) and box-and-whisker diagrams. In the studied komatiite-hosted Ni-Cu-PGE deposits, some of the Fe-oxides are secondary chromium magnetites and magnetites after magmatic chrome spinel, and therefore most Cr-rich compositions should be filtered out or the Ni-Cu-PGE field could be re-shaped for specific use with studied komatiite-hosted Ni-Cu-PGE deposits.

3) There is positive correlation between the Ni tenor of the deposit and Ni content in magnetites. This indicates that a high Ni content in magnetite can be due to post-magmatic oxidation of sulfides or it could be a primary feature related to a high Ni content of magma from which these Fe-oxides crystallized.

4) High-resolution laser ablation inductively coupled plasma mass spectrometry (HR-LA-ICP-MS) will be used later to obtain more precise analyses of trace elements and compare them with our EPMA data.

Acknowledgements

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References

Staged emplacement of the Turnagain Alaskan-type ultramafic-mafic Intrusion, British Columbia, Canada: Implications for Ni-Cu-PGE mineralization and the origin of zoned complexes

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Abstract. We report the first geochronological study of the temporal evolution of a zoned ultramafic-mafic complex, the Early Jurassic Alaskan-type Turnagain intrusion in British Columbia. Field mapping and preliminary geochronology results (U-Pb and 40Ar/39Ar) for ultramafic-mafic rocks comprising the Turnagain intrusion establish a multi-stage history of emplacement bearing on the origin of the zoned structure. Assembly of the Turnagain intrusion involved episodic emplacement and crystallization of four distinct batches of cumulates (Phases 1-4) over a protracted period (ca. >188-185 Ma). Significant Ni-sulphide mineralization in Phase 2 is distinctly earlier than minor Cu-PGE sulphide mineralization in the younger Phase 4 intrusion. Sulphide saturation and enrichment of chalcophile elements in Phases 2 and 4 apparently reflects evolution in independent mineral systems. The crudely zoned distribution of ultramafic cumulates (dunite-wehrlite-clinopyroxenite-hornblendite) in the Turnagain intrusion appears somewhat fortuitous as the zonal character is constructed by temporally distinct intrusive events. Realistic models for the origin of zoned complexes will require calibration by further geochronological studies. The dating also constrains the timing of regional tectonism. Eastward-directed thrusting and folding of the Turnagain intrusion and its wallrocks accompanying acccretion of the Quesnellia arc assemblage to the North American continent must be younger than ca. 185 Ma (late Early Jurassic).

1 Introduction

The Early Jurassic Turnagain Alaskan-type intrusion (25 km²) in northern British Columbia belongs to a global class of ultramafic-mafic intrusions emplaced in supra-subduction zone environments that are gaining prominence as an exploration target for magmatic Ni-Cu-platinum group element (PGE) mineralization (Nixon et al. 2015; Manor et al. 2016). The Turnagain body is unusually enriched in Ni-(Co-Cu-PGE) sulphides compared to typical Alaskan-type intrusions. Low-grade Ni-sulphide mineralization at Turnagain ranks ninth among the world’s largest deposits in terms of contained Ni metal, constituting a total resource of 1842 Mt @ 0.21 wt % Ni and 0.013 wt % Co (Mudd and Jowitt 2014).

The main Ni mineralization is hosted by wehrlite and clinopyroxenite, and the principal sulphide minerals are pyrrhotite, pentlandite and chalcopyrite. Platinum group minerals documented in the youngest part of the intrusion include platinum- and palladium-bearing arsenides, antimonides and tellurides (Jackson-Brown et al. 2014). The origin of the mineralization is directly related to contamination of parental arc magmas by crustal material. Critical contributions of sulphur and graphite from carbonaceous phyllite in the wallrocks led to the reduction of oxidized parental arc magmas and triggered sulphide saturation (Scheel 2007).

The Turnagain intrusion has been regarded as a typical Alaskan-type body zoned from a dunite-wehrlite core to a clinopyroxenite-hornblende clinopyroxenite-hornblendite margin (Clark 1980). The compositional and textural features of Alaskan-type intrusions are commonly related to crystal accumulation from fractionating mafic-ultramafic magmas residing deep in the crust. The origin of the zoning has been explained by re-intrusion of crystal cumulates to higher crustal levels promoted by diapiric uprise and/or regional deformation (e.g. Findlay 1969; Irvine 1974; Clark 1980). More recent studies draw attention to emplacement of zoned ultramafic suites in narrow conduit systems, rooted in the mantle, which serve as efficient traps for upgraded metal-laden magmas (e.g. Manor et al. 2016). Here, lithological zoning appears related to accretion of cumulates on conduit walls coupled with multiple injection of variably fractionated magmas (Manor et al. 2016 and references therein). The conduit model may be particularly relevant to small intrusive bodies, whereas the origin of zoning in the larger intrusions likely involves more complex processes.
Advances in U-Pb geochronology in recent years make it possible to quantitatively evaluate emplacement mechanisms of ultramafic intrusive suites and the origin of the zoning (e.g. Scoates and Wall 2015). In this study, we utilize U-Pb and 40Ar/39Ar geochronology in conjunction with field mapping and sampling of drill core to determine the internal architecture and temporal evolution of the Turnagain intrusion. To the best of our knowledge, this is the first geochronological study that attempts to systematically date the ultramafic-mafic cumulates of a zoned igneous complex. Our results indicate a protracted and multi-stage history of emplacement commencing prior to regional deformation. The sequence of intrusive events is inconsistent with the successive tapping and emplacement of cumulates derived from a single, continuously fractionating magma chamber. Instead, these results warrant a reappraisal of proposed emplacement models for zoned ultramafic-mafic intrusions such as typified by Alaskan-type intrusive suites.

2 Regional setting

Greenschist-facies graphitic strata that host the Turnagain intrusion have been interpreted to form part of the displaced North America cratonic margin (Cassiar terrane), and to conformably overlie Cambro-Ordovician stratigraphy of the miogeocline (Gabrielse 1998; Erdmer et al. 2005). The latter authors also documented a conformable relationship between the graphitic strata and overlying Mississippian and younger (?) metavolcanic and metasedimentary rocks. They concluded that the entire succession represents a volcanic arc or back-arc assemblage built on the edge of Ancestral North America.

A regional airborne electromagnetic (EM) survey conducted during mineral exploration in the area indicates that graphitic strata hosting the Turnagain intrusion show a marked EM response (conductivity) not shared by ultramafic or surrounding metavolcanic and metasedimentary rocks. Our mapping traverses east of the Turnagain intrusion demonstrate that the sharp EM boundary separates highly conductive graphitic rocks from poorly conductive strata of the miogeocline, and truncates...
the stratigraphic units mapped by Gabrielse (1998). We infer that this EM boundary represents a terrane-bounding fault that delineates the Early Jurassic thrust emplacement of accreted arc assemblages of Upper Paleozoic age (Yukon-Tanana terrane) onto the Ancestral North American margin.

3 Geology of the Turnagain Intrusion

A recent compilation of the geology of the Turnagain intrusion incorporating historical and modern exploration work is given by Nixon et al. (2012). The intrusion forms an elongate body (8 x 3 km) oriented within the regional structural trend (Fig. 1).

The northern and eastern margins of the intrusion are marked by a westerly dipping thrust fault that has emplaced ultramafic rocks onto Mississippian graphitic strata in the footwall. Intrusive contacts with hornfelsed wallrocks are largely preserved along the southern and western margins.

Geological mapping has established four distinct intrusive phases (from oldest to youngest): Phase 1, interlayered wehrlite and clinopyroxenite; Phase 2, mainly dunite and wehrlite with thin, localized occurrences of clinopyroxenite and hornblendite distributed along the margin; Phase 3, melanocratic to mesocratic diorite and lesser feldspathic hornblendite; and Phase 4 hornblende clinopyroxenite, magnetite clinopyroxenite and hornblendite cut by minor leuco-diorite dykes. Contacts between intrusive phases are sharp and locally exhibit intrusive breccias.

Phase 1 rocks are intruded by Phase 2 dunite- and clinopyroxenite within dunite form a steeply dipping trough or synform plunging steeply to the southeast. The original attitude of this structure may have been modified by motion along the adjacent thrust fault. Phase 1 rocks are intruded by Phase 2 dunite- and clinopyroxenite occupying the core of the Turnagain intrusion. The latter intrusive phase is the most voluminous and hosts the main Ni-sulphide mineralization. The dunite and wehrlite are generally massive although mappable units of wehrlite locally occur in dunite and vice versa.

Phase 3 diorite forms an elongate body separating Phase 2 from Phase 4 in the central part of the complex. Centimetre- to metre-scale layering of mesocratic and melanocratic diorite is well preserved in some outcrops. Intrusive breccias with dunite elastics derived from Phase 2 set in a dioritic groundmass are observed locally.

Phase 4 hornblende clinopyroxenite, magnetite clinopyroxenite and hornblendite form a poorly exposed body at the northwestern margin of the complex. These rocks are cut locally by thin leuco-diorite dykes. Examination of drill core reveals layering (centimetre- to metre-scale) locally involving thin horizons of magnetitite and Fe-Cu sulphides. These Cu-PGE-enriched sulphides are a current exploration target and potentially form an additional economic resource.

4 Geochronology

Intrusive phases of the Turnagain Alaskan-type complex were investigated by U-Pb and \(^{40}\)Ar/\(^{39}\)Ar geochronology. U-Pb dating of accessory minerals (zircon, titanite) by chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA- ID-TIMS) yields the following preliminary \(^{206}\)Pb/\(^{238}\)U dates (+2σ) that are interpreted as crystallization ages: Phase 2 hornblendite, 190.3±4.5 Ma (titanite); Phase 3 mela-diorite, 188.11±0.14 Ma (zircon); and Phase 4 clinopyroxenite (4a) and a leuco-diorite dyke (4b), 185.63±0.19 and 185.33±0.13 Ma (both zircon), respectively. \(^{40}\)Ar/\(^{39}\)Ar dating of Phase 2 wehrlite and hornblendite yields plateau dates of 188.6±1.2 Ma (2σ, phlogopite) and 187.4±1.5 Ma (hornblende), respectively, that represent cooling ages (nominally 500°C and 300°C for the closure temperatures of hornblende and biotite, respectively). The latter dates represent minimum ages for the emplacement of Phase 2 ultramafic cumulates.

5 Discussion and conclusions

The field observations and geochronological results for ultramafic-mafic rocks of the Turnagain Alaskan-type intrusion place important constraints on the internal architecture and temporal evolution of the complex, the timing of mineralization, and regional tectonic events.

Emplacement of the Turnagain intrusion occurred in discrete stages over a period of at least 3 million years (ca. 188-185 Ma). The geochronology results are concordant with the sequence of intrusive events recorded by geological relationships observed in the field. The span of intrusive activity must be regarded as a minimum since intrusive Phase 2 yields \(^{40}\)Ar/\(^{39}\)Ar cooling dates as old as 188 Ma; and the oldest Phase 1 component of the Turnagain complex has not yet been dated.

Mineralization in the Turnagain intrusion is hosted by two separate sub-intrusions. The main Ni resource is contained in the Phase 2 intrusion dated at 188-190 Ma, whereas the Cu-PGE-enriched sulphides in Phase 4 clinopyroxenites and hornblendites were emplaced several million years later (ca. 185 Ma). The dating results indicate the presence of two distinctive sulphide saturation episodes in the Turnagain intrusion that took place in independent mineral systems: an earlier event that produced substantial Ni-sulphide mineralization in the older Phase 2 cumulates; and a later event that gave rise to Cu-PGE mineralization in the younger Phase 4.

The crude zonal arrangement of internal lithologies appears somewhat serendipitous in that it is primarily governed by the episodic intrusion and deposition of discrete batches of cumulates derived from parental magma(s) at various stages of evolution. However, the localized occurrence of thin marginal units of hornblendite and clinopyroxenite within the volumetrically dominant
Phase 2 dunites and wehrlites must reflect second-order post-emplacement processes. Therefore, realistic models for the origin of zoned ultramafic-mafic complexes such as Alaskan-type intrusions are likely to be complex, and successful models for their evolution will require calibration by further detailed geochronological studies.

Regional thrusting and folding in the Turnagain area occurred in response to eastward tectonic transport, likely related to the accretion of outboard arc assemblages (Quesnellia) to the miogeoclinal margin of Ancestral North America. Regional deformation clearly postdates emplacement of the youngest Phase 4 intrusive component of the Turnagain intrusion. Thus, the accretion of Quesnellia to the North American continent is constrained to be younger than ca. 185 Ma (late Early Jurassic).

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References

Comparison between chemical composition of Cr-spinels forming massive and disseminated chromite ores: an example from the Vardar Zone, Kosovo

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Abstract. Massive and disseminated chromite ores were collected in the Prishtina district (Kosovo) in order to characterize variations in spinel chemistry. Analyses were carried out by WD-XRES using an EPMA. Compositions of chromite in samples with distinct microstructures differ in ranges of major element concentrations. Disseminated Cr-spinels not only contain more Mg than massive chromite, which is related to effective subsolidus reaction with silicates during reequilibration, but they are affected by serpentinization in contrast to chromite in rich ore. Studied chromitites show cataclastic texture and “subgrains” appeared as a result of brittle deformations in the disseminated ore type. The following substitutions were verified: Mg and Mn for Fe$^{2+}$, Al and V for Cr. Knowledge about differences in composition of chromite composing rich and poor ores can be useful during early stage of exploration.

1 Introduction

Ophiolite complexes often host podiform chromitites that are rocks containing a high volume of Cr- or Al-rich spinels and frequently form economically viable orebodies, as, e.g. on the Balkan Peninsula (i.e. Konjuh, Zlatibor, Radusa) (Grafenauer 1977). The main microstructures of chromitites can be classified into three groups: (1) massive (>80% of chromite), (2) semi-massive (30-80%) and (3) disseminated (<30%). Gradation between them is commonly observed in most ore bodies (González-Jiménez et al. 2014). Ophiolitic chromitites may show a wide range of specific primary microstructures (i.e. nodular, orbicular, antinodular, banded, vein, net, breccia, schlieren) (Fig. 1) some of which carry important information on the processes of crystallization (González-Jiménez et al. 2014; Prichard et al. 2015). What is important for the petrogenesis, chromite is among the first phases to crystallize from ultramafic magma and has high resistance to alteration, particularly compared with other high-temperature igneous minerals, such as olivine (Evans and Frost 1975; Barnes and Roeder 2001). Thanks to these features it has been used widely as a reliable “petrogenetic indicator” (the term coined by Irvine, 1965). However, chromite geochemistry must be interpreted cautiously because Cr-spinels may reequilibrate with the surrounding silicates during cooling (Roeder and Campbell 1985) and undergo alteration during serpentinization and later metamorphism, as indicated by several studies (i.e. González-Jiménez et al. 2009, Delura 2012; Kapsiotis 2014a; Kapsiotis 2014b).

This paper presents new data on chromite ores hosted in one of serpentinized ultramafic complexes located in the Prishtina district (Eastern Kosovo, Balkans) (Fig. 2), where the Cr-mineralization is poorly known. The aim of the present work is to preliminarily characterize chemical composition of Cr-spinels that form both massive (rich) and disseminated (poor) ores in the study area (Fig. 1), taking into account the features of podiform chromitites mentioned above. Furthermore, discussed are variations in primary magmatic chromite composition and alteration effects observed in the studied samples.

Figure 1. Field images of chromitites occurring in the study area. a Chromite pod hosted in serpentinite (evident sharp lithological contact is exposed). b Banded to schlieren type of chromite ore (alternating layers of chromite and serpentinite to irregular lensoid disseminations of chromite in matrix).

2 Geological background

Chromite mineralization in Kosovo occurs in the Mezozoic ultramafic complexes, spread mainly in two regional tectonic units – the Vardar Zone and the Mirdita Ophiolite Belt that developed during convergence and collision related to closure of the Tethys ocean (Elezaj and Kodra 2012). The study area belongs to the Vardar Zone and...
contains an ultramafic body assumed to be a fragment of an ophiolitic suite (Fig. 2). Chromium-bearing ultramafic rocks crop out there as a narrow, SSW-NNE elongated massif. In the course of field work several occurrences of small chromitite pods, lenses and veins (bodies from a few cm to more than 1.5 m long) as well as schlieren to banded ore and disseminated chromite have been documented in deformed and strongly serpentinized rocks (Fig. 1).

**Figure 2.** Simplified sketch map of ultramafic complexes related to ophiolites occurring in Kosovo (based on Beak Consultants GmbH 2006). The arrow shows the study area.

**3 Samples and analytical methods**

Geochemical in situ analyses of Cr-spinels were performed on two representative samples of massive and disseminated chromite ores (Fig. 3). In order to determine the compositional variations, 224 analyses were done for both samples. Measurements along microprobe profiles across selected chromite crystals were done to test possible changes in metals distribution. The chemical analyses were carried out using a JEOL SuperProbe JXA-8230 electron microprobe (EPMA) at the Laboratory of Critical Elements at the AGH-University of Science and Technology in Krakow (Poland). The EPMA was operated in the wavelength-dispersion mode at an accelerating voltage of 15 kV, a probe current of 20 nA, focused beam with a diameter of <1 μm. The counting times on peak and on both (+) and (-) backgrounds were 20 and 10 seconds, respectively. The following standards, lines and crystals were used: chromite (CrKα, LIF), kyanite (AlKα, TAP), diopside (MgKα, TAPH; CaKα, LIFL), rhodonite (MnKα, LIFL), rutile (TiKα, PETJ), V (VKα, LIFH), hematite (FeKα, LIFL), willemite (ZnKα, LIFH), Co (CoKα, LIF), cuprite (CuKα, LIFH), NiO (NiKα, LIFL) and albite (SiKα, TAP). The data were corrected according to the ZAF procedure using the original software.

In the microprobe analyses of chromite Fe is reported as FeO total and FeO (ferrous iron) and Fe2O3 (ferric iron) concentrations were determined assuming ideal spinel stoichiometry (AB2O4; cations calculated to 4 oxygens).

**4 Cr-spinels chemistry**

Based on Fe2+/Fe3+ vs. Al2O3 wt% discrimination diagram (Kamenetsky et al 2001) (Fig. 4a), the studied chromitites represent the supra-subduction zone environment. On TiO2 wt% vs. Al2O3 wt% diagram (Fig. 4b), the results of Cr-spinels analyses plot within the overlap area between spinels from the island-arc setting and the supra-subduction zone. They are characterize by following average values of atomic ratios: Cr# [Cr/(Cr+Al)] - 0.816, Mg# [Mg/(Mg+Fe2+)] - 0.454, Fe2+# - 0.546 [(Fe2+/(Fe2++Mg)], Fe3+ [Fe3+/(Fe3++Cr+Al)]= 0.027.

Results of microprobe analyses (EPMA-WDS) show that massive and disseminated chromite vary mainly in ranges of major elements concentrations (Fig. 5). Variations of Cr2O3, FeO total, Al2O3 and MgO values are greater in the poor chromite ore than in the rich chromite ore. Both, the lowest (50.422 wt%) and the highest (65.425 wt%) Cr concentrations were measured in disseminated chromite. Another significant difference is in the Al enrichment of spinels constituting the massive ore in contrast with the Mg enrichment of spinels disseminated in serpentinite. Differences in values between studied samples are 0.605 wt% and 0.794 wt% in average concentrations of Al and Mg oxides respectively. Increased values of FeO total (up to 39.512 wt%) were observed only in a few analyses of disseminated chromite crystals that have been affected by serpentinization (Fig. 7). The highest concentration of Fe2O3 (max. 15.457 wt%) were found close to the magnetite rim in altered spinels. No replacement of chromite into magnetite was noticed in the massive ore sample, in which average ferrie iron oxide concentration in Cr-spinels is 1.648 wt% (0.886 wt% less than in disseminated spinels). More differentiated Fe2+ values as well as Mg# values were observed in disseminated chromite (Fig. 6).

Minor but evident chemical heterogeneity in optically homogeneous chromite crystals was recorded by microprobe profiles. Noticeable tendency of Mg, Al, Fe2+ content increase at points localized directly beside crystals.
edges was observed, with spreads between maximum and minimum values up to 0.576 wt%, 0.997 wt%, and 1.216 wt%, respectively. Also Cr contents decrease up to 2.229 wt% appears close to chromite contact with serpentinite.

The presence of alteration effects in disseminated chromite and their absence in massive chromite are clearly visible on BSE (back-scattered electron) images (Fig. 7). Both ore types show cataclastic texture but in the disseminated type the dismemberment of chromite crystals is much more pronounced and expressed by numerous “subgrains” produced during brittle deformations (Fig. 7b). This indicates that poor ores with lower proportions of chromite in comparison to massive type are more sensitive to conditions changes and can be easily dismembered. Massive chromitite bodies may be protected from intense fracturing as well as serpentinization thanks to the stress and fluids absorption by the silicate phases surrounding them. Simultaneously, a chance for preservation of primary magmatic structures and composition in this case is greater than in ores with lower chromite-silicate ratio.

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Concentration of trace metals (here included in this group when the average value of oxide content is <0.1%) such as Cu, Ca, and Si were below detection limits in many analyses. Average concentrations of ZnO, CoO, and NiO do not differ significantly for the examined ore types. Low contents of these metals in the chromite lattice requires applying different analytical methods (i.e. LA-ICP-MS) with lower detection limits to properly and fully characterize their variations in both ore types.
examining composition of Cr-spinels in easy to collected pan concentrates. Through the careful examination of detrital spinels chemistry it may be possible to discriminate between promising ultramafic complexes, where massive chromite bodies may occur, and barren complexes, where chromite exist only as an accessory mineral or poor, disseminated ores.

Acknowledgements

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Coexistence of Ru-Os-Ir minerals and Ni-rich sulfide liquids in the Al-rich ophiolitic chromite deposit of Mercedita (eastern Cuba)

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Abstract. The Mercedita mine (Moa-Baracoa massif) is the largest deposit of ophiolitic chromite in Cuba. The chromitite is Al-rich (Cr# 0.41-0.54) and PGE-poor (55.8-165.9 ppb). The whole-rock PGE distribution is dominated by Os, Ir and Ru, which is consistent with the observation of Os-Ir-Ru PGMs inclusions in chromite. In previous work only a few grains of laurite (RuS₂) were identified on thin sections. Further processing of these PGM-bearing samples using a hydroseparation technique resulted in the improved concentration of PGMs. In addition to the PGM included in chromite, a set of new PGM were identified associated with Ni-rich sulfides, including millerite and heazlewoodite (?). We identified laurite (RuS₂), irarsite (IrAsS), erlichmanite (OsS₂) and native Os among the 33 new grains of PGMs recovered.

The genesis of the PGM is associated with the crystallization of chromite and the contemporaneous segregation of droplets of immiscible sulfide liquid from the parent basaltic melt. Coexistence of Os-Ir alloys and laurite with Ni-rich sulfides is explained as a result of the earlier/contemporaneous segregation of the PGMs and the immiscible Ni-rich sulfide liquids. Our new observations are in agreement with recent experiments indicating that PGMs associated with Ni-rich sulfides in mafic and ultramafic systems would form in equilibrium, contrary to canonical models in which sulfide liquids dissolve PGE to later exsolve them as PGM upon crystallization and subsolidus equilibrium of the monosulfide solid solution.

1 Introduction

The Moa-Baracoa ophiolitic massif (Eastern Cuba) contains more than a hundred chromite deposits (Proenza et al. 1999; Gervilla et al. 2005). The calculated reserves in the area reach 6.5 million tonnes (Silk 1988) and include most of the Cuban chromite reserves (chromite associated with chromiferous laterites or placers are not included). The Mercedita chromitite comprises at least 7 lenses of massive chromitite hosted in residual peridotites with layered gabbros representative of the crust-mantle transition zone of the ophiolite. It is the largest ophiolitic chromitite in Cuba containing chromite reserves of more than 5 million tonnes. This chromitite has been exploited intermittently since 1981, with an extraction of more than 500,000 tonnes of refractory grade chromite (Proenza et al. 1999).

Mercedita is a typical example of chromitite associated with ophiolitic sequences emplaced in the mantle-crust transition. Its particularity is the presence of multiple lenticular gabbro bodies included in the chromitite (Proenza et al. 1999, 2002). The ore bodies present a dunite envelope of variable width (between some centimeters and several meters), which are hosted in harzburgites (Fig. 1).

The Mercedita chromitite is Al-rich (refractory grade), with Cr# [Cr/(Cr+Al)] between 0.41 and 0.54, and impoverished in Platinum Group Elements (PGE) showing concentrations below 200 ppb (Ru being the most abundant element) (Proenza et al. 1998).

Due to the usually low PGE content of Al-rich chromitites, very few studies of Platinum Group Minerals (PGM) have been carried out in this type of rocks. Most PGM reported of ophiolitic chromitites of Cuba were identified in Cr-rich (metallurgic grade) chromitites of the Sagua de Tánamo and Mayari districts. These PGM were euhedral and included in larger chromite crystals (Figure 5a, b in Gervilla et al. 2005; González-Jiménez et al. 2011), suggesting their early crystallization at high-T from basaltic melts under relatively low /S₂. 

Figure 1. Schematic geological map of the Mercedita deposit showing the distribution of chromitite lenses (compilation by Proenza et al. 1998). In the lower left corner schematic map of Cuba showing the distribution of ophiolites massifs and the location of the Mercedita deposit.

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In spite of the low PGE content of the Mercedita chromitites, previous studies always found some PGM grains included in chromitites (Proenza et al. 1999). Using hydroseparation techniques in a 2 kg massive chromitite sample from Mercedita, different PGM have been also found included in Ni sulfides (Navarro-Ciurana et al. 2012). In this study, we aim to characterize these phases and their mineral associations.

2 Methodology

Thin sections from chromitite samples of Mercedita have been studied with optical microscope, scanning electron microscope (SEM) using both a Quanta 200 FEI XTE 325/D8395 and a field emission scanning electron microscope (FE-SEM) Jeol JSM-7100 at the Serveis Científics i Tecnologies, University of Barcelona (CCiTUB), Spain.

At the same institution, quantitative electron microprobe analyses (EMPA) were obtained with a JEOL JXA-8230 operating in wavelength-dispersive spectroscopy (WDS) mode with an accelerating voltage of 20 kV, a beam current of 10 nA, and a beam diameter of 1 μm. Pure metals were used as standards for Os, Ir, Ru, Rh, Pt, Pd, Co, and Sb as well as chromite (Al, Fe), periclase (Mg), NiO (Ni), S (S), GaAs (As), and wollastonite (Si). The following interferences RuL\(_\beta\)-RhL\(_\alpha\), RhL\(_\beta\)-PdL\(_\alpha\), RuL\(_\beta\)-PdL\(_\alpha\), and RhL\(_\alpha\)-PtL\(_\alpha\) were online-corrected.

Hydroseparation techniques (HS lab, Barcelona; http://www.hslab-barcelona.com/) have been used in the in order to separate PGE phases. The obtained grains have been mounted as polished monolayer on resin blocks (SimpliMet 1000) and studied with optical microscope, SEM and EMPA (CCiTUB). Powder of the same sample has also been analyzed by ICP-MS at Genalyses Ltd. (Maddington, Western Australia) after nickel sulfide fire assay collection following the method described by Chan and Finch (2001) in order to determine the PGE content.

3 Results

3.1 PGE geochemistry

Platinum Group Elements content have been analyzed in samples from different lenses of massive chromitite from the Mercedita mine. The total PGE content ranges between 55.8 and 165.9 ppb (Proenza et al. 1999) (Figure 2) representing a depletion from 10 to 100 times relative to the primordial chondrite values (Chondrite CI values from Naldrett and Duke 1980). The patterns are characterized by comparable values of Os and Ru (Ru being the most abundant PGE), a negative anomaly in Ir and a negative slope from Ru to Pd.

![Figure 2. PGE distribution of Mercedita chromitite samples normalized to chondritic values (CI chondrite from Naldrett and Duke 1980). The area corresponds to the data published in Proenza et al. (1999) and the black line corresponds to the sample processed with hydroseparation techniques in this study.](image)

3.2 PGE mineralogy

Platinum group minerals (PGM) and Ni-rich sulfides, including millerite (Ni\(_{0.97}\)S\(_{1.02}\)), heazlewoodite (Ni\(_{1.2}\)Fe\(_{0.01}\)S\(_{1.02}\)), pentlandite (Fe\(_{3.3}\)Ni\(_{4.8}\)S\(_{8.2}\)), and an unknown Fe-Ni-Cu sulfide ([Ni\(_{0.28}\)Fe\(_{0.30}\)Cu\(_{0.32}\)]\(_{0.96}\)S\(_{1.02}\)-[Ni\(_{0.72}\)Fe\(_{0.10}\)Cu\(_{0.10}\)]\(_{0.98}\)S\(_{1.02}\)), were found located in the interstices of larger chromite grains. These PGM and Ni-rich sulfides are often associated with Fe-Ni alloys (awaruite (FeNi\(_{3}\)) and taenite (FeNi)), Ni phosphide, native Ni and Cu-phases such as native Cu, chalcopyrite (CuFeS\(_2\)), and chalcocite (Cu\(_{1.83}\)Fe\(_{0.07}\)Ni\(_{0.03}\)S\(_{1.06}\)). These non-silicate phases can be from euhedral to anhedral morphologies with sizes up to 0.4 mm.

In Mercedita, PGMs were found as inclusions in chromite and in Fe-Ni sulfides. The characteristics of both types of PGMs are described below:

a) **PGMs in chromite**

Only seven grains of laurite (Ru\(_{S_{2}}\)), with grain sizes between <1 and 25 μm, were found in the studied samples (Fig. 3a). Laurite exhibits idiomorphic shapes with cubic to pentagonododecahedron habits. It shows considerable substitutions of Ru for Os and minor Ir with various compositions ranging from (Ru\(_{0.51}\)Os\(_{0.09}\)Ir\(_{0.99}\)S\(_{1.00}\) to (Ru\(_{0.85}\)Os\(_{0.15}\)Ir\(_{0.04}\)Rh\(_{0.02}\)S\(_{1.00}\)). Only PGM larger than 3 μm could be analyzed by EMPA. Rh contents are relatively important (usually >1 wt. %), whereas other elements, such as Pd, Pt and Ni are present in extremely low contents, frequently below the detection limit. The laurites in Mercedita have compositions comparable with other ophiolitic chromitites (e.g., Gervilla et al. 2005).
b) PGMs in Ni sulfides

33 PGM grains were found associated with Ni-rich sulfides. The principal PGM phases are (in decreasing abundance) laurite, irarsite, erlichmanite and native Os.

Subhedral and euhedral laurite (RuS₂) crystals with sizes up to 10 μm (generally around 2 μm) were found included in cores and rims (Fig. 3b), as well as in crosscutting fractures of millerite and heazlewoodite. Most of these laurite crystals are homogenous in composition, although some of them show reverse zoning with Os-rich cores and Ru-rich rims (González-Jiménez et al. 2009). Irarsite (IrAsS) forms subhedral grains (<1 μm in size) in rims or in crosscutting fractures of the Ni-rich sulfides (Fig. 3c). Erlichmanite (OsS₂) shows euhedral shapes and sizes up to 2 μm, whereas native Os presents sizes up to 1 μm and euhedral to anhedral morphologies.

4 Discussion and final remarks

The morphology of the PGE chondrite-normalized pattern of the Mercedita chromite deposit (Fig. 2) is similar (except for the Ir negative anomaly) to patterns reported for other Al-rich ophiolitic chromitites (e.g., Leblanc 1991). The PGE distribution is explained by the presence of laurite, more precisely an Os-rich laurite. This reflects both the abundance and the relative proportion of Os and Ru in the pattern, and also the scarcity of Rh, Pt and Pd.

The enrichment of Os, Ir and Ru (IPGE) relative to Rh, Pt and Pd (PPGE) also implies that only the first group was effectively concentrated during the formation of the Mercedita chromite deposit. Previous studies (Ballhaus and Sylvster 2000; Matveev and Ballhaus 2002) evidenced that IPGE concentration in chromitites is the result of the mechanical trapping of nanometric clusters of PGE or micrometric PGMs by the crystallizing chromite. The segregation of these PGE phases was related with the disturbance of fO2 in the parental melt as a result of chromite crystallization (Mungall 2002).

The idiomorphic shape of laurite crystals included in chromite from Mercedita suggests a free growth of the crystals from the melt and their later mechanical entrapment by the chromite growth (e.g. Stockman and Hlava 1984; Augé et al. 1988; Ferrario and Garuti 1990; González-Jiménez et al. 2014 and references therein). This implies a high temperature crystallization of laurite, previous or coeval with the chromite crystallization. The PGM included in chromite grains from the Mercedita deposit are dominated by Os-rich laurite (Fig. 3a). According to experimental results (Brenan and Andrews 2001; Andrews and Brenan 2002), Os-rich laurite can be formed in equilibrium with Ru-poor Os–Ir alloys at 1,200–1,300°C and log fS₂ from 2 to 1.3.

On the other hand, the coexistence of Ru-Os-Ir sulfides and alloys within Ni-rich sulfides (Fig. 3b and c) suggests the possible segregation of PGM contemporaneously with chromite but before the immiscible segregation of micrometric droplets of Ni-rich sulfide liquid. Segregated either as nanoparticles or as micrometric grains of PGMs, the presence of laurite as inclusions and at the margins of larger NiS crystals might indicate incomplete resorption of these PGMs into the lately segregated blebs of immiscible Ni-rich sulfide liquid.

Figure 3. BSE-SEM images of: a) Laurite (RuS₂) included in chromite; b) Laurite inclusions (1-2 μm) in Ni-sulfide, inclusions are mainly located in the rim and; c) Irarsite (IrAsS) inclusions (<1 μm) in Ni-sulfide.
According to experimental data (Stockman and Hlava 1984; Melcher et al. 1997; Garuti et al. 1999), Os-Ir-Ru alloys and sulfides can crystallize in equilibrium with Ni-rich sulfides from S-undersaturated basaltic melt at relatively high-T (1400–1300 °C) and low fS2. Alternatively, the coexistence of Ru-Os-Ir sulfides and alloys with Ni-rich sulfide melts in the Mercedita chromite deposit would reflect the contemporaneous segregation of immiscible PGE-rich and PGE-depleted sulfide melts during the event of chromite crystallization in the mantle. Recent experiments by Helmy and Bragagni (2017) noted that there is a window of T (1300 – 1020 °C) and fO2 in which PGM and sulfide liquids can be segregated in equilibrium from basaltic melt. This interpretation provides an alternative view to the conventional suggestion of PGE dissolved in sulfide melts and later exsolution as PGM upon cooling and subsolids re-equilibrium of Fe-poor Mss.

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Undiscovered mafic-ultramafic rock-hosted chromium resources in Finland

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Abstract. Chromium resources in undiscovered podiform and stratiform chromite deposits were estimated down to the depth of one kilometre in the bedrock of Finland using the three-part quantitative assessment method. Sixteen permissive tracts were delineated for stratiform and two tracts for podiform deposits. The tracts cover altogether 7430 km², which is two per cent of the total land area of Finland. An existing USGS minor podiform chromite grade-tonnage model was used to assess the undiscovered podiform resources in Finland. For stratiform chromite, a separate deposit volume model for each permissive tract and a general model of chromium content per unit volume were used. The estimated mean numbers of undiscovered stratiform and podiform chromite deposits in Finland are 9 and 23, respectively. The undiscovered stratiform and podiform chromite deposits are estimated to contain, at 50% probability, at least 350 Mt and 7600 t chromium, respectively. The assessment results indicate that at least 92% of the remaining chromium endowment within the uppermost 1 km of the Finnish bedrock is in poorly explored or entirely unknown stratiform chromite deposits. Practically all of the undiscovered resources are located in stratiform deposits in layered intrusions in northern Finland.

1 Introduction

Stratiform chromite deposits in South Africa and podiform deposits in Kazakhstan are estimated to contain approximately 95% of the known chromium resources of the World (Papp 2016). Chromium has been produced from five different types of deposits: stratiform deposits mostly associated with Archaean–Palaeoproterozoic mafic–ultramafic layered intrusions, podiform deposits mostly associated with Palaeozoic–Mesozoic ophiolites, small lenticular deposits associated with Archaean komatiitic sills, placer deposits, and laterites formed by the weathering of ultramafic rock containing chromite (Prendergast 2008; Mosier et al. 2012; Schulte et al. 2012).

Stratiform chromite deposits and occurrences in ~2.45 Ga mafic–ultramafic layered intrusions in northern Finland form the most important chromium resource of the country. The Kemi (Elijärvi) deposit belongs to the stratiform deposit type. Five partially explored stratiform chromite deposits with a preliminary resource estimate, and about 10 poorly explored occurrences are also known in Finland.

There are indications of podiform chromite deposits in the Palaeoproterozoic 1.96–1.95 Ga ophiolites in eastern and northern Finland. However, there are no well-known deposits of this type, and only two poorly known occurrences exist in eastern Finland.

We describe here the results of an assessment of undiscovered chromium resources in stratiform and podiform chromite deposits in Finland. The Geological Survey of Finland (GTK) has carried out assessments of undiscovered mineral resources in Finland since 2008 (Rasilainen et al. 2010, 2012, 2014, 2016a; Eilu et al. 2015). Detailed results of the assessment of chromium resources in Finland are reported in Rasilainen et al. (2016b).

The GTK assessments are based on the three-part quantitative assessment method developed by the U.S. Geological Survey (Singer 1993; Singer and Menzie 2010). The assessment process produces probabilistic estimates of the total amount of metals in situ in undiscovered deposits of selected types, down to the depth of one kilometre. The three-part method consists of (1) evaluation and selection or construction of descriptive models and grade-tonnage models for the deposit types under consideration, (2) delineation of areas according to the types of deposits permitted by the geology (permissive tracts), and (3) estimation of the number of undiscovered deposits of each deposit type within the permissive tracts. The estimated number of deposits is combined with the grade and tonnage distributions from the deposit models to assess the total undiscovered metal endowment.

2 Chromium deposits in Finland

2.1 Stratiform chromite deposits

Most of the known chromite deposits and occurrences in Finland are hosted by mafic–ultramafic layered intrusions in the northern part of the country (Alapieti et al. 1989; Mutanen 1997, 2005; Huhtelin and Alapieti 2005; Huhtelin 2015). These early Palaeoproterozoic (2.5–2.4 Ga) layered intrusions occur within a large area in the north-eastern part of the Fennoscandian Shield, in Finland, Russia and Sweden, and they straddle the Archaean–Proterozoic boundary within the shield. The emplacement of the intrusions was part of a global episode of igneous activity possibly related to the initial breakdown of the Neoproterozoic Kenorland supercontinent, and it produced several layered intrusions and mafic dyke swarms on other cratons as well (Alapieti and Lahtinen 2002; Iijina and Hanski 2005).

Two categories of stratiform chromite deposits can be distinguished in the Finnish 2.45 Ga layered intrusions. In
the first category, the massive chromitite seams and layers containing disseminated chromite occur in the lower ultramafic section of a layered intrusion. This is the most common chromite deposit type in the 2.45 Ga layered intrusions in Finland, and has been detected in the Kemi, Tornio, Penikat, Narkaus, Akanvaara and Koitelainen intrusions (Söderholm and Inkinen 1982; Alapieti and Lahtinen 1986; Iljina 1994; Mutanen 1997; Huhtelin and Alapieti 2005).

The Kemi deposit belongs to the first category of stratiform chromite deposits and contains the main chromium resource in Finland. The chromitite layer occurs throughout the entire length of the ultramafic basal part of the Kemi intrusion. The thickness of the chromitite layer varies from a few centimetres to over 100 m, and the average in the mine area is about 40 m. The deposit has proven ore reserves of 50.1 Mt with an average grade of about 26 % Cr₂O₃ and an average Cr/Fe value of 1.6–1.7 (Huhtelin 2015). Additional mineral resources estimated to the depth of one kilometre are 97.8 Mt (Outokumpu 2015).

In the second category of stratiform chromite deposits in Finland, the chromitite layers occur in the stratigraphically upper, anorhostitic–gabbroic, section of the layered intrusion. This type has only been observed in the Akanvaara and Koitelainen intrusions (Mutanen 1997, 2005). The upper chromitite layer (UC) in the Akanvaara intrusion is situated stratigraphically about 2 km above the base of the intrusion. The average thickness of the UC layer is about 1.14 m, the average Cr₂O₃ content is 23 %, and the Cr/Fe value is about 0.77 (Mutanen 1997).

### 2.2 Podiform chromite deposits

Podiform chromite deposits are mostly small magmatic chromite accumulations in ultramafic units of ophiolite complexes that are commonly thought to represent tectonically detached pieces of oceanic lithosphere, created in mid-oceanic ridge, transform fault or suprasubduction settings (Mosier et al. 2012). The pods typically consist of semi-massive to massive chromite, range from centimetres to hundreds of metres in size and show tabular, cylindrical and irregular shapes. They occur in the lowermost parts of the cumulate sequences, at mantle tectonite and cumulate sequence contacts, and in the uppermost parts of the mantle (tectonite) units of the hosting ophiolites.

In Finland, unquestioned ophiolites have been observed in the ca. 1.9 Ga oebducted Jormua–Outokumpu Allochthon within the North Karelia and Kainuu Schist Belts. The preserved area of the allochthon is about 5000 km², and it contains numerous 1.96–1.95 Ga ophiolite fragments (Kontinen 1987; Peltonen et al. 1998; Peltonen et al. 2008). Podiform chromite occurrences are only known from two ophiolite fragments of the Jormua–Outokumpu area: Vasarakangas within the Kylylahti ophiolite fragment (Vuollo et al. 1995) and Pitkänperä within the Jormua ophiolite (Kontinen and Peltonen 1998). Decimetre-size concentrations of massive chromite and schlieren and bands of heavily disseminated chromite occur in serpentinised hazburgite-dunites in the Nuttio area, Central Lapland, but clear examples of massive podiform chromite have not been observed there.

The Pitkänperä chromitite at Jormua occurs in a 100–400-m-wide, approximately 5 km long slice of mantle tectonite. The largest known chromitite pod is about one metre wide and over seven metres long in visible cross-section. Half a dozen smaller pods with a diameter of 0.1 to 1 m are known from the area immediately north. A representative whole-rock sample from a relatively unaltered core part of the Pitkänperä pod contains 34.41% Cr₂O₃ (A. Kontinen, unpublished data).

The Vasarakangs chromitite is only known from excavated blocks in a waste rock dump of an abandoned open pit, from which talc-carbonate rock was mined as ore. Tens of massive to nodular chromitite boulders up to one meter in size occur in different parts of the waste rockheap, which covers several hectares in area. Based on five whole-rock analyses from less altered blocks, Vasarakangas chromitite has an average Cr₂O₃ concentration of 40.6 % (Vuollo et al. 1995).

### 3 Deposit models

Little published information is available on ore tonnages for whole stratiform chromite deposits, which is mainly due to the great lateral continuity of the chromite layers throughout the entire layered intrusion. This lateral continuity imposes a strong correlation between the size of the hosting intrusion and the stratiform deposit tonnage. The scarcity of data makes it difficult to generate a normal grade-tonnage model, and the dependency of the stratiform deposit tonnage on intrusion size makes the application of a general grade-tonnage model problematic.

To avoid these complications, the standard three-part method estimation of the undiscovered metal tonnages was modified. A general chromium tonnage-volume model was created for Finnish stratiform chromite deposits. The model describes the chromium content per unit volume in stratiform chromite deposits in Finland. The volume of possibly existing undiscovered stratiform deposits was modelled separately for each permissive tract. The undiscovered chromium resources were estimated for each permissive tract by combining the general chromium tonnage-volume model and the estimated volume of undiscovered stratiform deposits using Monte Carlo simulation.

No well-known podiform chromite deposits exist in Finland, but the characteristics of the Jormua and Pitkänperä occurrences are conformable with the minor podiform subtype in the recently published grade-tonnage model for podiform chromite (Mosier et al. 2012). Hence, this model was used in the assessment of chromium resources in undiscovered podiform deposits in Finland.
4 Results and discussion

In total, 16 permissive tracts were delineated for stratiform and two tracts for podiform chromite deposits in Finland (Fig. 1). Altogether, the tracts cover approximately 7430 km$^2$, which is 2% of the total land area of Finland. The area covered by the stratiform tracts is 1458 km$^2$, and the size of the tracts varies between 2.3 km$^2$ and 450 km$^2$ with a median of 35 km$^2$. The two podiform tracts have a total area of 5971 km$^2$, most of which is taken up by the Outokumpu tract (5936 km$^2$). The Nuttio podiform tract covers only 35 km$^2$.

The number of undiscovered deposits was estimated for each permissive tract. The expected (mean) number of undiscovered stratiform chromite deposits for a permissive tract varies from zero to two deposits, and the sum of the mean estimates across all permissive tracts is nine deposits. The mean estimate of undiscovered podiform chromite deposits in Finland is 23 deposits, and it is highly dominated by the 21 deposits estimated to exist within the Outokumpu podiform chromite permissive tract.

The median estimate of undiscovered chromium resources in Finland is, at least, 350 Mt of chromium. Practically all of these resources are estimated to be in stratiform chromite deposits (Table 1). Undiscovered podiform chromite deposits are estimated to contain only 7600 t of chromium (at the 50% probability level). The dominance of the stratiform resources is due to the fact that the average size of an undiscovered stratiform deposit is estimated to be 790 Mt of ore, which is about 415,000 times larger than the average size of an undiscovered podiform deposit (1900 t of ore).

The identified chromium resources of Finland, located in the Kemi deposit, are 28.7 Mt chromium. The assessment results indicate that more than 90% of the remaining chromium endowment within the uppermost one kilometre of the Finnish bedrock is in poorly explored or entirely unknown stratiform chromite deposits in the Koitelainen, Akanvaara, Penikat, Tornio and Narkaus layered intrusions in northern Finland. The undiscovered resources are heavily dominated by the Koitelainen intrusion, which is estimated to contain a median undiscovered resource of 300 Mt chromium. This is 85% of the total median estimated chromium resources in Finland.

![Figure 1. Permissive tracts for stratiform and podiform chromite deposits in Finland. The names of the most important tracts and deposits mentioned in the text are shown on the map.](image)

### Table 1. Median and mean estimates of the undiscovered chromium resources in stratiform and podiform deposits in Finland.

<table>
<thead>
<tr>
<th>Deposit type</th>
<th>Median estimate (Mt Cr)</th>
<th>Mean estimate (Mt Cr)</th>
<th>Probability of mean or greater</th>
<th>Probability of none</th>
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<tbody>
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<td>Stratiform</td>
<td>350</td>
<td>1,100</td>
<td>0.18</td>
<td>0.04</td>
</tr>
<tr>
<td>Podiform</td>
<td>0.0076</td>
<td>0.017</td>
<td>0.41</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Mt: Million metric tons. The estimated amounts of metal are rounded to two significant digits.
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Outokumpu 2015. Outokumpu Oyj Toimintakertomus ja tilinpäätös 2014


Ni and Cu isotopic signatures of Cu-Ni-PGE sulfide mineralization in the Duluth Complex, Minnesota

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Abstract. Ni and Cu isotopes of major Cu-Ni-PGE sulfide deposits in the Duluth Complex were analyzed to gain insight into ore formation, isotopic fractionation processes, and the suitability of Ni and Cu isotopes as exploration tools. $^{\delta^{58}}$Ni (-0.97 ‰ to 0.21 ‰) shows least fractionated values of -0.07 ‰ for unmineralized intrusives, whereas sulfide mineralization exhibits values between 0.22 ‰ and -0.08 ‰. With increasing sulfide content, Ni isotopes become progressively lighter (0.15 ‰ to -0.97 ‰) while weathered outcrop material shows values between -0.23 ‰ and -0.87 ‰ and till records intermediate values (-0.02 ‰ to -0.77 ‰). $^{\delta^{65}}$Cu values (-1.28 ‰ to 0.36 ‰) show heavier isotopic signatures than other magmatic sulfide deposits in the region (> 0.69 ‰) with disseminated ore material being much lighter (-0.16 ‰). Surface material shows variable negative $^{63}$Cu due to preferential enrichment into weathering products. Early phases experience little $^{\delta^{58}}$Ni fractionation, but sulfides preferentially incorporate lighter Ni with rising sulfur content; surface samples also show preferred adsorption of lighter Ni isotopes. Ni isotopic signatures may be useful in distinguishing regions associated with Cu-Ni-PGE mineralization from barren areas. The significance of Cu isotopic values is less clear because a variety of poorly-understood processes (Cu source, sulfide fractionation) likely influence Cu isotopic signatures.

1 Introduction

Magmatic Cu-Ni-PGE sulfide mineralization occurs in a series of deposits along the western margin of the Duluth Complex in northeastern Minnesota (Fig. 1). The mineralization is concentrated within the gabbroic South Kawishiwi and Partridge River Intrusions of the Duluth Complex layered series that formed during the 1.1 Ga Midcontinent Rift event (Miller et al. 2002). The origin and formation of this regionally extensive mineralization has been the subject of significant research in the past, and several hypotheses of its formation have been proposed (e.g., Severson 1994; Peterson 2001; White 2010). Whereas the mineralogy, geochemistry, and formation of these deposits has been investigated in some detail, there is little information available on the metal isotopic signatures of these deposits or their behaviour during magmatic sulfide mineralization processes. Recent studies have started to explore the potential for terrestrial Ni isotopic fractionation between $^{60}$Ni and $^{58}$Ni, the two most abundant isotopes of nickel (Cameron et al. 2009; Gall et al. 2012; Gueguen et al. 2013; Ratié et al. 2015).

Results demonstrate that Ni isotopic fractionation exists in both high and low-temperature terrestrial material with a range of 2.1 ‰ (Gueguen et al. 2013; Hiebert 2014; Wasylenksi 2015). The mechanics of these isotopic fractionation events are not well understood, and may involve kinetic, equilibrium, or mass-independent processes (Kendall and McDonnell 1998; Schauble 2004; Wasylenksi et al. 2015). Isotopic differences between silicate and sulfide-rich igneous rocks suggest that different fractionation events may be involved in the formation of sulfide-bearing and sulfide-barren units.

Figure 1. Approximate extent of the Partridge River and South Kawishiwi Intrusions, hosts to major Cu-Ni-PGE mineralization (in red). Modified from Ripley (1986) and Miller et al. (2001).

Cu isotopes have been used in the past to characterize Cu mineralization in a variety of environments but very few data are available for magmatic systems (e.g., Malitch et al. 2014) and only one study on the Duluth Complex (Ripley et al. 2015).

Ni and Cu isotopes were analyzed from a range of sulfide deposits in the Duluth Complex to gain more insight into the genesis and evolution of these deposits and assesses the potential of using $^{\delta^{60}}$Ni as a new tool for studying the mineralogy, spatial extent, and surface signature of Cu-Ni-PGE mineralization in the Duluth...
Complex and elsewhere. In addition, Ni isotopes may be useful as an exploration tool as most of the deposits in the Duluth Complex are covered by thick layers of till and little outcrop exists.

Cu isotopes values were obtained to compare data with Ni isotopic signatures to determine if common fractionation processes exist between both metal, to what extent their behaviour differs during sulfide deposition, and to study the contribution of various Cu sources.

2 Sampling and analysis

Three main sample types were collected for analysis: main silicates, Cu-Ni sulfides (massive, disseminated), and secondary oxide. Sample material came from drill core, available surface outcrop, glacial till, and non-mineralized Duluth Complex gabbro for background values. In addition, selected non-Duluth Complex samples were also analyzed, including Ely Greenstone material and secondary Ni silicate material (garnierite).

Sample material was routinely prepared for whole-rock analysis (< 100 μm powder). In addition, electro-pulse disaggregation (EPD) was employed to produce mineral separates (olivine, sulfides) before a powder was produced. EPD enables the touch-free separation of individual mineral grains using high-voltage current (200 kV), which allows the separation of single crystal mineral grains and avoid contamination.

Ni isotope ratio measurements were performed on a Nu Plasma II MC-ICP-MS at the Sesame Lab at Indiana University using the double-spike technique (Wasylenki et al. 2015). Cu isotopes were analyzed using established methods at the Yale Analytical and Stable Isotope Center. Ni isotopic data have a 2 sigma precision of ± 0.03 ‰ and Cu isotopes a 2 sigma precision of ± 0.11 ‰.

3 Results

3.1 Ni isotopes

Ni isotope values generally fall within the range of previously published analogues (Fig. 2). The clear isotopic differences between sulfide and silicate samples (gabbro, olivine) support the hypothesis by Gueguen et al. (2013) and Hiebert et al. (2014) that a high temperature fractionation of Ni occurs in sulfide-bearing magmatic rocks. Isotopic signatures of EPD olivine and sulfide-poor gabbro indicate that the initial crystallization of olivine in the Duluth Complex reflects a mantle, bulk silicate earth signature (± 0 ‰), rather than a distinct fractionation event. The sulfide-poor gabbro outlier (0.22 ‰; Fig. 2) has been identified as a potentially late cumulate.

A trend of increasingly negative $\Delta^{60/58}$Ni values in samples with higher sulfide contents (sulfide-rich gabbro) is observed, with more negative values in semi-massive sulfide samples (~15 to 30 % sulfide) and values closer to zero in disseminated sulfides (~5 to 10 % sulfide), a relationship also noted by Hiebert et al. (2014) and typical of isotopic systems, including S, related to mixing between magmatic and crustal components (Lesher and Burnham 2001). Some samples do not follow this trend and either show signs of subsequent alteration (0.15 ‰; see Fig. 2) or represent disseminated sulfides.

3.2 Cu isotopes

$\Delta^{65/63}$Cu values for the Duluth Complex deposits range from -1.28 ‰ to 0.36 ‰ (Fig. 3), comparable to other data from the Duluth Complex (Ripley et al. 2015). Other magmatic Cu-Ni-PGE deposits in the area (Eagle, Tamarack; massive sulfides) show a heavier isotopic signature (> 0.69 ‰), with disseminated ore material from Eagle being much lighter (-0.16 ‰). Both massive and disseminated sulfides from all deposits in the Duluth Complex show similar Cu isotopic values (average: -0.32 to -0.35 ‰) but individual deposits are quite distinct.

Other magmatic sulfide deposits show similar isotopic
variations (except Sudbury); however, their average values are significantly more negative (-0.7 to -1.5 ‰). Surface material generally shows variable negative enrichment of 65Cu, attributed to weathering processes and the preferential enrichment of lighter Cu isotopes into the weathering products.

4 Discussion

As published Ni isotopic values of crustal rocks are generally > 0.2 ‰ (Gueguen et al. 2013), a mixing scenario between crustal and mantle Ni (around 0 ‰; Ripley et al. 2015) does not readily explain measured Ni isotopic variations in the Duluth Complex or increasingly negative Ni signatures as function of sulfide content. The available isotopic data seem to suggest that after the initial crystallization of olivine (0 ‰), sulfide minerals forming in high-temperature mafic melt preferentially incorporate 58Ni relative to 60Ni, with higher concentrations of sulfide leading to more 58Ni enrichment. Studies of other stable metal isotopic systems have indicated a number of reasons for this fractionation, including bond strengths, vibrational differences, or space requirements in the dense sulfide crystal lattices (e.g., Kendall and McDonnell 1998; Schauble 2004). Alternatively, a mixing scenario between crustal material, believed to have supplied sulfur to the sulfide melt, and mantle material in the Duluth Complex, would require crustal rocks to possess a distinctly negative Ni isotopic signature in contrast to currently available data.

During surficial weathering, oxidation reactions release Ni 2+ and Ni 3+ Ni is preferentially incorporated into secondary oxides while 60Ni remains in solution, leading to an isotopically negative fluid. Later secondary phases that precipitate out of groundwater, river or seawater are enriched in 60Ni. (Fig. 4).

Due to the difference in Ni isotopic values between unmineralized material (average: -0.05 ‰) and sulfide-bearing samples (up to -0.97 ‰ with increasing sulfide content), Ni isotopes may be useful to distinguish barren magmatic systems from mineralized systems because of the preferential incorporation of isotopically light Ni into sulfide-bearing rocks.

In addition, Ni isotopic data vary noticeably from deposit to deposit in the Duluth Complex, with values in the South Kawishiwi Intrusion shifting from an average of 0.0 ‰ in the northeast to -0.46 ‰ in the southwest. This difference may reflect the origins hypothesis of Peterson (2001), who theorized that a magmatic conduit (Nickel Lake Macrodike - NLM; see Fig. 1), supplied most of the melt responsible for the mineralization. If the geographic variation in Ni isotope values, it is speculated that different deposits experienced distinct temperature and crystallization conditions during formation, with the northernmost deposits staying hotter for longer due to their proximity to the NLM or that a different source of S (and a portion of Ni-Cu) was involved. These variables would affect the completeness of the sulfide/silicate equilibration reactions, leading to the shift in isotopic values. Ni isotopic signatures of other rock-forming minerals known to incorporate Ni (clinopyroxene, Fe-Ti oxides) may provide additional insight into crystallization processes, sulfide melt segregation, and potential high-temperature isotopic fractionation.

The significance and usefulness of Cu isotopes in the Duluth Complex is less clear since a variety of processes (Cu sourcing, sulfide fractionation) likely influenced the overall Cu isotopic signature. In addition, the processes controlling Cu isotopic fractionation at high temperatures are poorly understood and few Cu isotopic values are available from magmatic sulfide systems. Figure 3 shows that some data from the Duluth Complex lie between conventional mantle values (around 0 ‰) and Duluth Complex sediments (~ 1 ‰). A melt fractionation between these crustal rocks and a mantle source would explain these and data from other deposits (Eagle, Noril’sk). The majority of values from the Duluth Complex (massive and disseminated), however, as well as most other magmatic sulfide deposits, fall to the left of this mixing range. If a ‘maximum’ mantle-derived value of -1.5 ‰ is assumed (red line in Fig. 3; Ripley et al. 2015) the majority of available data fall into this expanded mixing range; some data however cannot be explained this way. Whether this discrepancy is due to limited sampling or a magmatic isotopic fractionation process remains to be determined.

With these limitations in mind, a mixing diagram of mantle-derived and sedimentary Cu in the Duluth Complex is presented in Figure 5. A range of Cu isotopic reservoirs are used to assess the relative contribution of sedimentary and magmatic Cu in the Duluth Complex. Potential contributors include Cu assimilation from crustal rocks (~ 1 ‰), nominal mantle reservoir (0.0 ‰), mantle-derived magmas (up to -1.9 ‰), and magmatic fraction (unknown). To explain the values from the Duluth Complex, results require Cu isotopic contributions from crustal rocks up to 64 ‰, mantle contribution up to 96 ‰, and magmatic fraction (unknown) up to 32 ‰ (not shown). Other deposits show more restricted ranges but generally require a higher percentage of magmatic Cu fractionation due to their more negative isotopic values.
While sedimentary contributions to the Cu isotopic signature of several percent seems feasible, significantly higher values are not easily explained by other geochemical and isotopic evidence.

This uncertainty underscores the current lack of knowledge about magmatic Cu isotopic processes and the need to obtain additional data to gain more insight into the contribution of various Cu sources. Once these processes are better understood, the formation of individual deposits may then be studied by computing the relative contributions of metal sources using metal isotopes.

Acknowledgements

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Palladium antimonides – an experimental investigation

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Czech Geological Survey

Abstract. Palladium antimonides were experimentally investigated at 400°C. We have synthesized the binary phases in the system Pd-Sb and evaluated them by means of X-ray powder-diffraction analysis, reflected light and electron microscopy. The experiments were performed using the evacuated silica-glass tube method. The following phases were confirmed to be stable at 400°C: Pd_20Sb_7, Pd_{31}Sb_{12}, Pd_{8}Sb_{3}, Pd_{5}Sb_{2}, Pd_{2}Sb, PdSb, and PdSb_2. The crystallographic data are summarized herein. The synthetic analogue of ungavaite (Pd_{3}Sb_{2}) was not observed at 400°C and at higher temperatures. The following phases can be expected to occur in nature: Pd_{20}Sb_{7}, Pd_{31}Sb_{12}, Pd_{8}Sb_{3}, and at higher temperatures. The phases are confirmed to be stable at 400°C. We have synthesized the binary system Pd-Sb, using the evacuated silica-glass tube method. The following phases in the system Pd-Sb, based on the run products were characterized by X-ray powder diffraction, in polished sections examined in reflected light, and with electron-microprobe techniques (EMPA).

2 Techniques and methods

2.1 Experimental

Experiments were performed in evacuated and sealed silica glass tubes in horizontal tube furnaces. Charges of about 200 mg were carefully weighed out from the native elements (palladium powder, 99.95% purity and antimony pebbles, 99.999% purity). The starting mixtures were first melted at 1000°C for three days. Then, the run products were ground in an agate mortar under acetone and reheated to 400°C (for 70 days). After heating, quenching occurred by dropping the capsules in cold water. Phases in the run products were characterized by X-ray powder diffraction, in polished sections examined in reflected light, and with electron-microprobe techniques (EMPA).

2.2 Electron probe microanalyses

EMPA were performed with a CAMECA SX-100 electron probe microanalyser in a wavelength-dispersion mode using an electron beam focussed to 1-2 µm. Pure elements were used as standards. Concentrations were quantified on the Pd_Lα and Sb_Lα with an accelerating voltage of 15 keV, and a beam current of 10 nA. In a sample, compositional data were collected from several grains within a polished section.

2.2 X-ray diffraction analyses

The X-ray diffraction patterns (XRD) were collected in Bragg-Brentano geometry on Bruker D8 Advance diffractometer equipped with the Lynx Eye XE detector and CuKα radiation source. The data were collected in the in the angular range from 10 to 140° 2θ.

3 Results and discussion

Eight binary phases in the system Pd-Sb, based on the
phase diagram proposed by Kim and Chao (1996), were reinvestigated in this study. A list of experimental runs with products are listed in Table 1. Minerals belonging to the system are summarized in Table 2. The list of synthetic Pd-Sb phases and relevant crystallographic data are summarized in Table 3. The following phases were confirmed to be stable at 400 °C: Pd$_{20}$Sb$_7$, Pd$_{31}$Sb$_{12}$, Pd$_8$Sb$_3$, Pd$_5$Sb$_2$, Pd$_2$Sb, PdSb, and Pd$_2$Sb$_2$.

Table 1. Results of selected experimental runs in the Pd-Sb system.

<table>
<thead>
<tr>
<th>Run No</th>
<th>Starting composition (at.%)</th>
<th>Phase assemblages at 400°C (*600°C)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
<td>Sb</td>
</tr>
<tr>
<td>2</td>
<td>75.00</td>
<td>25.00</td>
</tr>
<tr>
<td>13</td>
<td>74.07</td>
<td>25.93</td>
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<tr>
<td>6</td>
<td>72.73</td>
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</tr>
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<td>1</td>
<td>66.66</td>
<td>33.33</td>
</tr>
<tr>
<td>5</td>
<td>62.50</td>
<td>37.50</td>
</tr>
<tr>
<td>3</td>
<td>57.14</td>
<td>42.86</td>
</tr>
<tr>
<td>7</td>
<td>50.00</td>
<td>50.00</td>
</tr>
<tr>
<td>8</td>
<td>40.00</td>
<td>60.00</td>
</tr>
</tbody>
</table>

Table 1. Results of selected experimental runs in the Pd-Sb system.

Naldrettite (Pd$_x$Sb$_{2-x}$) has a synthetic analogue primarily synthesized by Bälz and Schubert (1969) at 500 °C. It melts incongruently at 580 °C (Kim and Chao 1996) and below this temperature it coexists with Pd$_2$Sb$_2$ or with PdSb (Fig 1a). For some reason the phase Pd$_2$Sb is missing in the phase diagram compiled by Massalski (1990).

Sudburyite has a synthetic analogue PdSb, which melts congruently at 805 °C (Kim and Chao 1996). Ungavaite (Pd$_x$Sb$_{2-x}$) has no synthetic analogue in the system Pd-Sb so far known. Our attempts to prepare the phase “Pd$_x$Sb$_{2-x}$” at 400, 600, and 700 °C were not successful. The run products at 400 °C resulted in association of Pd$_2$Sb + PdSb, and at 600 °C in Pd$_5$Sb$_2$ + Pd$_3$Sb$_{12}$, at 700 °C we observed parts of melting. It is possible that the phase is not quenchable or it belongs to a low-temperature phase that requires long term heating. Some further investigations, particularly at low temperatures are needed.

Stibiopalladinite has a suggested stoichiometry of Pd$_{5+x}$Sb$_{2-x}$. New XRD data, as suggested by Cabri (2002), on natural samples are needed in order to propose an exact synthetic analogue. It is interesting to note that the unit-cell volume of synthetic phase Pd$_2$Sb$_2$ shows a relationship to that of stibiopalladinite: $V_{\text{stibiopalladinite}} \approx 2V_{\text{PdSb}_2}$. Although the $a$ parameters are nearly identical in both phases, the $c$ parameter of Pd$_2$Sb$_2$ is roughly half of the $c$ parameter of stibiopalladinite. The powder diffraction patterns of both phases show similarities to a certain extent; however, as was also mentioned by Cabri and Chen (1976), their diffraction intensities differ substantially.

Figure 1. BSE (backscattered electron) images illustrating the assemblages of synthetic (a) sudburyite (PdSb) and naldrettite (Pd$_x$Sb$_{2-x}$), (b) the phase Pd$_2$Sb$_2$ and sudburyite (PdSb); quench from 400 °C.

Based on experimental results we believe that other palladium antimonides (tentatively assuming Pd$_5$Sb$_2$ as stibiopalladinite and considering that mertierite II has As in the structure) can be found as new minerals in nature as Pd$_{20}$Sb$_7$, Pd$_{31}$Sb$_{12}$, Pd$_8$Sb$_3$, and Pd$_2$Sb$_2$. Their formation also at low temperatures cannot be excluded.
Table 2. Pd-Sb minerals and their crystallographic data

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal formula</th>
<th>Crystallographic data</th>
<th>Unit-cell parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>naldrettite</td>
<td>Pd₄Sb</td>
<td>orthorhombic</td>
<td>Cmc2₁</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a (Å) 3.3906</td>
<td>1</td>
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<td></td>
<td>b (Å) 17.5551</td>
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<td></td>
<td>c (Å) 6.957</td>
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<td>Z 8</td>
<td>1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ungavaite</td>
<td>Pd₄Sb₃</td>
<td>tetragonal</td>
<td>P4₁2₁2, P4₁2₂, P4₁2₂, P₄₂₁₂, P₄₂₂₂ or P₄₃₃</td>
<td>8 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a (Å) 7.7388</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>stibiopalladinite</td>
<td>Pd₅₋ₓSbₓ</td>
<td>hexagonal</td>
<td>P₆₃/mmc, P₆₃mc or P-62c</td>
<td>12 3</td>
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<td>a (Å) 7.598</td>
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<td>b (Å) 28.112</td>
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<td>sudburyite</td>
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<td>P₆₃/mmc</td>
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<td>a (Å) 4.083</td>
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<td>b (Å) 5.602</td>
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<td></td>
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<td></td>
<td>c (Å) 2</td>
<td></td>
</tr>
</tbody>
</table>

Note.: 1) Cabri et al. (2005), 2) McDonald et al. (2005), 3) Cabri and Chen (1976), 4) Cabri and Laflamme (1974)

Table 3. Synthetic Pd-Sb phases at 400 °C and their crystallographic data

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition range Sb (at. %)</th>
<th>Exp No</th>
<th>Composition</th>
<th>Crystallographic data</th>
<th>Unit cell parameters</th>
<th>Primary ref.</th>
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<tbody>
<tr>
<td>Pd₂₀Sb₇</td>
<td>25.51-25.91 Sb₁₃</td>
<td>Pb₂₀Sb₄₀Sb₉₆₆₆</td>
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<td>a (Å) 11.7264(3)</td>
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<tr>
<td>Pd₃₁Sb₁₂</td>
<td>27.83-28.29 Sb₁₂</td>
<td>Pb₃₀₀₇Sb₁₂₂₃</td>
<td>hexagonal</td>
<td>R-3c</td>
<td>a (Å) 7.6106(1)</td>
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<tr>
<td>Pd₈Sb₃</td>
<td>27.04-27.24 Sb₆</td>
<td>Pb₈V₄₂₀Sb₂₉₉₆₆₆₆</td>
<td>hexagonal</td>
<td>R-3c</td>
<td>a (Å) 7.6082(2)</td>
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<tr>
<td>Pd₅Sb₂</td>
<td>28.27-28.78 Sb₄</td>
<td>Pb₅S₀₈₂₀Sb₀₂₀₀₀</td>
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<td>P₆₃cm</td>
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<td>PdSb</td>
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<td>Pb₂₀₂₀Sb₁₀₀₀₀</td>
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<td>49.69-50.04 Sb₇</td>
<td>Pb₁₀₃₀₂₀Sb₁₀₀₀₀</td>
<td>hexagonal</td>
<td>P₆₃/mmc</td>
<td>a (Å) 4.0772(1)</td>
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<tr>
<td>PdSb₂</td>
<td>66.20-66.29 Sb₈</td>
<td>Pb₁₀₃₀₂₀Sb₁₀₀₀₀</td>
<td>cubic</td>
<td>Pa-3</td>
<td>a (Å) 6.4606(1)</td>
<td>6</td>
</tr>
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</table>


4 Conclusions

The following phases were confirmed to be stable at 400 °C: Pd₂₀Sb₇, Pd₃₁Sb₁₂, Pd₈Sb₃, Pd₅Sb₂, PdSb, and PdSb₂. The phases PdSb and PdSb₂ have mineral analogues naldrettite and sudburyite, respectively. The exact synthetic analogue of stibiopalladinite is not yet clear. Mineral ungavaite (Pd₄Sb₃) has no synthetic analogue known at 400 °C and above this temperature. The phases Pd₂₀Sb₇, Pd₃₁Sb₁₂, Pd₈Sb₃, and PdSb₂ can be expected to be found in nature likely in close association with other PGMs, particularly with known palladium antimonides. Those phases can be expected in magmatic Cu-Ni-PGE mineral deposits, associated with mafic and ultramafic igneous rocks, however the formation at low temperatures is also probable.

Acknowledgements

This contribution honours the memory of prof. Hazel Prichard. Financial support through the internal project from the Czech Geological Survey is gratefully acknowledged.

References


Gersdorffite as a PGE collector in massive ores in the Ban Phuc Ni-Cu-(PGE) sulfide deposit in the northern Vietnam

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Abstract In the Ban Phuc Ni-Cu-(PGE) sulfide deposit in northern Vietnam, the whole-rock PGE concentrations are decoupled from the numbers of platinum-group minerals (PGM). In the massive ores no or few PGM are found. On the other hand, more PGM are located in disseminated sulfide ores in which PGE concentrations are lower. The massive ores commonly contain gersdorffite. The gersdorffite has been found to contain all six PGE and, along with BMS, is likely to be the host for PGE in the massive ores. This is an example of a growing number of cases where massive ores have been found to contain PGE in arsenic-bearing minerals, either PGM including sperrylite and members of the irarsite-hollingworthite-plaratsite solid solution series or in gersdorffite/cobaltite. We suggest that the presence of As in a magma will cause early removal of PGE. The presence of arsenic in mafic-ultramafic magmas in low and high level plutonics and lavas results in the formation of early arsenic-bearing PGM and euhedral, 10-60 μm, PGE-bearing sulfarsenide.

1 Introduction

Arsenic is known to form PGM including common minerals such as sperrylite and the PGE sulfarsenide solid solution series of irarsite-hollingworthite-plaratsite with irarsite commonly rimming either of the other two. In addition to the Ir, Rh and Pt sulfarsenides, orarsite and ruarsite are relatively common.

Ir, Rh and Pt are also known to form PGM arsenide or sulfarsenide enclosed in Ni-Fe-Co sulfarsenide which form the gersdorffite-cobaltite solid solution series. Studies have shown that As has an affinity for the PGE and if present in the magma will cause early crystallization of PGE depleting the PGE concentrations of subsequent base metal sulfides. The details of the timing of this PGE collection and the exact mechanism are not entirely clear. Some authors consider that the PGE arsenide crystallized early before the formation of an immiscible sulfide liquid (Merkle 1992), whereas others suggest that the PGE arsenide crystallized from the immiscible sulfide liquid (Dare et al., 2010). Some workers also propose the separation of an immiscible As-rich liquid from the immiscible sulfide liquid (e.g. Holwell & McDonald 2007). Arsenic is a deleterious element in base metal sulfides and therefore the processes that determine its distribution are of interest to companies involved in extraction and processing of these ores.

Our initial study of the Ban Phuc Ni-Cu-(PGE) sulfide deposit in the northern Vietnam involved analysis of PGE in a suite of samples, followed by a search for PGM in both PGE-rich massive sulfide ores and disseminated sulfide ores hosted in dunite. A lack of PGM in the massive ores led to a laser ICP-MS study to determine alternative hosts for the PGE in these ores.

2 Geological background

2.1 The Emeishan large igneous province (LIP)

The Emeishan LIP in the western part of the Yangtze Block and the eastern margin of the Tibetan Plateau is bounded to the south by the Indochina Block. The Emeishan LIP is mainly composed of flood basalts and mafic-ultramafic intrusions. The flood basalts crop out chiefly in the Yunnan, Sichuan and Guizhou Provinces in China and the Song Da region in northern Vietnam. The volcanic sequence ranges in thickness from several hundred meters in the east to nearly 5 km in the west (Chung & Jahn 1995) and is mainly composed of low-Ti and high-Ti flood basalts, with minor picrite, tephrite and basaltic andesite (Xu et al. 2001), all of which are believed to have formed by melting associated with the Emeishan plume (Chung & Jahn 1995).

Permian flood basalts and associated mafic-ultramafic intrusions form a narrow (< 20 km), NW-trending belt more than 350 km long in the Jinping (China) - Song Da (northern Vietnam) district. This belt is bounded in both China and northern Vietnam by the Ailao Shan-Red River fault zone to the northeast and the Ailao Shan-Song Ma suture to the southwest (Chung et al. 1997). The flood basalts crop out in the Nam Muoi River area (>30 km long and ~3 km wide), the Ta Khoa area both in the northern Vietnam (60 km long and 10 km wide) and the Jinping area (~150 km²), and represent the southernmost part of...
the Emeishan LIP. The lava sequence unconformably overlies the early Permian limestone, and is concordantly overlain by the early Triassic limestone and shale with coal measures (Glotov et al. 2001).

Numerous mafic-ultramafic intrusions intruded Ordovician and Devonian strata in the Jinping-Song Da district. The Ban Phuc and Baimazhai intrusions host Ni-Cu-(PGE) sulfide ore deposits (Glotov et al. 2001; Wang & Zhou 2006).

2.2 The Ban Phuc Ni-Cu-(PGE) sulfide-bearing ultramafic intrusion

The Ban Phuc intrusion intruded the core of the Ta Khoa anticline. The axis of the fold is NW-striking and extends for ~50 km, with a width of up to 20 km along the Song Da rift. The fold is composed of early- to middle-Devonian schist, quartzite, gneiss, marble, siliceous limestone, and amphibolite belonging to the Ta Khoa Formation in the core and is covered by Permian lavas in the limbs. The core part of the fold experienced significant erosion and the strata in the core part are aligned nearly vertically.

The Ban Phuc intrusion is a NW-trending elongated body corresponding to the strike of the Ta Khoa Formation. It is about 940 m long and 220-420 m wide and has a 470 m downward extension, with an outcrop area >0.25 km² (Fig. 1a). It intruded along the trend of a discontinuous unit of limestone. The intrusion is relatively wide in the northwestern margin where only the flat base of the intrusion is preserved. It narrows and extends to the southeast part where it has an oval-like cross-section dipping steeply northeast, roughly concordant with the country rocks.

The intrusion is composed of dunite overlain by wehrlite (Fig. 1b). Two main types of mineralization are recognized in the host intrusion and country rocks: (1) vein-like massive and minor disseminated sulfide ores in the hornfels schist and altered ultramafic dikes on the southern contact zone (Fig. 1a); (2) disseminated sulfide ores at the base of the dunite and in the walls of the intrusion (Fig. 1b). The estimated reserves of metals are 119,400 tons Ni, 40,500 tons Cu, 3,400 tons Co, 14 tons Te, and 67 tons Se.

The vein-like massive sulfide ore body in the hornfels schist occurs along a shear-controlled vein structure in the southern margin of the intrusion. This vein mainly forms a single structure with minor offshoots and bifurcations. It has a NW-SE strike, steep dip of 70-90° to the southeast and rarely to the southwest (Fig. 1b) and cuts lithological layering of the country rocks at a low angle but appears conformable in some sections. The vein is 750 m in length and has an average width of 1.26 m. It has an inverted triangular form in plan view and extends downwards at least 450 m (Fig. 1b). The average grade of massive sulfide in the vein is 2.68% Ni, 1.19% Cu and 0.06% Co. The massive ores that were analyzed in this study have an average of ~4.1 wt.% Ni and 0.3 wt.% Cu.

The disseminated sulfide ores in the hornfels schist and altered ultramafic dikes abutting the massive sulfide ores form a halo surrounding the massive sulfide vein, which vary from a few centimeters to several meters in extent. The disseminated sulfide ores in the vein contain 0.69% Ni, 0.62% Cu and 0.02% Co in average.

The disseminated sulfide ores in the dunite form concave layering which is defined by low-grade, Ni-rich sulfide layers, conformable with the base and foot walls of the intrusion (Fig. 1b). In the wider basal zone preserved at the northwestern margin of the intrusion these are flat layers with only minor convexity, but in the southeastern section the layers are tightly packed and strongly concave, extending into the footwall wall of the intrusion. The disseminated sulfide ore bodies have thickness varying from 2 to 40 m with the average of 0.8% Ni.

3 Petrography

In the Ban Phuc Ni-Cu-(PGE) sulfide deposit there are three types of sulfide ores, massive and densely disseminated ores in the hornfels schist, and disseminated ores in the dunite.

Massive sulfide ores in the hornfels schist have 50 to 80 wt.% sulfides, and are mainly composed of pyrrhotite (70%), pentlandite (10%) and chalcopyrite (5%), as well as minor gersdorffite, magnetite and silicates. Most massive ores have subhedral granular textures. Pyrrhotite varies in size from 1 to 3 mm. Flame and embayed textures formed by replacement processes are present in the margin of the pyrrhotite. Pentlandite occurs in granular masses with a grain size of 0.06-2 mm, and as fine inclusions in pyrrhotite. Chalcopyrite forms irregular grain aggregates up to 3mm in size, and inclusions in pyrrhotite.

Densely disseminated or vein-like sulfide ores in the hornfels schist contain more chalcopyrite with sulfides ranging from 11 up to 67 wt.% close to the massive ore body. These sulfide ores are mainly composed of pyrrhotite (25%), chalcopyrite (30%), violarite and pentlandite (15%), pyrite (10%) and minor gersdorffite. Chalcopyrite occurs as anhedral grains or intergrowths with pyrrhotite.

The disseminated ores in the dunite at the base of the intrusion contain 1 to 8 wt.% sulfides, which occur as blebs and patches in the angular interstices between silicates.

4 Whole-rock PGE, Ni, Cu and S contents

Massive sulfide ore from the Ban Phuc deposit has Pt ranging from 4.6 to 51.6 ppb and Pd ranging from 12 to
118 ppb with Pt/Pd of 0.1 to 1.4 (Fig. 2). The sample of Cu-rich breccia ore has a Pt value of 18,079 ppb and Pd of 26.9 ppb. In contrast the disseminated ores in dunite have Pt and Pd values that have a less extreme range of 251-801 ppb Pt and 316-1444 ppb Pd with Pt/Pd of 0.4 to 0.8 (Fig. 2). Both the disseminated and massive ores that are located near country rock have high Pt concentrations compared to Pd with Pt/Pd of 94 and 97, whereas the Cu-rich breccia ore has the highest Pt/Pd of 672 (Fig. 2).

In the Ban Phuc deposit, the disseminated ores have steep patterns with weak negative Ir anomalies. Ni is enriched relative to Ir, whereas Cu is depleted relative to Pd (Fig. 3). The massive ores have low PGE values so give trough shaped patterns have remarkably different patterns; three samples show trough-like patterns with very negative Pt anomalies, one sample also shows a trough-like pattern but with a very negative Ru anomaly (Fig. 3). Sulfide ores close to the country rocks have steep patterns with very negative Ru anomalies and positive Pt anomalies (Fig. 3).

The samples of disseminated ores contain <3 wt.% S. Sulfide contents that were calculated based on the S contents in the rocks vary from 1.1 to 7.5 wt.%, whereas the massive sulfide ore samples have 19.9 to 29.9 wt.% S, with sulfide contents ranging from 52 to 79 wt.%. The sulfide ores near the country rocks have highly variable S (S = 4.08 to 25.6 wt.%), with sulfide contents varying from 11 to 67 wt.%.

The massive ore samples from the Ban Phuc deposit contain 2.6 to 6.3 wt.% Ni and 0.05 to 0.8 wt.% Cu. The Ni/Cu ratios range from 7.7 to 49. The massive ores have a positive correlation of Cu and Ni and generally show a trend from Ni-rich to Cu-rich, indicating fractionation of the sulfide melt. The disseminated ore samples contain 0.3 to 1.5 wt.% Ni and 0.02 to 0.2 wt.% Cu. The Ni/Cu ratios of the disseminated ores range from 6.1 to 19 and they also show a trend from Ni-rich to Cu-rich. The sulfide ores near the country rocks have 0.6 to 3.5 wt.% Ni and 0.8 to 1.6 wt.% Cu with Ni/Cu of 0.6 to 3.8.

5 Grain size and compositions of platinum-group minerals and PGE-bearing sulfarsenide mineral (gersdorffite)

Five froodite grains are enclosed within silicates in disseminated ores including one from near the country rocks. The grains range in size from 1×1 to 10×5 μm and have rounded outlines and are slightly elongate (Fig. 4a and b). Froodites shown in Fig. 4b are stoichiometric in composition, whereas three others are irregular in shape, and are heterogeneous in composition with Sb substituting for Bi in their compositions. In one case a composite grain of froodite and a Sb-rich Pd-bismuthide occurs surrounded by silicate (Fig. 4b).

Four sperrylite crystals are observed in the disseminated ores including one from near the country rocks. The sperrylite grains in these ores are irregular in shape and range from 8×5 to 20×5 μm in size. They contain minor Sb. These crystals are enclosed in silicates or in one case pentlandite (Fig. 4c).

Two Au-Ag electrum grains are observed in the disseminated ores (Fig. 4d). They are very small with a grain size of ~4×4 μm and are associated with silicate minerals and magnetite (Fig. 4d). Both grains contain more Ag than Au, and minor S.

The gersdorffite crystals in the samples are light ivory in color in reflected light. In the massive ores of the Ban Phuc deposit they are usually small and perfectly formed euhedral grains from 5 to 60 μm maximum diameter with an average of 33×25 μm in size. Most grains are enclosed in pyrrhotite. Euhedral gersdorffite grains in the sulfide ore from near the country rocks range from 4 to 50 μm in diameter averaging 30×26 μm in size (Fig. 5).
The gersdorffite grains in the massive ores contain on average 14.6 wt.% Ni and 14.3 wt.% Co, whereas the gersdorffite grains in the sulfide ores from near the country rocks have lower Co averaging 11.4 wt % and higher Ni values averaging 17.2 wt.% than those in the massive ores.

One euhedral gersdorffite grain was found to contain all 6 PGE at ppm levels with Pt highest at 634 ppm, and Os and Ru lowest (Fig. 6). The primitive mantle-normalized patterns approximately copy those in the whole rock but are elevated (Fig. 7). Where the PGE are evenly distributed within the gersdorffite, Ag, Te and Bi form two peaks on both margins of the gersdorffite. The surrounding pyrrhotite has very low levels of PGE except for 6 ppm Pt and even this is 100 times less than in the gersdorffite. All the PGE in the chalcopyrite are less than 1 ppm. Compared to surrounding BMS, Sb, Te, Bi, Re, Ag and are also elevated in the gersdorffite as well as slight elevations for Se and Au (Fig. 6).

In many massive BMS ores Pd-PGM are common and are thought to have exsolved from the BMS during cooling. In these ores Pd-bearing PGM are absent in the massive ores because the Pd is still present in solid solution in the BMS. It has been suggested that exsolution of Pd to form PGM requires slow cooling, as for example would have taken place in a large complex such as the Bushveld complex (Barnes et al. 2004). In these much smaller intrusions there may not have been time for the Pd-PGM to have exsolved from the BMS.

There are now several examples of PGE-rich Ni-Cu ores in which As has caused early crystallization of PGM including the Ban Phuc ores and other mafic and ultramafic layered intrusions such as the Platreef (Holwell & McDonald 2007). The same process appears to affect komatiitic Cu-Ni-PGE massive ores that are As-bearing. Recently there have been several descriptions of PGE associated with magnetite layers in the upper parts of layered intrusions such as the Bushveld, Rincon del Tigre, Skagaard, Stelland the Freetown complex. Where these occurrences are As-bearing there is evidence of early crystallization of As-bearing PGM. Sperrylite in the Jacare Sill has been recorded enclosed both in magnetite and in olivine suggesting early crystallization (Sá et al. 2005). In contrast in the Freetown complex the PGE-bearing high level horizons are barren of As and here the PGM are predominantly PGE-sulфides and Pt-Fe alloys and these are located interstitial to the silicates suggesting late crystallization of the PGE.

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Sulfide textural variations and multiphase ore emplacement in the Eagle’s Nest Ni-Cu-PGE deposit, McFaulds Lake greenstone belt, Ontario, Canada

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Abstract. The Meso to Neoarchean McFaulds Lake greenstone belt (aka ‘Ring of Fire’) in northern Ontario is best known for its world-class chromite endowment, but it also hosts significant magmatic Ni-Cu-PGE mineralization at the Eagle’s Nest deposit. Mineralization at Eagle’s Nest occurs in a dynamic feeder system that contains multiple generations of sulfide textures, consistent with its interpretation as a magmatic feeder. Abundant disseminated, oikocrystic net-textured, and inclusion net-textured sulfide mineralization formed first and was consolidated enough to be cross-cut by abundant late-stage websteritic melts and by minor late-crystallizing massive sulfide melts. Understanding the fundamental characteristics of mineralization at Eagle’s Nest will provide critical information about the evolution of this large Cr and Ni-Cu-PGE ore system associated with Archean komatiitic magmatism in the Superior Province.

1 Introduction

The Eagle’s Nest deposit of the ultramafic to mafic Ring of Fire intrusive suite in the 2.8-2.7 Ga McFaulds Lake greenstone belt (Fig. 1) contains 20 Mt @ 1.7% Ni, 0.98% Cu, and 4.4 g/t Pd+Pt (Burgess et al. 2012) and is one of the largest Ni-Cu-PGE deposits discovered in Canada in the last 25 years. It is hosted by a subvertical (originally subhorizontal) ultramafic body dominated by komatiitic pyroxenite and peridotite that is ~200 m long (thick), up to 50 m thick (wide), and ~1600 m deep (long) and contains mainly net-textured sulfide mineralization with only minor disseminated and massive sulfide mineralization (Mungall et al. 2010). Textural, mineralogical, and geochemical variations within the deposit provide critical information on the mode of emplacement and crystallization of the Fe-Ni-Cu sulfide mineralization at the Eagle’s Nest deposit.

2 Geologic setting

The Eagle’s Nest deposit occurs within the feeder system of the Double Eagle intrusive complex, which is part of a 15 km long by up to 3 km wide (thick) by >1 km deep (wide) ultramafic-dominated sill complex of the Ring of Fire intrusive suite composed of at least two discrete sill bodies (Fig. 2). In both complexes, the intrusion is differentiated with a thicker lower ultramafic sequence composed of komatiitic dunite, lherzolite, websterite, and chromitite (Blackbird and Black Horse chromite deposits in DEIC and Big Daddy, Black Creek, Black Label, and Black Thor chromite deposits in BTIC) overlain by a thinner mafic sequence composed of melanogabbro, mesogabbro, leucogabbro, and lesser anorthosite.

3 Sulfide textures

The sulfide mineralization at Eagle’s Nest is composed mainly of pyrrhotite-pentlandite-chalcopyrite and occurs predominantly as various textural facies of net-textured sulfide mineralization (ranging 5-12% S) with minor disseminated (2-5% S), rare semi-massive (12.5-30% S), and minor massive (>30% S) textures (Fig. 3). Disseminated textures occurs as fine, dispersed sulfides in close proximity to blebby and wispy sulfides in otherwise barren rock, interlayered with net-textured/massive sulfides (Fig. 3a). Net textures sensu stricto are rare, but occur as thin films of sulfide surrounding serpentinitized olivine. Most contain pyroxene oikocrysts and can be subdivided into leopard-net textures containing dark altered pyroxene oikocrysts (Fig. 3b) and pinto-net textures...
containing light altered pyroxene oikocrysts (Fig. 3c). Disrupted-net textures have been invaded by websterite (Fig. 3d). Inclusion-net textures contain inclusions of olivine/dunite, magnetite, and silicate-oxide facies iron formation (Fig. 3e). Semi-massive textures are rare, but fine-grained semi-massive sulfides transgress net/leopard/pinto-textured sulfides. Massive sulfides occur as large lenses tens of meters thick, as well as 3-70 cm thick veins and veinlets (Fig. 3f).

Locally, massive sulfides contain a wide range of clasts including barren peridotite, pyroxenite, magnetite, net-textured sulfide, and rare siliceous material. Clasts are often associated with zones of chalcopyrite, which is concentrated along contacts, alteration zones, or along veins and faults. Commonly, clasts are relatively homogeneous and exhibit a similar grain size with < 2 mm difference, whereas in zones where clast size vary considerably, up to 5 mm size differences can exist.

### 4 Contact relationships

Contacts between barren peridotites and peridotites containing fine, more-or-less uniformly distributed disseminated sulfides are normally gradational. Contacts between late websterite and leopard/pinto/inclusion net-textured sulfides are irregular but relatively sharp (Fig. 4a), whereas contacts between massive and semi-massive/net-texture are irregular, with massive infiltrating net texture (Fig. 4b, 4c, 4d). These types of contacts occur adjacent to both thin veins (<1 m) and thicker (>1 m) lenses of massive sulfides.

### 5 Discussion

The textures and cross-cutting relationships indicate at least three phases of ore formation/modification: 1) formation of disseminated and net/leopard-net/pinto-net/inclusion-net textured ores in the subhorizontal magmatic conduit, most likely involving sulfide localization processes described by Lesher (in review), sulfide percolation processes discussed by Barnes et al. (2017), and later local sulfide melt mobilization forming sulfide schlieren; 2) emplacement of semi-massive and massive sulfide melts containing clasts derived from other parts of the system (barren dunite, net-textured ores) and country rocks (magnetite, iron formation); 3) emplacement of late websterite melt, which may be related to the similar
lithology described by Spath et al. (2015) in the nearby Black Label area.

The websterite relatively sharply cross-cuts early net-textured facies without mobilizing sulfides, indicating that the olivine/pyroxene network behaved relatively rigidly, but does not cut semi-massive or massive sulfides, possibly because they were still ductile at the time. Cross-cutting, infiltrating relationships between massive and net-textured mineralization suggest late-stage mobilization of massive sulfides; this is because sulfide melts crystallize at lower T (<1100 °C) than silicates (1400-1200 °C), so will remain mobile to lower temperatures.

The inclusions in net-textured mineralization also indicate that the system was dynamic, because it was able to carry clasts. It is likely that rounded clasts were incorporated earlier and/or carried further, and that angular clasts were incorporated later and/or carried less far. Finally, because no “exotic” xenoliths are present (all appear to be host and local footwall lithologies) this suggests ore formation occurred close to the site of emplacement.

The evidence for multiphase emplacement indicates a relatively long-lived ultramafic system, consistent with Eagle’s Nest representing a feeder within the Double Eagle Igneous Complex.

6 Conclusions

Ni-Cu-PGE mineralization at Eagle’s Nest includes a wide range of textures including disseminated, disrupted-net, pinto-net, leopard-net, inclusion-net, semi-massive, and massive. The contacts between the textures, the presence
of clasts of barren/net texture in massive sulfides, and the intrusion of olivine pyroxenite into leopard-net mineralization suggest a dynamic, multi-phase emplacement history. By understanding the underlying characteristics of mineralization at Eagle’s Nest, further insight can be gained into the evolution of this large Cr and Ni-Cu-PGE ore system in the Superior Province that is associated with Archean komatiitic magmatism.

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Figure 4. Contact relationships. a websterite/net-textured contact, b massive/net-textured contact, c massive/net contact with clast of net-textured sulfide, d massive/net textured contact with large clast of magnetite. NQ (47.5 mm diameter) core.
S03. Key controls on the quality (size and/or grade) of metal deposits in volcanic and sedimentary basins

Convenors:
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SGS
Mineral deposits in time: products and indicators of Earth's tectonic and environmental history

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**Abstract.** Although it has been known for several decades that some types of mineral deposits have episodic distributions through time, better constraints on the ages of mineralisation and a better knowledge of Earth's history have improved our understanding of how metallogenesis is linked to Earth's tectonic and atmosphere/hydrosphere evolution.

The temporal distribution of deposits reflects a combination of formation and preservation, with erosion removing older examples of deposits formed at shallow levels (<5 km) in the crust (e.g. porphyry copper deposits) from the geological record. The distributions of deposits that typically form in convergent margins have a close association with periods of supercraton/supercontinent assembly during Earth's history, and deposits that require the involvement of oxidised surficial or basinal fluids form only after the Great Oxidation Event.

For some deposit classes, characteristics of deposits within the class also change with time. For volcanic-hosted massive sulfide deposits, the lithological make-up of the host packages, the geochemistry of associated volcanic rocks and the mineralogy of the ores and alteration assemblages change with time. These changes not only provide clues to changes in tectonic processes and environmental conditions over time, but also influence the physical properties and explorability of the deposits.

**1 Introduction**

It has long been recognised that mineral deposits change in their abundance and characteristics through geological time (e.g., Meyer 1981). As the amount and quality of geochronological data from mineral deposits have increased and our understanding of how Earth has evolved has progressed, it has become more apparent that the distribution of deposits through time and, moreover, changes in their characteristics reflect the tectonic and environmental evolution of Earth (e.g. Lambert et al. 1992; Goldfarrb et al. 2010; and many others).

In this contribution we present the distributions of a range of ore deposit types through time as a series of histograms, and discuss how these distributions reflect changes in tectonics and in the atmosphere/hydrosphere. Then we focus on volcanic-hosted massive sulfide (VHMS) to discuss how this deposit type has changed through time, and how these changes reflect the evolution of the Earth and could affect exploration models.

**2 Secular distribution of mineral deposits**

Figure 1 illustrates the secular distributions of mineral deposits for a range of deposit types, including porphyry copper, VHMS, orogenic gold, pegmatite, carbonate-hosted Zn-Pb (Mississippi Valley- and Irish-types), clastic-dominated (shale-hosted) Zn-Pb-Ag, and some uranium (paleoplacer and unconformity-related) deposits. These deposit types were selected because they form in different tectonic settings and local paleo-environments, so that comparing and contrasting their distributions gives insight into Earth's evolution.

**2.1 The importance of preservation**

The distributions presented in figure 1 reflect not only the patterns of deposit formation but also their destruction by subduction and erosion. The contrasting distributions of porphyry copper and orogenic deposits best illustrates the importance of preservation. The vast majority of porphyry copper deposits present in the geological record formed between 100 Ma and the present, with only a tiny fraction having formed before 250 Ma. In comparison, major orogenic gold deposits have formed episodically since ~2720 Ma and the youngest major deposit (Muruntau) present at the Earth's surface formed at ~288 Ma (Morelli et al. 2007). The different distributions for these deposits, both of which form along convergent margins, reflect not only the periods of ore formation, but the level in the crust in which they form, and their susceptibility to subsequent erosion. Because porphyry copper deposits form in the upper few kilometers of the crust (Seedorf et al. 2005),
they are more likely to be lost as the arcs in which they formed are eroded by later orogenesis. Although rare and economically minor, porphyry copper deposits are known through much of Earth’s history, with the oldest example being the ~3320 Ma (R Thorpe, in Williams 1999) Spinifex Ridge deposit. Orogenic gold deposits, on the other hand, form at deeper levels in the crust (mostly 6-12 km), generally during orogenesis (Groves et al. 1998). Accordingly, these deposits are more likely to be preserved, and the lack of young deposits may just reflect that, for the most part, present day erosion levels have not reached the levels at which these deposits formed. To support this concept, minor young orogenic deposits, such as ~32-11 Ma deposits in the European Alps (Pettke et al. 1999), are known in areas with recent extreme uplift.

Deposits can also be lost through tectonic processes like subduction. In the last four decades abundant black smokers, the modern equivalent of VHMS deposits, have been discovered along mid-oceanic ridges (Hannington et al. 2005). But as the oceanic crust formed along these ridges will mostly or totally be lost to subduction, these deposits will not be preserved in the geological record. Accordingly, the distribution of VHMS deposits shown in figure 1 is inherently biased, although it may be a reasonable record of VHMS deposits formed in back-arc basins or rifted arcs along convergent margins, which are more likely to survive into the geological record.

2.2 Mineral deposits and the supercontinent cycle

Figure 1 shows that the present distribution of some deposit types closely follows periods of amalgamation of supercratons and supercontinents. These deposit types, which include VHMS, orogenic gold and pegmatite deposits, are thought in general to form along convergent margins (Huston et al. 2016). Porphyry copper deposits might also be expected to show a similar distribution, but the loss by erosion biases the observed distribution. This pattern holds entirely for the assembly of Kenorland, Nuna and Pangea, and the pattern also holds for the early assembly of Amasia, the next postulated supercontinent. In fact, multiple modes in the VHMS and pegmatite data between 600 Ma and 300 Ma may reflect the initial assembly of Gondwana and Euramerica (first mode) and the assembly of these two entities into Pangea (second mode). The only exception to this generalisation is Rodinia assembly, which is not characterised by a spike in VHMS or orogenic gold deposits, but is characterised by a spike in pegmatites. This may suggest that Rodinia assembly involves different tectonic processes to the other supercontinents (e.g. introversion or advancing accretion orogenesis: Pehrsson et al. 2014).

In some cases there appears to be a slight progression in the age of deposit types associated with supercontinent assembly. This is illustrated between 2750 Ma and 2500 Ma where VHMS deposits formed earliest, followed by orogenic gold and then pegmatites. This progression is also observed in some individual provinces. In the Eastern Goldfields Superterrane in Western Australia, VHMS
2.3 Mineral deposits and the Great Oxidation Event

A number of deposit types do not show a strong relationship with the supercontinent cycle, particularly those that form in basins. Rather, the distribution of these deposits seems to be more related to the Great Oxidation Event (GOE) at ~2350 Ma, as discussed by Meyer (1981) and Lambert et al. (1992). For example, the major basin-hosted uranium deposit type prior to the GOE was paleoplacer uraninite. Uraninite is stable and forms paleoplacers under reduced atmospheric and hydrospheric conditions, but in oxidised conditions after the GOE, basinal fluids became oxidised and uranium could be easily transported in these fluids. Hence, after the GOE, uranium deposits are largely hydrothermal and include such types as unconformity-related deposits (Figure 1) and sandstone-hosted deposits (not shown).

The other types of basin-hosted deposits formed from oxidised fluids are carbonate-hosted (Mississippi Valley-type) and siliciclastic-carbonate clastic-dominated deposits (cf. Huston et al., 2016 and references therein). These deposits start after the GOE (the oldest examples of these types have ages of 2100 and 2020 Ma, respectively) and are most abundant during the Mesoproterozoic and Phanerozoic, during which time the atmosphere and the upper part (at least) of the hydrosphere was oxidised (Farquhar et al., 2010).

Unlike the other basin-hosted deposits, Mississippi Valley-type carbonate-hosted deposits also have a general correlation with supercontinent assembly with strong peaks that correspond to Pangea and Amasia assembly and minor peaks associated with late Nuna and Rodinia assembly. This relationship may reflect the origin of these deposits as the distal products of orogenesis (orogenic gold) and post-orogenic extension (pegmatites).

3 Temporal changes in the characteristics of VHMS deposits and their host successions

Barrie and Hannington (1999) proposed a classification of VHMS deposits according to host succession lithology. This classification defines deposit classes: bimodal-mafic, pelitic-mafic, mafic, bimodal-felsic and siliciclastic-felsic. Figure 2a shows the proportions of these classes in the three major periods of VHMS formation/preservation (2800-2600 Ma, 2000-1700 Ma and 600-0 Ma). This diagram shows that the proportion of felsic-dominated host successions, particularly siliciclastic-felsic, increases from older to younger, which mirrors the increasing importance of bimodal-mafic deposits in older successions. The relative proportion of mafic and pelitic-mafic classes of deposits is, in fact, lower in older than younger deposits.

The geochemical characteristics of volcanic rocks within the host successions have also changed with time. Although mostly in mafic-dominated bimodal successions (Fig. 2a), in detail Archean deposits are mostly associated with tholeiitic rhyodacite to high-silica rhyolite, whereas younger deposits have a progressively closer association with calc-alkaline dacites and rhyolites (Lesher et al., 1986; Lentz, 1998; Piercey et al., 2001; Hart et al., 2004).
economic characteristics of the ores. As an example, the greater abundance of pyrrhotite in older ores may enhance discoverability using magnetic data.

4 Conclusions

Mineral deposits types have an episodic distribution through time, which is the consequence of preservation as well as secular changes in tectonic processes and the surficial environment on Earth. These processes also cause variations in the characteristics of deposit classes. The temporal distribution of mineral deposits be used to constrain how tectonic and environmental processes have changed over time.

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The bimodal fluid evolution of the Nimbus Zn-Ag deposit: an Archean VHMS with epithermal characteristics

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Abstract. The Nimbus Zn-Ag VHMS deposit represents an exceptional mineralised occurrence in the Yilgarn Craton. While other VHMS systems in the craton are restricted to paleo-rift zones, Nimbus is associated to a plume-related stratigraphy (Hollis et al. 2017). Furthermore, the epithermal characteristics resulting from low temperature and shallow water conditions allowed the development of an unusual mineralisation dominated by Ag-rich sulfosalts. In this study we take advantage of state-of-the-art in-situ techniques to investigate the fluid evolution of this peculiar VHMS system. From the trace element compositions and S-isotope signatures we suggest that Nimbus experienced a bimodal fluid evolution consisting of (i) an initial intense interaction between deep-magmatic fluids and seawater that developed barren pyritic lenses, and (ii) a subsequent closure of the hydrothermal system during which the Ag-rich ore formed sourcing sulfur almost entirely from a deep-magmatic source.

1 Geological setting

In the Archean Yilgarn Craton, volcanic-hosted massive sulfide (VHMS) mineralisation is predominately restricted to zones of thin juvenile crust as recently identified by regional (Nd, Pb and Hf) isotope studies (Huston et al., 2014; Mole et al. 2014). Interpreted as Archaean paleo-rift zones, one such zone trends N-S through the Eastern Goldfields Superterrane and is associated with the high grade ca. 2690 Ma Teutonic Bore, Jaguar and Bentley VHMS deposits (Hollis et al. 2015). Until recently, the plume-related lower portions of the stratigraphy were considered unprospective since only minor VMS-like occurrences (e.g. historic Anaconda mine) and barren pyritic lenses were recognised.

Figure 1. Modified section of the 1:500,000 geological map of Western Australia provided by the Geological Survey of Western Australia.

The Nimbus Ag-Zn-(Au) VHMS deposit, located approximately 10 km east of Kalgoorlie (Figure 1), represents the first notable exception to this paradigm. It is hosted in a NW-trending and steeply-dipping bimodal-felsic package of volcanic rocks with a Fl-affinity (felsic
volcanic rocks, ocean-plateau like low-Th basalts, Piercey (2011) which have been identified as coeval with the 2704 Ma plume magmatism responsible for world-class Ni-komatiite mineralisation (Hollis et al. 2017).

The mineralisation, assessed at 12.1 Mt at 52 g/t Ag, 0.9% Zn and 0.2 g/t Au, consists of a series of stacked plunging sulfide-bearing lenses. The ore mineralogy is characterised by sphalerite associated with abundant Ag-Sb-Pb-As sulfosalts, arsenopyrite, and rare chalcopyrite. The intense and pervasive hydrothermal alteration affecting the deposit is dominated by quartz-sericite-carbonate assemblage that shift to chlorite predominantly in the basin. These features, largely preserved after a low greenish metamorphic overprint, have been interpreted by Hollis et al. (2017) as the result of a shallow water and low temperature VHMS system with the Nimbus deposit consequently showing hybrid epithermal characteristics.

2 Methodology

Thirty-five samples representing the different sulfide occurrences were systematically examined by reflected light microscopy.

The mineral chemistry of sulfides and sulfosalts were defined by Wavelength Dispersion Spectroscopy (WDS) analyses using a JEOL 8530F microprobe at the Centre for Microscopy, Characterisation and Analysis (CMCA), University of Western Australia. S, As, Sb, Se, V, Fe, Ti, Au, Te, Cu, Pb, Ni, Zn, Co, Ag, Cd, Bi and Hg were quantified following the analytical conditions illustrated in Hassan and Roberts (2017).

Trace elements in pyrite and sphalerite were acquired by Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) performed at UQAC-LabMaTer, Université du Québec à Chicoutimi, Canada. 34S, 34V, 35Cr, 52Fe, 53Co, 54Ni, 61Cu, 62Zn, 63Ga, 74Ge, 75As, 85Rb, 88Sr, 90Zr, 99Mo, 107Ag, 111Cd, 118Sn, 121Sb, 129Te, 137Ba, 151Gd, 177Hf, 181Ta, 182W, 191Pt, 202Hg, 209Tl, 209Pb, 209Bi, 232Th and 238U were collected following a procedure similar to the one described in Duran et al. (2015).

Quadruple sulfur isotope (32S, 33S, 34S, and 36S) analyses were collected with the Cameca IMS1280 large geometry ion probe at the CMCA. In-situ S-isotope measurements were acquired on pyrite, chalcopyrite, arsenopyrite and pyrrhotite with the use of matrix-matched reference materials following the analytical procedure described in LaFlamme et al. (2016).

3 Ore mineralogy and mineral chemistry

At Nimbus the hydrothermal mineralisation occurs in lenses with distinct compositions.

Several lenses are composed of massive pyrite seemingly replacing quartz-feldspar phryc dacite (Figure 2). Such textures display a characteristic “colloform” morphology even though they formed by replacement and not through open-space precipitation. Barren “colloform” pyrite present three subsequent stages of crystallisation identifiable as: (a) early pyrite forming inclusion-rich aggregates on which grown (b) radial clean pyrite and a (c) late stage pyrite related to a series of crack-seal events that fragmented the previous texture (Figure 2).

Ore-bearing lenses consist of a sphalerite, pyrite assemblage associated with polymetallic sulfides, galena and arsenopyrite. Sulfides and sulfosalts occur with a variety of textures that range from massive to infilling brecciated dacite, stockwork, vein and stringer.

The microprobe study of sphalerite and pyrite established the absence of chemical zonation at the micron scale. It also provided reliable quantifications of the major and minor elements that validated the in-situ trace element data acquired by LA-ICP-MS.

Furthermore, EPMA analyses allowed the accurate determination of the chemical composition of several sulfosalts such as Ag-rich boulangerite (Pb2.24Sb4.08Ag0.06S11.03), bournonite (stoichiometric - PbCuSbS3), pyrofylpinite (Ag2.98Pb0.98Sb1.19S3), Ag,Zn-rich tetrahedrite (Ag2.36Zn0.58Cu7.20Fe1.76Sb3.98S3) and previously unrecognized Zn,Bi-rich meneghinite (Pb1.46Cu0.43Zn0.28Sb0.27B6.11S13.96).

Sporadic pyrite-bearing siltstone which displays peperitic relationships to both mafic and felsic units occurs within the mine sequence, indicating all were broadly coeval. Sedimentary-hosted pyrites are evenly spread in the silicate groundmass and present a distinct cubic shape.
4 Multiple S-isotopes systematic

The results from multiple S-isotopes analyses reveal different signatures for each of the main sulfide occurrences (Figure 3).

The “colloform” pyrite is characterised by a negative $\Delta^{34}\text{S}$ ranging from -1.71 to -0.15% (mean -0.80%) and by a wide variation in $\delta^{34}\text{S}$ from -4.61 to 5.01‰.

Sulfide associated with the Zn-Ag mineralisation display a consistent “near-ZERO” $\Delta^{34}\text{S}$ signature averaging at 0.11‰ with few outliers attaining positive values up to 0.42‰ (Figure 4). Ore related sulfides spread on the $\delta^{34}\text{S}$ axis between -4.79 and 5.72‰ with positive values prevailing the negatives. Interestingly, negative $\delta^{34}\text{S}$ signatures are carried by arsenopyrite and only occasionally by pyrite. Regardless of the ore-textures, the analysed samples equally cover the $\delta^{34}\text{S}$ spread with the exception of stringer sulfides that show a distinct positive $\delta^{34}\text{S}$ signature of about 4‰.

Analyses on pyrite in siltstone cluster with both $\Delta^{34}\text{S}$ and $\delta^{34}\text{S}$ positive values at about 3.12 and 5.31‰ respectively.

5 In situ LA-ICP-MS analyses

Sediment-hosted pyrite displays an average trace element concentration of 1154ppm with a standard deviation of 330ppm. In particular average concentrations of Sb, As, Pb, and Ni reach 40, 677, 90 and 308ppm respectively.

In comparison with siltstone-hosted pyrite, massive “colloform” pyrite presents a similar trace element content of 1109ppm with a larger standard deviation of 520ppm. Higher contents were measured in the early pyrite aggregates (see “a” in Figure 2) and in the fibrous and concentrically pyrite (see “b” in Figure 2). On average, concentrations of Sb, As, Pb, and Ni attain 256, 550, 100 and 175ppm respectively.

Ore-related pyrite presents an irregular distribution for most of the trace elements due to the presence of numerous outliers greater by two to three orders of magnitude. Such anomalous concentrations, likely to be due to sulfosalts inclusions, range from 605 to 5763ppm for the first and third quartile respectively. Stringer pyrite are an exception to this paradigm showing a consistent high Ni content that attains concentration up to thousand parts per million (Figure 5).

The sphalerite trace element content is characterised by a consistent Ag content of about 25ppm and levels of Cd, Hg and Pb attaining 1005, 1665, 1185ppm respectively. In particular, the level of Cd and Hg are largely variable among samples but consistent within the samples (Figure 5). Moreover, the Cd-Hg ratio varies among samples regardless of the sulfide textures.

6 Discussion

The combination of in-situ techniques for characterising the sulfide trace element contents and S-isotope signatures allows insight pertaining to the fluid evolution of VHMS deposits or more generally hydrothermal systems (e.g. Sharman et al. 2015).

At Nimbus, barren pyrite lenses are characterised by a consistent negative $\Delta^{34}\text{S}$ signature that testify a major input of sulfur derived from Archean seawater sulfate.
(Farquhar and Wing 2003). Furthermore the trace metal contents of As, Pb and Ni in the “colloform” pyrite resemble the ones measured in ocean-derived Archean sedimentary pyrite (Large et al. 2017).

The siltstone-hosted pyrite show a distinct positive S-isotope signature suggestive of Archean sedimentary sulfides that sourced photochemical-derived reduced sulfur (Farquhar and Wing 2003). The euclidean shape is likely to be the consequence of a dissolution re-precipitation process in a closed-system as both trace elements and S-isotopes are strongly homogeneous and still typical of sedimentary sulfides.

Ore-related sulfides display a “near-positive” isotopic signature. Such unusual definition has the purpose of highlighting that the $\Delta^{34}S$ signature, although below the 0.15‰, clearly leans to positive side of the $\Delta^{34}S$ axis. Compared with other S-isotope studies on Archean VHMS occurrences, such as the Noranda district (Sharman et al. 2015), the Kidd Creek deposit (Jamieson et al. 2012) or the Teutonic Bore complex (Chen et al. 2015), ore-related sulfides at Nimbus are the ones and only that do not present a mixing relation with sulfur from seawater sulfate. Furthermore, the $\Delta^{34}S$ distribution of the ore-related sulfides, and more directly the positive outliers, is indicative of a contribution, although minor, of sulfur from the intercalated siltstone.

The variable Cd-Hg contents in sphalerite, and in particular the Cd-Hg ratios are suggestive of different fluid compositions among lenses. Such feature may be due to discrete fluid pulses or, in view of the ore distribution in well-defined lenses, to a degree of compartmentalisation of the hydrothermal system.

7 Conclusion

This study reveals a well-defined bimodal fluid evolution of the Nimbus Zn-Ag VHMS deposit. Multiple S-isotope and trace element analyses on “colloform” massive pyrite demonstrate that at first the hydrothermal system formed barren pyritic lenses sourcing the large majority of the sulfur and metals from ocean seawater. The consistent “near-positive” $\Delta^{34}S$ signature from ore-related sulfides indicates that the barren pyrite lenses sealed the hydrothermal system that then evolved sourcing the ore-related sulfur from a deep magmatic source. The positive ore-related $\Delta^{34}S$ outliers suggest only a minor role of sedimentary sulfur in the deposit formation. Finally, trace elements content in sphalerite support a compartmentalised evolution of the system as proposed by Hollis et al. (2017).

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Enhancing understanding of Irish Zn-Pb mineralization: a closer look at the Island Pod orebody, Lisheen deposit

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Abstract. Irish-type deposits are a series of Zn-Pb orebodies, formed from the carbonate replacement of Lower Carboniferous limestone, triggered primarily by fluid mixing. Current understanding of the complex fluid flow and mixing dynamics associated with mineralization is limited. By applying clumped O-C isotope analysis to these deposits, these processes can be constrained. Preliminary paragenetic studies of the Island Pod orebody (0.4 Mt @ 20% Zn & 1.6% Pb) have yielded textural evidence for early fluid mixing of sulphide-rich fluids, in a quiescent, far-from equilibrium environment, resulting in the rapid precipitation of dendritic galena and intergrowths of dolomite and sphalerite. Initial clumped O-C analysis has revealed temperatures of 100–170°C for hanging-wall white matrix breccias that accompanied ore formation. This technique will be used to constrain temperature variations across the orebody, thus yielding information on how the fluid evolved as precipitation continued. A more detailed paragenetic study is underway and will form the foundation of future clumped O-C isotope and Zn-Cu-S isotope analysis.

1 Introduction

Irish-type deposits have produced globally significant quantities of zinc (Ashton et al. 2015). Since the 1960s there have been five such Zn-Pb orebodies mined in Ireland and over twenty sub-economic prospects discovered (Fig. 1). With the closure of the Lisheen mine in 2015, the only operational mine in Ireland is at Navan (Fig. 1).

Irish-type Zn-Pb deposits are a series of stratabound orebodies, which are carbonate-hosted and structurally controlled. Mineralization is typically found adjacent to normal faults. Irish Zn-Pb deposits formed from carbonate replacement of Lower Carboniferous limestone, when metal-bearing, hydrothermal fluids (up to 200°C) ascended on normal faults to mix with sinking, cooler (<50°C) hypersaline brines carrying bacteriogenically reduced dissolved sulphide (Wilkinson et al. 2005). The Lower Carboniferous marine limestones conformably overlie non-marine Devonian-Carboniferous rocks, with metals most likely sourced from the Lower Paleozoic basement beneath the deposits (Walshaw et al. 2006).

Many of the complex processes involved in the formation of these deposits are still poorly understood. Good progress has been made with understanding the composition of fluids involved in mineralization (Wilkinson et al. 2005). However, little has been done on identifying possible geochemical or isotopic haloes and understanding fluid processes involved in ore formation.

We aim to increase the understanding of these Zn-Pb deposits through the application of clumped O-C isotope techniques.

2 Island Pod orebody, Lisheen

The Lisheen deposit (23 Mt @ 13.3% Zn & 2.3% Pb; Fig. 1) consists of several discrete, stratabound orebodies that are strongly controlled by an extensional, left-stepping, ramp-relay fault array to the south (Fig. 2). The Island Pod (0.4 Mt @ 20% Zn & 1.6% Pb) is a small, satellite, body of
high-grade mineralisation located approximately 900 m to the northeast of the Derryville Zone orebody (Fig. 2). It was first intersected by drilling in 2005 but only properly evaluated by drilling in 2011.

The authors are initially focusing on the Island Pod orebody, where limited work has been carried out on understanding the fluid regime associated with ore deposition. We present the first detailed paragenetic study of this orebody, incorporating detailed optical, SEM and cathodoluminescence work.

When compared to the other orezones at Lisheen (Main Zone, Derryville, Bog Zone; Fig. 2), the Island Pod exhibits some unique features, including:
1) weak extensional structural control on the highest quality and thickest ore;
2) most mineralization is located some 20 m above the base of the Lower Carboniferous Waulsortian Formation host rock, rather than, as is typical, being at the base of the Waulsortian Formation in contact with the older Argillaceous Bioclastic Limestone (Hitzman et al. 2002);
3) there is rapid, lateral variation on a small (< 10 m) scale, where adjacent boreholes can have a zinc concentration difference of ~ 40 %;
4) mineralization is not obviously associated with the replacement of hydrothermal black matrix breccias, as observed elsewhere in Irish Waulsortian-hosted deposits (Hitzman et al. 2002).

3 Textural studies and paragenesis

Paragenetic studies of the Island Pod orebody have been carried out through detailed optical and SEM petrography of a restricted number of samples from the subeconomic halo laterally surrounding the main mineralization. This study has identified a sulphide mineralogy of pyrite, sphalerite, galena for the available samples.

Preliminary textural studies of the main sulphide lenses have revealed distinctive textures such as dendritic galena, associated with dolomite and colloform sphalerite (Fig. 3), and intergrowths of colloform sphalerite and dolomite (Fig. 4). These textures suggest that as the composition of the mineralizing fluid evolved over time, the system moved towards equilibrium, allowing precipitation rates to slow, causing dendritic and intergrowth textures to cease, and more equant crystals of galena to form. Based on the textures observed within the Island Pod subeconomic halo, an initial paragenesis can be determined; colloform sphalerite/pyrite → dendritic galena → sphalerite/dolomite intergrowths → coarse grained galena → rhombohedral dolomite associated with a later/non-euhedral pyrite. Very fine-grained pyrite, possibly framboidal, was also observed associated with colloform sphalerite.

Figure 3. SEM image of branching galena. The branching galena can be seen interacting with dolomite and sphalerite. Coarse, later galena is also observed here (bottom, left corner).

At higher stratigraphic levels in the sub economic halo, stringer mineralization exhibits a simpler paragenesis; coarse, euhedral pyrite → three generations of carbonate → disseminated sphalerite → disseminated pyrite. Galena is not observed and sphalerite is only present in minor, disseminated amounts. Coarse, early pyrite is followed by at least three generations of carbonate, ranging from fine to coarse grained. Late, disseminated sphalerite, followed by dispersed pyrite is also seen, typically associated with finegrained carbonate veins. This may represent a residual fluid that was devoid of dissolved sulphide.

In other Zn-Pb deposits, dendritic and colloform sphalerite intergrowth textures have been interpreted as representing early, rapid sulphide precipitation events...
resulting from supersaturated fluid in a far- from-equilibrium, quiescent environment (Fowler and L’Heureux 1996; Wilkinson et al. 2005). Specifically, Wilkinson et al. (2005) discussed these textures in relation to the main ore stage in the Main, Derryville and Bog Zones at Lisheen (Fig. 2). They interpreted these textures as resulting from rapid crystallization from a sulphide supersaturated fluid, due to fluid mixing.

In order to constrain a more representative paragenesis, a detailed and thorough investigation is under way based on a new suite of samples (~130) collected from the Island Pod orebody and its surrounding zones of sub-economic mineralization.

Figure 4. SEM image displaying intergrowths of sphalerite and dolomite, the sphalerite often displaying a colloform texture.

4 Clumped O-C isotope and fluid inclusion study

Previous thermometry studies of carbonates have been based on δ18O measurements of carbonate minerals (Huntington et al. 2011). However, this method is dependent on both the crystallization temperature and the isotopic composition of the fluid(s).

In carbonate minerals, the heavy isotopes of O and C (13C, 18O) are seen to ‘clump’ or bond more frequently to each other than if bonding frequency was random (Wang et al. 2004). The extent of this ‘clumping’ is temperature dependent, but importantly is independent of fluid isotope composition and chemistry of the carbonate minerals. Thus, clumped O-C isotope analysis offers a novel and reliable method for determining the temperature of fluids associated with Irish Zn-Pb formation (Hollis et al. 2017, this volume).

This method is being used to constrain fluid flow and mixing processes, along with temperature variations across orebodies.

Preliminary clumped O-C isotope data from the Island Pod orebody have revealed temperatures of 100-170°C for hanging-wall white matrix breccias and a more extensive programme of clumped O-C isotope analysis of carbonate samples from the Island Pod deposit is planned. All samples are being characterized prior to clumped isotope analysis to determine the relative timing of clumped isotope precipitation to mineralization.

We will present new data from across the Island Pod orebody, for all main phases of carbonate formation. Complimentary fluid inclusion data obtained will also be presented and will be the first fluid inclusion constraints from the Island Pod. We will establish whether ore forming processes were similar to those operating elsewhere in the Irish orefield.

5 Conclusions

Preliminary paragenetic work on the Island Pod orebody suggests that an early, rapid precipitation event occurred, which resulted in dendritic galena and intergrowths of sphalerite and dolomite. These textures have also given an indication of the local direction of crystal growth, which may relate to fluid flow direction. This early mineralization likely occurred in a calm, far-from equilibrium environment, from a sulphide supersaturated fluid, that resulted from early fluid mixing in the system. As the fluid composition evolved, due to changes in mineralization environment, including fluid composition and temperature changes, through new pulses of fluid to the system or/and crystallization of early sulphides altering the fluid chemistry, sulphide minerals precipitated as coarser and more equant crystals. Late, disseminated pyrite and sphalerite grains, often concentrated around carbonate veins, possibly highlight fluid conduits and the crystallization of residual fluid which contained minor sulphides.

Clumped O-C isotope analysis will advance preliminary deposit understanding provided by detailed paragenetic studies. Initial clumped data has revealed temperatures of 100-170°C for hanging-wall white matrix breccias. This technique is being used to constrain data on the fluid regime that led to mineralization in the Island Pod orebody, including fluid flow and mixing processes. Using the clumped isotopic techniques, temperature variations from across the Island Pod will be determined for each carbonate generation, further enhancing our understanding of fluid processes in Irish-type deposits that are associated with Zn-Pb mineralization.

6 Future work

Future Zn-Cu-S isotope analysis of the different sulphide generations will provide new insights into the dynamic fluid mixing processes, complementing the clumped O-C data obtained from carbonate analysis. This data will then be applied to the larger scale to enhance understanding of the fluid regime responsible for the investigated deposits. The genetic relationships between economic deposits and their sub-economic haloes will also be investigated.
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Metal-enriched pelitic units in the Proterozoic sediment-hosted Vazante Zn district, Minas Gerais, Brazil: Sources of base-metals for the carbonate-hosted deposits?

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Abstract. The Proterozoic meta-sedimentary Vazante Group, Minas Gerais Brazil contains a number of Zn-Pb sulphide and Zn-silicate deposits hosted by dolomite sequences that are stratigraphically and spatially associated with meta-pelitic rocks. The dolomite-hosted Zn deposits are thought to have formed during the Neoproterozoic Brasiliano orogeny. Whole rock-geochemical analyses reveal that carbonaceous phyllites belonging to the Serra do Garrote Formation (stratigraphically below the dolomites) are locally enriched in Zn (up to 0.46% Zn, 3 to 6x background concentration), and have anomalous concentrations of other elements such as Cu, V, Hg and U. These elements also commonly associated with the dolomite-hosted Zn deposits. The anomalous zones are associated with hydrothermal pyrite, sphalerite and chalcopyrite that formed prior to the Brasiliano orogeny. Textural evidence also indicates that pre-existing sulphides were later remobilized during the Brasiliano deformation event. The mineralogical, textural and geochemical evidence, as well as the timing of events, suggest that the meta-pelitic rocks of the Serra do Garrote Formation are one of the candidates to be the metal sources for the dolomite-hosted deposits in the Vazante Belt.

1 Introduction

The Proterozoic Vazante – Paracatu Zn-(Pb) mining district, Minas Gerais, is a 200 km-long, N-S trending zone (Fig. 1) that accounts for most, if not all of the zinc production in Brazil (Viviani et al. 2001). It contains a number of Zn-deposits hosted in dolomitic carbonates belonging to the Proterozoic Vazante Group, which comprises a mixed silicilastic – carbonate sequence (Dardenne and Freitas-Silva 1999; Dardenne 2000). These deposits include: 1. The Vazante – North Extension Zn silicate mines (65 Mt @ 20% Zn; willemite ore), located in the south of the district, and 2. The Morro Agudo Zn – Pb sulphide mine (20 Mt @ 5% Zn, 2% Pb) along with the adjacent Ambrosia and Fagundes sulphide deposits (no current published resources) located in the north of the district (resource estimates provided by Votorantim Metais).

Results from previous studies indicate, that even though the styles of Zn-mineralization hosted in dolomitic rocks in the district may differ (strata-bound to fault-controlled Zn-Pb sulphides in the North, versus fault-controlled Zn-silicates in the South); the compositions of the metalliferous fluids associated with ore deposition were similar (Appold and Monteiro 2009; Monteiro et al. 2007). However, little is known about potential source rocks for base metals and associated trace elements within the region, and this is an emerging area of research.

Figure 1. Regional geological map of the Vazante Zn district, Brazil showing distribution of carbonate hosted Zn-sulphide (red stars) and Zn-silicate (orange stars) deposits, and the associated strata of the Vazante Group (modified from Monteiro et al. 2006). Drill holes sampled in this study are plotted in black circles with locations provided by Votorantim Metais.

The carbonate sequences of the Vazante Group are underlain by, overlain by, and interlayered with packages of fine-grained, meta-pelitic rocks. The aim of this study is to test the hypothesis that certain meta-pelitic units were the sources of base metals. To achieve this goal, we
investigated the mineralogical and geochemical evolution of the meta-pelitic units of the Vazante Group by a combination of textural and mineralogical investigation, lithochemical characterization.

2 Geological Setting

2.1 The Vazante Group

The marine sedimentary rocks of the Vazante Group were deposited during the Proterozoic on the western margin of the São Francisco palaeocontinent during the Proterozoic (Dardenne 2000, and references therein). The best constraints on the age of the Vazante Group come from U–Pb ages of detrital zircons from meta-pelitic units, which give an upper age limit of 1300 – 1100 Ma (Rodrigues et al. 2012). The Vazante Group in the study area (Fig. 1) contains three principal sequences of meta-pelitic rocks: 1. The Serra do Garrote Formation that occurs stratigraphically below the dolomitic units, 2. The Lapa Formation that overlies the dolomitic units, 3. A number of meta-pelitic units interlayered with the different dolomitic units of the Serra do Poço Verde Formation formations (Fig. 1). These units are all encountered within the study area.

2.2 Structural setting

Zn-Pb mineralization hosted in the Vazante Group dolomites is interpreted to be associated with an orogenic event, the Neoproterozoic Brasiliano orogeny (= 600 Ma, Dardenne and Freitas-Silva 1999; Rostirolla et al. 2002; Monteiro et al. 2007). The Brasiliano orogeny resulted in the development of a regional tectonic fabric, Sn (referred to as S2 by previous workers) that is easily observed in the meta-pelitic units of the Vazante Group (Dardenne 2000) during the Brasiliano Orogeny.

3 Geochemical signatures of the Serra do Garrote Formation and other pelitic units

Twenty-five exploration drill-holes, provided by Votorantim Metais (locations of drill holes in Fig. 1) were mapped and sampled. These holes were selected to intersect the pelitic units belonging to the Serra do Garrote Formation, Serra do Poço Verde Formation and the Lapa Formation.

In total, 316 samples of meta-pelitic rocks from the Vazante Group were collected. Samples were analysed for their whole-rock major and trace element geochemistry at ALS laboratories. Major elements concentrations were analysed by X-ray fluorescence spectroscopy (XRF) on fused rock powders, trace element concentrations by inductively-coupled plasma mass-spectrometry (ICP-MS), and organic C using a LECO analyser and furnace.

The use of molar Al/Ti ratios, elements that are immobile in this system, delineated three different subunits within the Serra do Garrote Formation (Table 1). The G1 and G2 subunits contain the highest average Zn concentrations (594 and 376 ppm Zn respectively), whereas G3 contains less Zn on average (165 ppm Zn).

<table>
<thead>
<tr>
<th></th>
<th>Serra do Garrote G1: Mean (n = 78)</th>
<th>Serra do Garrote G2: Mean (n = 83)</th>
<th>Serra do Garrote G3: Mean (n = 39)</th>
<th>Serra do Garrote Background (n = 200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Ti</td>
<td>≤ 34.5</td>
<td>34.5 – 38.7</td>
<td>&gt; 38.7</td>
<td>36.35</td>
</tr>
<tr>
<td>Zn ppm</td>
<td>594</td>
<td>376</td>
<td>165</td>
<td>101</td>
</tr>
<tr>
<td>Cu ppm</td>
<td>97</td>
<td>78</td>
<td>43</td>
<td>28</td>
</tr>
<tr>
<td>Hg ppm</td>
<td>0.262</td>
<td>0.144</td>
<td>0.059</td>
<td>0.035</td>
</tr>
<tr>
<td>U ppm</td>
<td>5.74</td>
<td>3.49</td>
<td>2.24</td>
<td>2.36</td>
</tr>
<tr>
<td>V ppm</td>
<td>223</td>
<td>203</td>
<td>116</td>
<td>97</td>
</tr>
<tr>
<td>C organic (wt %)</td>
<td>1.40</td>
<td>0.81</td>
<td>0.41</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 1. Average concentrations of Zn, Cu, Hg, U, V and Organic C associated with the G1, G2 and G3 subunits of the Serra do Garrote Formation as defined by their Molar Al/Ti ratios.

Elements such as Cu, Hg, U, V and Organic C, show positive correlation with Zn in the Serra do Garrote Formation. The phyllites belonging to the G1 and G2 subunits of the Serra do Garrote Formation (n = 161) have higher background concentrations of these elements compared to the G3 subunit (Table 1) and other pelitic units of the Vazante Group. Previous studies have documented the association of these elements with the carbonate-hosted ore deposits in the Vazante district (Monteiro et al. 2007; Slezek et al. 2014).

4 Mineralogical characterization of zones of hydrothermal alteration in the Serra do Garrote Formation

Mineralogical characterization of the Serra do Garrote Formation used a combination of optical microscopy, scanning electron microscopy (SEM), and XRF. The meta-pelitic rocks of the unaltered Serra do Garrote Formation form phyllites which are composed of clay-sized muscovite (detrital?) + chlorite (detrital?) + silty quartz-grains (detrital), with varying amounts of organic matter, and early, disseminated, very finely crystalline pyrite (Py1). The phyllites are strongly foliated (Sn) and commonly folded and crenulated (Sn+1).

Zones of anomalous zinc concentration (>150 ppm Zn) are characterized by the occurrence of different generations of fine, crystalline pyrite + sphalerite ± chalcopyrite in early quartz ± chlorite layers or veinlets which can occur in all of the G1, G2 and G3 subunits.

There are multiple generations of hydrothermal pyrite associated with different stages of base-metal sulphide. Two styles of sulphide mineralization were identified. The first style comprises bands of hydrothermal
quartz and chlorite. The bands contain hydrothermal pyrite (Py2a), intergrown with sphalerite (Sp1) that contains chalcopyrite (Cpy1) inclusions. Sp1 occurs in higher proportions relative to Py2a in some bands, while other bands contain just Py2a (Fig. 2a).

The second style is characterized by the presence of inclusion-poor, subhedral pyrite (Py2b) that commonly displays growth zonation patterns, and/or anhedral, inclusion-rich pyrite (Py2c) (Fig. 2b). Observed mineral inclusions in Py2c are sphalerite (Sp2), chalcopyrite (Cp2), Ti-oxides, quartz or chlorite (Fig. 2b, c). Py2c is commonly observed overgrowing/mantling Py2b (Fig. 2b, c, d).

These features are commonly crenulated by Sn, resulting in folding and transposition of bands and layers; and the formation of boudins. These features indicate that the mineralization associated with base-metal enrichment of the Serra do Garrote Formation occurred prior to the orogenic event, which is called the late-D2 or D3 by previous authors (Slezak et al. 2014, and references therein).

All generations of early and hydrothermal pyrite (Py1, Py2a, Py2b, Py2c) are then overgrown, replaced and/or pseudo-morphed by syn-deformation pyrite (Py3, early to syn Sn+1). Py3 is associated with a new generation of sphalerite (Sp3) and chalcopyrite (Cp3) that mantle all earlier sulphides (Fig. 2d), suggesting that pre-Sn hydrothermal mineralization was then remobilized during the orogenic event. The interpreted paragenetic sequence is summarized in Fig. 3.

5 Discussion and conclusions
This is the first documented occurrence of base-metal enrichment in the siliciclastic units of the Vazante Group. This supports a new exploration target in the Vazante district using the trace element geochemistry of G1 and G2 subgroups as vectors. The metal enrichment in the phyllites of the Serra do Garrote Formation is due to hydrothermal alteration event, associated with pyrite and base-metal sulphides that predates the Brasiliano Orogeny, and the formation of the regional foliation, Sn.

Zn- and Cu-sulphides were (locally) remobilized from the Serra do Garrote Formation during the orogenic event (syn-Sn). The timing of remobilization coincides with the proposed timing of the formation of the carbonate-hosted Zn deposits.

The genetic-link between siliciclastic- and carbonate-hosted Zn-Pb deposits has been debated for a long time (Wilkinson 2014, and references therein). The documented mineralogical, textural and geochemical evolution of the Serra do Garrote Formation, and the timing of events relative to the formation of the regional Zn deposits, suggests that this unit is a potential candidate to be a source of base metals and ore-related elements. These elements were then transported by hydrothermal fluids and concentrated in the carbonate rocks during the Brasiliano Orogeny. Further work must be done to test this hypothesis.

Acknowledgements
The authors gratefully acknowledge Votorantim Metais for logistical and partial financial support for fieldwork, whole-rock geochemical analyses, and for collaboration with their exploration staff. G.R. Olivo’s NSERC discovery grant and a Queen’s Graduate Scholarship funded the Ph.D. research of N.A. Fernandes. G.R. Olivo’s NSERC discovery grant and the Queen’s Facility for isotope research (QFIR) are acknowledged for covering fieldwork and analytical costs.
References


Metamorphogenic base metal mineralization at the margin of a nappe complex: the example of Kupferberg, Germany

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Czech Geological Survey

Abstract. New data on pyrite chemistry, petrology and most importantly Cu and S isotope data reveal a two-stage genetic model for the Kupferberg Cu-Zn deposit in eastern Germany, with the principal Cu mineralization being related to the expulsion of syn-orogenic fluids from beneath a high-grade metamorphic nappe complex. The deposit consists of several sulfide lenses bound to Early Palaeozoic volcano-sedimentary strata at the margin of the allochthonous Münchberg nappe complex. The main Cu ore is texturally late chalcopyrite, mostly within pyrite-rich carbonaceous and calcareous shale in two different tectonostratigraphic units that became juxtaposed during the Variscan Orogeny. Copper isotope analyses yielded a narrow δ65Cu range of -0.26 to 0.36 ‰ for all ore types suggesting a hypogene origin for the principal chalcopyrite mineralization. 34S values of the ore lenses in the two different tectonostratigraphic units differ distinctly, whereas little difference exists between strongly mineralized ore types and local pyrite-rich beds. This indicates a strata-internal mobilization from pyrite-rich shales that became overthrust by the allochthonous nappe complex. Syn-tectonic fluid expulsion is further indicated by several positive Cu-anomalies along the southwestern margin of the nappe complex. The recognition of syn-orogenic Cu mineralization below a high-grade nappe complex raises the possibility of similar, potentially economic base metal deposits to occur at the base of metamorphic nappe complexes also elsewhere in the world.

1 Introduction

Kupferberg, about 120 km northeast of Nürnberg, hosts Bavaria’s largest known Cu-Zn deposit, which for several centuries was the economic motor for the whole region. Several of the stratiform, sulfide-enriched lenses were mined between the 13th and 19th century with a boom in the 17th century when the St. Veits shaft was exploited.

Similar stratiform ore lenses in metamorphic rocks (e.g. Broken Hill type deposits) are widely regarded to be syngenetic deposits, affected by recrystallization and local mobilization. Here we present evidence for the epigenetic origin of the Kupferberg deposit, and thereby provide the case for a possible formation of base metal deposits during syn-metamorphic thrust tectonics.

2 Geological setting

The Cu-Zn deposit of Kupferberg is located in the Saxothuringian Zone of the Palaeozoic Variscan basement in northeastern Bavaria. The various ore bodies constituting the deposit are located on either side of the boundary between the allochthonous metamorphic Münchberg nappe complex and underlying para-autochthonous Early Palaeozoic volcano-sedimentary rocks. More specifically, the ore lenses occur in both an Early Palaeozoic subgreenschist-facies volcano-sedimentary succession, the so-called Randschiefer Formation and in the adjacent greenschist-facies Prasinit-
Phyllit Formation of the Münchberg nappe complex. The former constitute ore bodies in the area of Kupferberg, the latter those in the area of Neufang (Fig. 1).

The Randschiefer Formation appears at the southwestern margin of the Münchberg nappe complex as an up to 3 km wide belt, dipping 40° to the northeast. The Randschiefer Formation is a shale-dominated collage of various Cambrian to Early Devonian rock types.

The greenschist-facies Prasinit-Phyllit Formation emanated from silty shales as well as mafic to intermediate volcanic rocks (Franke et al. 1995). U-Pb zircon age data of the mafic rocks support a Devonian age of approximately 400 Ma (Koglin et al. 2014). A further difference between the two formations exists in the geochemical character of the metavolcanic rocks. These are alkaline in the Randschiefer Formation but subalkaline in the Prasinit-Phyllit Formation (Okrusch et al. 1989; this study). To the southwest the Randschiefer Formation is truncated by a northwest-southeast trending fault zone, the so-called Franconian Lineament, which separates the Variscan basement rocks (including the study area) from the unmetamorphosed Triassic sedimentary rocks of the Central European Basin.

The stratigraphic position of the ore lenses within the Randschiefer Formation seems to vary on a small scale. Dill (1985) noted the lenses to be bound to black shales, whereas exploration drilling (Urban and Vaché 1972) intersected sulfide layers in at least two different stratigraphic positions with varying host rocks, including metabasalt and basaltic tuff. In numerous places the sulfide-enriched lenses are spatially associated with a rhyolitic tuff bed.

The ore lenses are dominated by quartz, carbonate, pyrite and chalcopyrite, with minor amounts of sphalerite and chlorite. Galena is very rare (Ibach 1940). Trace element concentrations in different pyrite types indicate the presence of at least one hydrothermal pyrite generation (mean Co/Ni = 35) that is texturally associated with chalcopyrite. The other pyrite types being syn-sedimentary/early diagenetic are distinctly lower in Co/Ni (mean = 3.7) (Höhn et al. 2017).

Locally, volumetrically insignificant sulfide veins cut across stratiform ore lenses and their host rocks. They are undeformed and thus clearly post-orogenic.

3 Results

3.1 Copper isotopes

Chalcopyrite-rich samples from the Randschiefer Formation (St. Veits shaft) yielded a δ65Cu range from -0.22 to 0.36 ‰. Chalcopyrite-poor samples from the same locality gave somewhat lower ratios between -0.26 and 0.06 ‰. Two δ65Cu values obtained on chalcopyrite-poor material from the Prasinit-Phyllit Formation (Goldener Falke adit) are -0.12 and 0.11 ‰ (Fig. 2).

Native copper and malachite could be extracted in suitable amounts only from the Randschiefer Formation (St. Veits shaft). The δ65Cu values of native copper as well as malachite show distinctly wider ranges than the results obtained for the chalcopyrite samples. The values for native copper are -0.01 and 1.75 ‰, whereas the data obtained on malachite are -0.35 and 1.26 ‰.

3.2 Sulfur isotopes

The δ34S values of samples from the Kupferberg deposit (Fig. 2) are all positive between 0.7 and 4.2 ‰. The δ34S ratios for the samples from the Randschiefer Formation (St. Veits shaft) are between 2.0 and 4.2 ‰ (mean = 3.1 ‰, σ = 0.7). This group is uniform without significant differences between the chalcopyrite-rich (mean δ34S = 3.2 ‰, σ = 0.6) and pyrite-rich samples (mean δ34S = 3.1 ‰, σ = 0.9). The samples from the Prasinit-Phyllit Formation (Goldener Falke adit) yielded δ34S ratios between 0.7 and 2.6 ‰ (mean δ34S = 1.4 ‰, σ = 0.8) and thus are significantly lower than those obtained for the samples from the Randschiefer Formation.

3.3 Cu contents in regional stream sediments

Previously collected geochemical data for stream sediments (Fauth et al. 1985) were processed and plotted for the region around the Münchberg nappe complex. The distribution of Cu in these recent sediments largely reflects the bedrock geology (Fig. 3). It shows that the Central European Basin (CEB) and the Fichtelgebirge are generally depleted in Cu, whereas the Saxothuringian Vogtland Syncline is slightly enriched. Most of the positive Cu-anomalies are located along the margin of the allochthonous Münchberg nappe complex with a dominance at the southwestern border.

3.4 High-tech metals gallium, germanium and indium in the Kupferberg deposit

A total of 84 trace element analyses were performed on the most abundant sulfides of the Kupferberg deposit to
estimate its potential regarding the so-called high-tech metals Ga, Ge, and In (Table 1).

![Image: Cu contents of recent stream sediments (ppm)]

**Figure 3.** GIS analysis of Cu in stream sediments (Fauth et al. 1985) and locations of historic mine sites in northeastern Bavaria. CEB = Central European Basin

In general, sphalerite can incorporate several thousand ppm of Ga (Cook et al. 2009), but the sphalerite from Kupferberg contains on average only 6.2 ppm Ga. Chalcopyrite is even lower in Ga, whereas pyrite contains an order of magnitude less Ga. Up to 3000 ppm of Ge have been reported for low Fe-sphalerite elsewhere (Melcher et al. 2006), but at Kupferberg its Ge content is several orders of magnitude lower. With 0.6 ppm Ge, pyrite is the most Ge-rich sulfide at the studied deposit. By the substitution $\text{Cu}^+\text{In}^{3+} \leftrightarrow 2 \text{Zn}^{2+}$, several wt.-% In can be incorporated into sphalerite (Cook et al. 2009). Although sphalerite at Kupferberg contains about 2300 ppm of Cu, only 5.2 ppm of In were measured.

### 4 Interpretation and conclusions

The narrow $\delta^{66}\text{Cu}$ range and trace element analyses of pyrite from the Kupferberg deposit (Höhn et al. 2017) are best explained by hydrothermal Cu input into both the Randschiefer and the Prasinit-Phyllit Formations. It further indicates the influence of metamorphism on the ore itself (Ikehata et al. 2011) and constrains the timing of the Cu mineralization to the last orogenic event. The spatial association of the ore bodies with a rhyolitic tuff bed further supports this notion. The Cambrian age of the tuff bed within the Ordovician Randschiefer Formation inevitably proves the existence of a Variscan thrust plane along strike and dip of most of the known ore lenses.

<table>
<thead>
<tr>
<th></th>
<th>Sphalerite (n=35)</th>
<th>Chalcopyrite (n=26)</th>
<th>Pyrite (n=23)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium</td>
<td>6.18</td>
<td>3.55</td>
<td>0.155</td>
</tr>
<tr>
<td>Germanium</td>
<td>0.046</td>
<td>0.564</td>
<td>0.600</td>
</tr>
<tr>
<td>Indium</td>
<td>5.19</td>
<td>1.59</td>
<td>0.459</td>
</tr>
</tbody>
</table>

The distinct S-isotopic difference between the pyrite-rich beds from the Randschiefer and the Prasinit-Phyllit Formation (Fig. 2) excludes a common S source and suggests that pyrite-rich shales of different age and different stratigraphic units were juxtaposed tectonically, during the emplacement of the Münchberg nappe complex onto the para-autochthonous units of the Vogtland Syncline. This led to the tilting of the incompetent, shale-dominated Randschiefer Formation, which follow the bowl shape of the allochthonous complex and thus the similar 40° NE dip on both sides of the thrust plane. The remarkable similarity of S isotope data from the most chalcopyrite-rich ore lenses of the Randschiefer Formation to the local pyrite-rich beds supports strata-internal mobilization. The shale-dominated pyrite-rich strata of the Vogtland Syncline in the footwall of the main thrust plane present themselves as most obvious candidate for the source of metamorphogenic fluids that were expelled along the thrust plane of the overlying nappe complex. This is supported by several sediment-hosted pyrite occurrences all around the Münchberg nappe complex. The low In content of sphalerite from the Kupferberg deposit also fits to a non-magmatic fluid source (Cook and Ciobanu 2015), whereas the low Ga and Ge contents may be indicative of relatively high temperatures (>300 °C) of the mineralizing fluid (Melcher et al. 2006; Cook et al. 2009).

The distribution of Cu in stream sediments of northeastern Bavaria shows a strong connection between anomalous Cu-enrichment and the margin of the Münchberg nappe complex. The high number of positive Cu-anomalies (including Kupferberg) at the southwestern margin likely reflects the movement of the allochthonous complex (greenschist-facies D3-deformation-phase after Franke et al. 1995) in southwesterly direction.

The recognition of this relatively unusual type of truly metamorphic base metal mineralization opens up the...
possibility of similarly formed, potentially economic base metal deposits to occur at the base of major thrust planes beneath high-grade metamorphic complexes elsewhere in the world.

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References


Clumped C-O isotope temperature constraints for carbonate precipitation associated with Irish-type Zn-Pb orebodies

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Abstract. Ireland hosts the greatest concentration of discovered zinc per square kilometre on Earth, with production from 5 carbonate-hosted deposits, including the giant Navan deposit. Clumped C-O isotope analyses of carbonates offer a powerful new technique to directly deliver accurate fluid temperatures and precise calculations of fluid O isotope compositions, offering a significant opportunity to refine the evolving genetic models, and develop new vectoring tools for exploration. We present the first clumped C-O isotope results for paragenetically-constrained carbonate generations from a number of Irish-type Zn-Pb deposits. Preliminary analysis of hanging-wall white matrix breccias from Lisheen show non-systematic temperature variation (~100 to 170°C), with fluid $\delta^{18}O_{v-SMOW}$ increasing with temperature. Significant variations in temperature at the thin section scale may be indicative of fluid mixing and/or multiple phases of WMB dolomite brecciation. Post-ore pink dolomite at Lisheen, and crosscutting calcite veins formed at significantly lower temperatures (67 to 42°C). Temperatures of 61 to 110°C were obtained for sphalerite-bearing calcite veins in the hanging-wall of the Randalstown Fault near Navan. These veins contain coarse sphalerite interpreted to have been remobilised from the nearby Navan orebody by a single, cool fluid (Marks, 2015). Clumped C-O data will also be presented for samples from Galmoy, Kilbricken and Castlegard (“Pallas Green”), from which existing fluid inclusion constraints are available.

1 Irish-type Zn-Pb deposits

Irish-type Zn-Pb deposits are the mainstay of the Irish mining industry. In the last fifty years, five orebodies have been mined (Tynagh, Silvermines, Navan, Galmoy and Lisheen) and over twenty prospects discovered (e.g. Kilbricken, Pallas Green) (Fig. 1). With the closure of the Lisheen mine in late 2015 there is now a sense of urgency to establish robust vectors to Zn-Pb mineralization.

There is now a consensus that Irish-type Zn-Pb deposits are syn-diagenetic ores formed by the replacement of Lower Carboniferous limestones during shallow burial. Conditions required for their formation include dense networks of normal faults that allowed ascending, warm, metal-bearing fluids equilibrated with Lower Palaeozoic basement to mix with sinking, cooler, hypersaline brines that carried bacteriogenically reduced sulphide of ultimate seawater origin (Wilkinson and Hitzman 2015).

2 Clumped C-O isotope analysis

It is well established that temperature-dependent mineral-fluid C and O isotope fractionations occur when carbonates crystallize from aqueous fluids. Mineral C-O isotope compositions are therefore controlled by crystallization temperature and the isotopic composition of the fluid, as well as the speciation of carbon and oxygen. However, the heavy isotopes of these two elements ($^{13}C$, $^{18}O$) are now known to bond in carbonate minerals measurably more frequently than expected by stochastic (i.e. random) distribution (Huntington et al. 2011).

Clumped C-O isotope analysis relies on the degree of ordering of rare $^{13}C$ and $^{18}O$ isotopes in the carbonate mineral lattice. This degree of “clumping” is an inverse function of temperature, with an increasingly random distribution at higher temperatures (Huntington et al. 2011). Although the technique has been traditionally applied to low-temperature Earth systems (i.e. to obtain accurate paleo-temperature constraints from ice-cores, soil, bones and teeth), it is rapidly moving into higher temperature fields of Earth Science.

One of the most useful aspects of the clumped isotope technique is that in addition to providing temperature constraints for carbonate crystallization, $\delta^{13}C$ and $\delta^{18}O$ may be simultaneously determined. Fluid $\delta^{18}O$ may be calculated, because temperature is known, rather than modelled, elucidating processes responsible for
mineralization (Dennis et al. in press).

Figure 1. A simplified geological map of Ireland showing significant mined Zn-Pb deposits in Ireland and the Pallas Green and Kilbricken prospects.

3 Methods

Approximately 110 samples were obtained from drillcore across the Lisheen Zn-Pb deposit, including the Lisduff Oolite Member, and Waulsortian-hosted Main Zone, Derryville and Island Pod orebodies (Fig. 2). These samples were examined in thin section to identify carbonate generations according to the paragenesis of Wilkinson et al. (2005). Carbonate powders were obtained from thin section-matched billets using a hand held drill.

Samples of sphalerite-bearing carbonate veins from the hanging-wall of the Randalstown Fault, to the west of the Navan deposit, were also analysed. These samples were previously characterised by Marks (2015). Additional carbonate powders from Galmoy, Kilbricken and Castlegarde (“Pallas Green”) (Fig. 1) were sampled from doubly polished wafers, previously characterised for fluid inclusion analysis (e.g. Eyre 1998; Wilkinson 2010, unpublished). Material sampled from fluid inclusion wafers was picked and crushed using an agate mortar and pestle.

Carbon dioxide was produced by reacting ~4 mg of carbonate powder with 102% orthophosphoric acid in vacuo at 25°C for a period of 12 hours for calcite and 5 days for dolomite. The evolved CO$_2$ was collected by cryo-distillation according to the methodology of Dennis et al. (in press). Potential hydrocarbon and chlorocarbon contaminations were stripped using porapak Q ion exchange resin at -20°C.

Sample gases were analysed for their isotope values, δ$^{18}$O - δ$^{13}$C on a custom-built MIRA (multiple isotope ratio analyser) dual-inlet mass spectrometer at the University of East Anglia (UEA), with analytical conditions as in Dennis et al. (in press). Details for calculating Δ47 are provided in Huntington et al. (2011). Temperatures are calibrated using natural and synthetic biogenic and inorganic calcites using the following in house equation (Dennis et al. in press):

\[ \Delta 47 = (0.0389 \times 10^6/T^2) + 0.2139, \]

where T is in Kelvin.

External precision for sample analysis is estimated as ± 0.014 ‰, with temperature errors corresponding to ± 2°C at Earth surface temperatures, rising to ± 12°C at 200°C. Sample contamination is monitored through Δ48 and Δ49 (Dennis et al. in press). Fluid δ$^{18}$O$_{V-SMOW}$ values were calculated according to Kim and O’Neill (1996) for calcite, and Horita (2014) for dolomite.

Figure 2. Orebodies and main structural elements of the Lisheen Zn-Pb deposit (modified after Kyne et al. 2017).

4 Preliminary results and conclusions

All data referred to in this section are plotted on Figure 3. Navan:

- Temperatures of 61 to 110°C (n=4; mean 92 °C) were obtained for sphalerite-bearing calcite veins in the hanging-wall of the Randalstown Fault near Navan. These veins contain coarse sphalerite interpreted to have been remobilised from the nearby orebody by a single, cool fluid (Marks, 2015).
- Calcite δ$^{18}$O$_{V-SMOW}$ for these samples varies from +16 to +21 and calculated fluid δ$^{18}$O$_{V-SMOW}$ ranges from -4.6 to +6.0 (mean 0.3) with higher values associated with higher temperature.
- One sample yielded a Δ$^{47}$ temperature of 89°C,
consistent with existing fluid inclusion constraints (81°C mean, range 68-92°C: Marks, 2015). This highlights the potential of the clumped technique to reproduce temperatures obtained by conventional fluid inclusion analysis. Fluid inclusions from other samples will be analysed in coming months.

Lisheen:
• Samples of coarse white dolomite, drilled from white matrix breccias (WMBs) of the high-grade Island Pod orebody (Doran et al. 2017 – this volume), yielded δ13CVPDB (+2.6 to +3.3) and δ18OVSMOW (+21.2 to +24.4) values similar to the rest of the deposit (i.e. Main Zone, Derryville, Bog Zone).
• The coarse white dolomites from Island Pod WMBs also have similar δ13C and δ18O isotopic compositions to clasts of regional dolomite from the same samples, and regional dolomite elsewhere in the deposit, similar to results reported by Wilkinson (2003). This suggests that the WMB dolomite may have been buffered by early regional dolomite or was precipitated from a fluid with similar δ18O, heated to ~180°C (see below).
• Temperatures of 98 to 172°C were obtained for the Island Pod WMB dolomites. The samples were all collected from one drillhole (from directly above mineralization to ~80 m in the hanging-wall). There is no systematic variation in temperature, or carbonate δ13C or δ18O towards mineralization in the preliminary dataset.
• Calculated fluid δ18OVSMOW values for WMBs dolomites range from +0.7 to +8.6, with higher values associated with higher temperatures, as at Navan. Interestingly, the WMB samples plot on the same array as the post-ore carbonates described below. This array is consistent with fluids in isotopic equilibrium with regional dolomite, calculated from Horita (2014) over a range of temperatures and δ18O of +19.5 to +26 (data from Eyre 1998; Hitzman et al. 1998).
• Samples of black dolomite drilled from black matrix breccias (BMBs) at Lisheen also yield similar δ13C and δ18O isotopic compositions to clasts of regional dolomite from the same samples and across the deposit (Fig. 3).
• A temperature of 67°C was obtained for post-ore pink dolomite from the Lisheen deposit, with a fluid δ18OVSMOW value of -0.7.
• A late white calcite vein yielded a temperatures of 63°C, with a calculated fluid δ18OVSMOW value of -2.6.
• Temperatures of 42 and 43°C were obtained for late yellow calcite (which crosscuts the late white calcite), with fluid calculated δ18OVSMOW values of -3.5 to -6.2.

4 Future work
The preliminary clumped C-O isotope results presented here highlight the potential of the technique to better understand the formation of both Irish-type and MVT Zn-Pb deposits. Additional samples will be analysed in the coming months (March-May 2017). These include samples from the following deposits, for which existing fluid inclusion data are available: (1) Galmoy – white matrix breccias; (2) Kilbricken – ore stage calcite; (3) Castlegard – ore stage calcite; (4) Lisheen – regional dolomite, white matrix breccias, pink dolomite, late calcite; (5) Rathdowney Trend – regional dolomite, black matrix breccias (6) Navan – ore stage carbonates.

We will also analyse samples of black matrix breccia from across the Lisheen deposit (i.e. Lisduff oolite, Main Zone, Derryville Zone: Fig. 2) to determine whether systematic temperature or fluid δ18O variations occur away from faults which helped focus hydrothermal fluids from depth.

Figure 3. Compiled and new C and O isotope data from the Lisheen Zn-Pb deposit (includes data from Eyre, 1998; Hitzman et al. 1998). New data is represented by large symbols.

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Contrasting fluid types involved in the genesis of ca. 1.89 Ga, syngenetic polymetallic sulfide deposits, Falun and Zinkgruvan, Bergslagen, Sweden

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Abstract. Metamorphosed polymetallic sulfide deposits in Bergslagen, Sweden, are currently divided into 1: Strata-bound volcanic-associated limestone-skarn Zn-Pb-Ag-Cu-Au sulfide deposits (SVALS) and 2: Stratiform ash-siltstone-hosted Zn-Pb-Ag sulfide deposits (SAS). It has not been completely resolved if these deposit types formed from similar hydrothermal fluids. Recent investigations at the Falun SVALS deposit and the Zinkgruvan SAS deposit suggest that fluids of contrasting pH, $f_{O_2}$, salinity and T were involved in their origin. Whereas Falun formed by cooling and neutralization of acidic (pH<4), hot (300–400°C) and reducing fluids carrying metals and sulfur together, Zinkgruvan formed by reduction of oxidized brines at a near-neutral pH. Falun is a vent-proximal, synvolcanic carbonate-replacement deposit with similarities to VMS and skarn deposits, whereas Zinkgruvan is a post-volcanic, exhalative deposit with similarities to some SEDEX deposits. Our results suggest that the different character of SVALS and SAS deposits in part are functions of fundamental differences in fluid chemistry, controls on sulfide precipitation and relationship to volcanism.

1 Introduction

The Bergslagen ore district has a mining tradition extending back more than a millennium. Most deposits have been mined for iron, hosted by iron oxides in marble/skarn, banded iron formations and iron oxide-apatite deposits (Fig. 1). Polymetallic sulfide deposits were originally mined for Cu and Ag but following technological advances during the last centuries, Zn and Pb became main commodities. At present, three deposits are in production; the 65 Mt Zinkgruvan Zn-Pb-Ag-Cu deposit, the 144 Mt Garpenberg Zn-Pb-Ag-(Cu-Ag) deposit and the 1.15 Mt Lovisa Zn-Pb deposit. Historically important deposits include the 28–35 Mt Falun Zn-Pb-Cu-(Au-Ag) deposit, the 6.8 Mt Saxberget Zn-Pb-Cu-(Au-Ag) deposit, the ~5 Mt Sala Zn-Pb-Ag deposit and the 6.7 Mt Stollberg ore field (Allen et al. 1996).

The deposits are hosted by a volcanosedimentary succession deposited at ca. 1.91–1.89 Ga in a back-arc basin on continental crust (Allen et al. 1996). The succession as well as the hosted mineral deposits underwent polyphase ductile deformation, regional metamorphism (mainly amphibolite facies) and intrusion by multiple generations of plutonic rocks at ca. 1.9–1.8 Ga during the Svecokarelian orogeny (Stephens et al. 2009). The resulting post-ore modifications have induced significant uncertainties regarding the original timing and mechanisms of ore formation.

Sundblad (1994) obtained contrasting Pb isotope trends for the Zinkgruvan and Falun deposits, whereby it was speculated that these deposits formed from different ore-forming systems. This contrasted with the prevailing view at the time that sulfide deposits in Bergslagen share a common volcanic-exhalative origin (e.g. Hedström et al. 1989). Allen et al. (1996) subsequently showed that massive sulfide deposits in Bergslagen can be divided into two end-members; 1: stratiform ash-siltstone-hosted ZnPb-Ag sulfide deposits (SAS; Zinkgruvan) and 2: strata-bound volcanic-associated limestone-skarn Zn-Pb-Ag-Cu-Au sulfide deposits (SVALS; Falun, Garpenberg, Sala etc.). Facies analysis showed that SVALS deposits are replacive, vent proximal deposits whereas SAS deposits are exhalative deposits formed distal to volcanic vents.

Recent investigations at Falun (Kampmann et al. 2017) and Zinkgruvan (Jansson et al. 2017) have added to this...
two-fold division by recognizing that fundamentally different fluids and trapping mechanisms were involved in their origin, and that the relationship to volcanism differs. These differences can account for a number of features, such as the differences in associated alteration, the affinity of SVALS and SAS deposits to former limestone and silty-muddy facies respectively, as well as the rarity of large SAS as opposed to SVALS deposits in Bergslagen.

2 The Falun deposit

The Falun pyritic Zn-Pb-Cu-(Au-Ag) sulfide deposit has been one of Sweden’s most important metal producers for several hundred years until 1992. Approximately 28–35 Mt of ore grading 5 % Zn, 2 % Pb, 0.6–4 % Cu, 13–35 g/t Ag and 0.5–4 g/t Au were produced. The deposit occurs in an area of Bergslagen, which is dominated by metamorphosed, rhyolitic subvolcanic intrusions and volcanlastic rocks including pumiceous facies. The massive sulfide deposit is situated in the core of a sheath fold, surrounded on all sides by altered stratigraphic footwall rocks or shear zones (Fig. 2). The altered volcanic rocks currently consist of variable amounts of e.g. anthophyllite, biotite, cordierite, garnet, quartz, which comprise metamorphic products after syn-volcanic chloritization, sericitization and silicification. Kampmann et al. (2017) demonstrated an original zonation from distal sericite to increasing chlorite towards the Falun deposit. The Fe-content in original chlorite was shown to increase towards the core of the alteration system, where the footwall locally hosts stringer-type Cu-Au mineralization.

Similar to other SVALS deposits, field relationships at Falun strongly suggest a synvolcanic origin, a volcanic vent-proximal position and sub-seafloor massive sulfide deposition by carbonate replacement (cf. Allen et al. 1996). The latter is exemplified carbonate rock relics in the massive sulfide mineralization. Kampmann et al. (2017) concluded that most features can be attributed to sub-seafloor replacement in a VMS system, but that hybrid metasomatic skarn features may have resulted from the prograde volcanic-magmatic evolution at ca. 1.89 Ga.

3 The Zinkgruvan deposit

From 1857 to present, ~41 Mt of stratiform sulfide ore grading 10.6 % Zn, 2.9 % Pb and 58 g/t Ag have been mined at Zinkgruvan (Jansson et al. 2017). The deposit is located on the refolded, overturned limb of an east-west-trending major syncline (Fig. 3). The 5–10 m thick main sulfide bed has been traced for a strike extent of over 5 km and to a depth of 1.6 km. The deposit is situated in the upper part of the Zinkgruvan formation; a unit recording the regional transition from deposition of dominantly felsic, juvenile volcanic rocks to argillitic to turbiditic rocks (Allen et al. 1996). Beneath the ore horizon, the Zinkgruvan formation is dominated by metatuffite interbedded with dolomitic marble. Marble interbeds are less abundant above the ore horizon, where graphite-bearing pyrrhotite and garnet-rich units after former black shale and reduced silicate-facies iron formation occur.

A lateral metal zonation exists in the stratiform ore, wherein Zn/Pb increases from proximal to distal (Hedström et al. 1989). Dolomitic marble in the most proximal position locally hosts stratabound, low grade cobaltiferous and nickeliferous Cu ore, from which 1 Mt at 2.5 % Cu, 0.4 % Zn and 25 g/t Ag have been mined to date (Jansson et al. 2017). In contrast to Falun, feldspar-destructive alteration is absent. Instead, the main alteration style in the footwall comprised semi-regional, pervasive K-feldspar alteration, which converted rhyolitic dacitic volcanic rocks to ‘microcline-quartz rocks’ the whole-rock K2O of which commonly exceeds 10 wt.%. These rocks carry accessory tourmaline.

The Zinkgruvan deposit formed at a tectonic transition from active, but waning, volcanism and extension, to a
post-volcanic stage of thermal subsidence. A syngenetic-exhalative origin was favored by Jansson et al. (2017), who noted similarities with both MacArthur-type SEDEX deposits (Cooke et al. 2000) and VMS deposits.

4 Inferences of fluid composition

Kampmann et al. (2017) showed that the protoliths of the metamorphosed, altered volcanic rocks at Falun formed from feldspar-destructive alteration, driven by acidic \((S^++H^+)\) hydrothermal fluids at temperatures of 300–400° C. Low \(f_O^2\) in the fluids was inferred based on 1) paucity of Fe\(^{3+}\)-bearing minerals in altered rocks, 2) Au endowment, 3) traces of cassiterite in the stringer zone and 4) elevated trace Sn in sulfides. It was suggested that the fluids carried metals and sulfur together, and that stringer-type Cu-Au mineralization formed as result of cooling. The massive sulfide ore was inferred to have formed as a result of a sharp drop in metal solubility following neutralization upon sub-seafloor interaction with limestone (Fig. 4, cf. Allen et al. 2010). A modified seawater origin for the fluid ± a magmatic-hydrothermal contribution was inferred.

In contrast, Jansson et al. (2017) inferred near neutral pH ore-forming fluids at Zinkgruvan based on widespread K-feldspar alteration and evidence that the ore-forming fluid transgressed a thick former limestone unit prior to depositing the stratiform Zn-Pb-Ag ore. A high \(f_O^2\) in the fluids was inferred based on widespread hematite-staining in the deeper parts of the K-feldspar-altered zone (Fig. 3). The K-feldspar alteration, boron-enrichment, low aspect-ratio of the ore and considerations of metal solubilities were used to argue that the ore-forming fluids were saline brines which ponded on the seafloor. No estimate of fluid \(T\) could be given, albeit consideration of Zn and Pb solubilities in saline, oxidizing fluids led to the conclusions that the temperature was not necessarily higher than e.g. 150-250° C (cf. Cooke et al. 2000). The ore-forming was interpreted to be evaporated seawater, sourced distal from Zinkgruvan. Sulfide deposition as a response to reduction of brine \(SO_4^{2-}\) and/or mixing with \(H_2S\) at the seafloor was inferred (Fig. 4), based on sulfur isotopes and the presence of reduced lithologies in and above the ore horizon. The Cu ore was suggested to have formed when the ascending brine interacted with organic matter and/or reduced pore waters in the vent zone.

5 Discussion

Allen et al. (1996) showed that interplay between volcanotectonic subsidence and volcaniclastic sedimentation commonly maintained shallow marine environments in Bergslagen. Thus, stromatolitic limestone rather than deeper marine clay facies formed during pauses in volcanism, and periodicity in volcanism established interbedding between volcanic rocks and limestone.

Under these circumstances, synvolcanic systems involving ‘Falun-type’ fluids would more likely form sub-seafloor SVALs deposits by interaction with buried limestone than exhalate to form SAS mineralization. The formation of exhalative deposits would necessitate that fluids bypassed sub-seafloor neutralization, and vented into deeper basins where the hydrostatic pressure was sufficiently high to preclude substantial boiling. This explains why SVALs deposits are relatively common with several >1 Mt deposits, and why their exhalative counterparts appear rare and/or less endowed. Furthermore, continuous burial meant that limestone could act as a trap to mineralizing fluids at several different stages in the volcanic-magmatic evolution, explaining the complex history and common hybrid VMS- and skarn-like features at many SVALs deposits (cf. Jansson et al. 2015).

In contrast, a ‘Zinkgruvan-type’ hydrothermal fluid had a greater capacity of retaining its metal load up to the point of exhalation, owing to a near-neutral pH, lower \(T\) and the paucity of interbedded reduced strata (reductants) in the volcanic succession. Despite several known SAS deposits (Allen et al. 1996), most deposits have a known tonnage < 1 Mt and Zinkgruvan alone accounts for > 95 % of the
combined tonnage of the group (cf. Allen et al. 1996). This may reflect the rarity of deeper, anoxic environments favorable for bacterial sulfate reduction and organic matter accumulation at the time of hydrothermal activity. It was not until the waning stages of volcanism that basin subsidence started to outpace detrital volcaniclastic input, whereby widespread deeper marine environments could be sustained. Thus, formation of large deposits from ‘Zinkgruvan-type’ fluids more strongly depended on specific windows in the basin evolution.

The underlying differences imply that fundamentally different exploration strategies should be employed. Exploration for SVALS deposits should target areas where vents for ‘Falun-type fluids’ intersect former limestone units. Exploration for SAS deposits, on the other hand, should focus on localizing depocenters in areas where widespread hydrothermal activity persisted to the late- to post-volcanic stages in basin evolution.

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Segmented fault arrays and their control on the formation of Irish Zn-Pb deposits

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Abstract. 3D analysis was used to investigate the structural controls of two Irish Zn-Pb deposits, Lisheen and Silvermines. Left-stepping segmented fault arrays were identified as the controlling structural on the geometry of, and fluid flow within, the deposits and the region. Four relay ramps were identified at Lisheen, two intact, one incipiently breached and one fully breached, while five relay ramps, two intact and three incipiently breached, were identified at Silvermines. The scale at which these ramps form and their associated degree of breaching were found to play an important role in ore body geometry and localisation. Locally, fluid flow in fully intact relays is focused migrates both vertically and laterally into areas of structural complexity in the hangingwalls of the bounding segmented faults. Smaller scale, fully breached ramps may act as zones of up-fault fluid flow and as points of ingress for mineralising fluids to enter host lithologies. At the regional scale, the geometry and periodicity of segmented fault arrays can be used to more effectively target mineralisation. Ultimately, fault segmentation and relay ramp geometries play a key role in the development of Irish Zn-Pb deposits.

1 Introduction

The importance of various structures within Irish Zn-Pb deposits has long been recognized. However, the detailed analyses of these structures, and their control on mineralization, has yet to be fully understood. By not detailing the structural context in which geophysical and geochemical vectors occur, often times the processes behind individual deposit formation remain enigmatic. Here, we investigate the fundamental structural controls on location and geometry of, and fluid migration within, two Irish Zn-Pb deposits; Lisheen and Silvermines.

Both deposits are hosted in the Lower Carboniferous marine carbonate transgression of the Irish Midlands (Fig. 1). In studies of Lisheen, Hitzman et al. (1992) and Fusciardi et al. (2003) recognized the importance of segmented fault arrays and relay ramp geometries (Fig. 2) on the formation of Irish Zn-Pb deposits. Segmented fault arrays have been described at Silvermines by Andrew (1986) who noted trends of several synchronous, interrelated WNW striking, N-dipping faults closely related to mineralisation. Using current and legacy data sets coupled with 3D modelling and analyses, this study aims to accurately and quantifiably constrain segmented fault arrays in relation to deposit formation.

2 Geological setting

The Lower Carboniferous marine transgressive carbonate sequence overlies Devonian-Carboniferous terrigenous clastics, Old Red Sandstone, sitting unconformable upon deformed Silurian metasediments (Wilkinson and Hitzman 2014). These underlying basement rocks were deformed in the late Silurian-Early Devonian by the Caledonian orogeny resulting in NE-SW structural fabrics which were subsequently inherited by the overlying Carboniferous sequence (Worthington and Walsh 2011).

The Lisheen deposit sits within the south dipping (10°) northern limb of the Littleton syncline which complicates earlier extensional structures (Fusciardi et al. 2003). Within the deposit, the Lower Carboniferous sequence begins with a series of mixed clastic sediments and carbonates overlain by an argillaceous bioclastic limestone (ABL) unit. Here, the ABL has three members; 1) the Lower Calcarenite, 2) the Lisduff Oolite and 3) the Upper ABL. Directly atop the ABL sits the Waulsortian Reef Limestone, the primary host for mineralisation (Hitzman et al. 2002). Finally the succession is overlain by a cherty grainstone unit known as the Crosspatrick Formation.

The Silvermines deposit lies on the southern limb of the Kilmastulla syncline (Andrew 1986). The Lower Carboniferous succession within the area commences with an interbedded biomicarenite and calcareous shale, known as the Basal Shale unit, followed by the greenish-grey Ballyvergin Shale unit. Above these units sits the ABL, an interbedded biomicarenite and calcareous shale, known as the Basal Shale unit, followed by the greenish-grey Ballyvergin Shale unit. Above these units sits the ABL.
Figure 2. Schematic model of an intact relay ramp showing the bounding segmented normal faults and accommodation structure.

which, at Silvermines, is subdivided into five members; 1) the bioclastic calcarenite and shaley Basal Fragmental Member, 2) the Lower Dolomite Member, an oolitic biosparrenite that hosts mineralisation, 3) the fossiliferous, biosparrenite Bioclastic Limestone Member, 4) the Muddy Limestone Member, and 5) the nodular biomicritic Muddy Reef Member (Andrew 1986). Atop the ABL unit sits the Waulsortian Reef Limestone, the main host to mineralisation within Silvermines (Philcox 1984). Finally, the sequence is overlain by the Cherty Limestone unit.

3 Mineralization

Mineralisation within the Irish Zn-Pb deposits generally occurs within the hangingwalls of segmented normal faults as stratiform ore bodies (Bonson et al. 2012). Zn-Pb-Ag (Cu, Ni, Ba) mineralisation at Lisheen is hosted within Waulsortian reef limestone with minor amounts found in the Lisduff oolite where the two units are juxtaposed. The deposit is subdivided into six mineralised zones: 1) Main Zone, 2) Derryville Zone, 3) Bog Zone Central, 4) Bog Zone East and 6) The Island Pod (Fig. 3). Ore bodies are stratiform, occurring within 20 meters of the Waulsortian-ABL contact, and consist of a number of massive sulphide lenses surrounded by semi-massive, vein and/or disseminated sulphide mineralization (Fusciardi et al. 2003).

Zn-Pb-Ba (Ag, Cu) mineralization at Silvermines is hosted within both the Lower Dolomite unit and the Waulsortian Reef limestones. Five mineralised zones have been recognised within the deposit; three major zones 1) G-Zone, 2) B-Zone, and 3) K-Zone and two minor zones 4) C-Zone and 5) Shallee (Fig. 4). Ore bodies at Silvermines occur either in the fault planes of normal faults (i.e. the lower G-Zone) and/or in stratiform lenses within the host lithologies. Mineralisation occurs as massive sulphide or as disseminated or vein style mineralization.

4 Methods

To best model the complex geometries of the Lisheen and Silvermines deposits, using their associated dense and spars datasets, we have combined a series of 3D modelling techniques and software packages. This was done to optimize the accuracy and efficiency of the modelling process. Various modelling packages including Maptek’s Vulcan and Midland Valley’s MOVE as well as implicit packages Paradigm’s SKUA-GoCAD + Mira Geoscience plugin and Aranz Geo Ltd’s Leapfrog Geo were used.

Figure 3. Plan view of the left-stepping segmented fault array, and relay ramps, at Lisheen. The red faults represent the major normal faults which were later complicated by the navy blue, oblique-slip faults and finally by the thin black NNW-trending strike-slip faults.
5 Results

3D analysis of the deposit models, and field observations, identified left-stepping segmented fault arrays and associated accommodation structures as the fundamental structural framework (Fig. 3 and 4). Within both deposits displacements along segmented normal faults decrease rapidly away from points of maximum displacement. Most notably, these segmented fault arrays have a distinct spatial relationship with the position of various ore zones.

5.1 Lisheen

At Lisheen, segmented normal faults strike EW and dip northward (Fig. 3). 3D analysis established the presence of four relay ramps; two larger, fully intact ramps (MZ-DVIL and DVIL-BZW), and two smaller breached to fully breached ramps (BZW-BZE and MZ; Fig. 3). All four ramps dip shallowly to the W-NW and total displacements across the ramps decrease eastward from 220m to 160m. Displacement on the segmented normal faults brings the Lisduff oolite in the footwall in contact with the overlying Waulsortian Reef Limestone in the hangingwall. It is at this juxtaposition where both units are mineralised.

The geometry of the SE edge of the Main Zone ore body parallels the base of the MZ-DVIL relay ramp (Fig. 3). A similar geometry is observed for the Derryville ore body whose SE boundary is defined by the base of the DVIL-BGW ramp (Fig. 3).

5.2 Silvermines

Normal faults within the segmented fault array at Silvermines strike NW and dip NE (Fig. 4). 3D analysis identified five main relay ramps: the largest ramps (GZ-BZ1, BZ1-BZ3 and BZ3-COO) are incipiently breached and two medium ramps (BZ1-BZ2 and BZ2-BZ3) are fully intact (Fig. 4). In general, relay ramps at Silvermines dip shallowly to the NW. Similar to the segmented fault array at Lisheen, whose displacement decreases eastward, total displacement across the fault array at Silvermines changes, from 370m in the west to 298m in the east.

Issues with legacy data sets from Silvermines (i.e. less drilling definition, historical analytical capabilities, etc.) meant that 3D modelling of the detailed geometries of individual ore bodies was slightly less achievable than for those at Lisheen. Nevertheless, the locations of each ore body, as well as their extents, was delineated from the diamond drillhole records, historic reports, publications, and underground mapping (Fig. 3). 3D modelling shows that the main portions of the G-Zone and B-Zone ore bodies occur within Waulsortian reef limestone at the base of the GZ-BZ1 and BZ1-BZ3 relay ramps (Fig.3). Unlike Lisheen, mineralisation in these two ore bodies continues half-way up the ramps. K-Zone and C-zone ore bodies, hosted within the Lower Dolomite Unit, are located within GZ1-BZ1 and BZ1-BZ3 ramp breaching structures and do not migrate down the ramps.

6 Discussion

6.1 Scale of relay ramps and degree of breaching

Larger scale relay ramps at Lisheen (MZ-DVIL and DVIL-BZW), and some large-medium scale relay ramps at Silvermines (BZ1-BZ3 and BZ1-BZ2), have fault separations, and corresponding ramp lengths, substantially greater than their total displacements. These ramps are fully intact implying that the strain accommodated by the ramps did not exceed their failure threshold. Other larger-
medium scale relay ramps at Silvermines (GZ-BZ1, BZ1-BZ2 and BZ3-COL) have increased displacements relative to fault separations, circumstances which have, as expected. Let to fault propagation and relay breaching.

Smaller fully breached relays at Lisheen (MZR and BZW-BZE) accommodate similar fault displacements as their larger intact counterparts but their ramps have experienced higher strains ultimately leading to ramp failure and potentially significant fault rock generation.

6.2 Scale of relay ramps and fluid flow

In the case of the larger scale, fully intact relay ramps, fluid flow is focused away from the ramps and into bounding segmented faults. The spatial locations of the mineralised bodies are found to be concentrated within the hanging walls of the segmented normal faults and at the base of the relay ramps. These observations suggest that fluid migration was restricted to the lowermost hangingwall and could not continue up the ramp (Fig. 3).

On the opposite side of the spectrum are the smaller scale, fully breached relay ramps. In this case, ramp zones are highly fractured due to increased strain resulting from their high fault displacement to low separations. These smaller scale ramps become potential zones for up-fault fluid flow and may act as points controlling the ingress of fluids into host lithologies.

In between these two extreme cases exists a continuum. Incipiently breached ramps focus fluids both away from ramps into bounding normal faults and also into areas along the breaching fault (i.e. K-Zone at Silvermines).

We attribute the scale of segmentation to the nature of the faulted sequence, with particular units promoting segmentation during upward fault propagation from underlying pre-existing Caledonian basement structures.

6.3 Scale of relay ramps and targeting

The presence of various scales of relay ramps within the Lisheen and Silvermines deposits suggest a means by which to vector to further mineralisation. At differing scales, relay ramps control the location of ore bodies; whether that is at the base of, and within, the bounding segmented faults of larger-scale, incipiently and fully intact relay ramps or within the structurally complex, fully breached small-scale relay ramps.

An understanding of the scale and geometries of segmented fault arrays can be used to determine local ore body geometries and to target potentially favourable locations. Using displacement and amount of structural complexity encountered, one can determine the location within a segmented fault array and/or the scale of the relay ramp. From here, determinations can be made as to the location of further mineralization i.e. whether to step out to locate the bounding segmented faults, or to target the structurally complex zones within a smaller scale relay ramp.

7 Conclusions

Segmented fault arrays play a critical role in deposit formation controlling both the locations of feeders and the distribution of ore bodies. Within individual deposits, the scale of fault segmentation varies, which has a direct impact on the nature of the linking structures. The degree of breaching of relay ramps is controlled by the scale of segmentation (and corresponding separation and ramp length) relative to fault displacement, and plays a crucial role in the creation of porosity for upwelling fluid flow.

Understanding the structural controls of both the Lisheen and Silvermines deposits have allowed us to investigate the processes by which they formed. Key characteristics including relay ramp scale, breaching, structural geometries and location of best ore grades allow for more precise target generation. Knowledge of the scale of relay ramps and their links to ore body locations will allow exploration and mining companies to more effectively vector to mineralization.

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Interpreting geochemical paleoredox proxies in mudstones associated with Sediment-Hosted Massive Sulphide (SHMS) deposits

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Abstract. In this study, a suite of geochemical redox proxies have been used to evaluate ambient basinal conditions during a period of Late Devonian hydrothermal activity in the Selwyn Basin (Canada). Organic-rich mudstones were collected from two correlated drill-holes; one intersects a 35 m thick sequence of SHMS mineralization, while the other intersects un-mineralized strata. All samples contain a high proportion of reactive Fe (Fe_HR/Fe_T > 0.38), indicating water column anoxia. Greater pyritisation in the mineralised succession (median Fe_PY/Fe_HR = 0.86), relative to un-mineralised samples (median Fe_PY/Fe_HR = 0.72), could represent more locally stagnant, euxinic conditions. However, δ^{10} Mo_NIST values (0.33 to 0.69‰) are uniform between both drill-holes and substantially lower than coeval Late Devonian seawater (≈ 1.5‰). The low abundance (<5 ppm) of Mo in mineralised samples indicates hydrothermal Mo input was negligible; in the un-mineralised mudstones fractionation of authigenic Mo from seawater is consistent with deposition under non-euxinic conditions. In the absence of water column euxinia, high primary productivity and enhanced organic carbon burial were the key variables for promoting sulfate reduction in the sub-surface and trapping metals; therefore, when, how and where these conditions develop in sedimentary basins are the most important consideration when targeting prospective host rocks for SHMS systems in the geologic record.

1 Introduction

Understanding ore formation processes in sedimentary basins requires development of precise geochemical constraints for both ambient basin conditions and hydrothermal input. Broadly speaking, this is fundamental for evaluating trends in the paleogeographical and secular distribution of sediment hosted base metal (SHMS) deposits, which represent anomalous tonnages of base metals and reduced sulphur within the geologic record. Many SHMS deposits are hosted in organic rich mudstones that contain abundant pyrite, and determining the conditions of pyrite formation (diagenetic, hydrothermal) can have major implications for models of ore formation.

In this study we focus on samples of organic rich mudstone from Late Devonian stratigraphy of the Selwyn Basin. Globally, this was an important period for both organic rich mudstone deposition and also hydrothermal activity (e.g. Iberian Pyrite Belt, Selwyn Basin; Goodfellow and Lydon 2007). Central to many previous studies has been the idea that pyrite and base metal sulphides (PbS, ZnS) precipitated in stagnant, restricted basins following venting of hydrothermal fluids (sedimentary-exhalative model; Goodfellow et al. 1993). Nevertheless, uncertainty remains over the precise relationship between ambient paleoredox conditions and sulphide formation (e.g. Gadd et al. 2016; Magnall et al. 2016). We look to address this problem using a multi-proxy approach that combines lithogeochemical (Fe speciation, Mo) and isotopic techniques (Mo). These techniques, although commonly used in lithogeochemical studies of un-mineralised basins (e.g. Gordon et al. 2009), have not yet been applied in mineralised systems. The results presented here are therefore relevant to all studies of marine paleoredox in mineralised basins.

2 Regional geology

The Selwyn Basin (Canada) comprises clastic sedimentary rocks deposited along the western passive margin of ancestral North America between the Late Neoproterozoic and Late Devonian. There are 3 major periods of organic rich mudstone deposition and SHMS mineralisation hosted by Lower Paleozoic Selwyn Basin stratigraphy (Goodfellow 2007). At Macmillan Pass (YT), two SHMS deposits (Tom, Jason) are hosted by organic rich, variably pyritic mudstones of the Earn Group.

Subsequently, island arc accretion during the Mesozoic...
led to Selwyn Basin strata being deformed in the Cordilleran fold and thrust belt. At Macmillan Pass, deformation is localised within fold hinges, and primary hydrothermal and sedimentological features are generally well preserved.

3 Samples

Samples from the hydrothermal vent complex at Tom were collected from TYK-1, TYK-2 and T91-14 (e.g. Fig. 1A). Samples of organic rich mudstone (e.g. Fig. 1B) were collected from two correlated drill-holes; TYK-5 intersects ~35 meters of stratabound sulphide and barite mineralisation at the Tom deposit, and 76-17 is located between the Tom and Jason deposit and intersects strata from an un-mineralised sequence within the basin. Details of the stratigraphic correlation are given in Magnall et al. (2015).

Figure 1. Hand sample photographs of a mineralised (massive sulphide and iron carbonate) sample (A) from the vent complex (Tom deposit) and a sample of organic rich mudstone (B) from DH76-17. Scale bar is 2cm.

4 Geochemical redox proxies

Samples from the Tom vent complex and un-mineralised mudstones from DH_TYK-5 and DH 76-17 were analysed for major, minor and trace elements at ACME (Vancouver) and Actlabs (Ontario). Splits of the mudstone rock powder were used for generating iron speciation data, at Leeds University following the protocol described in Poulton and Canfield (2005). Similarly, Mo isotope data was produced on the same mudstone sample splits at the W. M. Keck Foundation Laboratory for Environmental Biogeochemistry (ASU).

4.1 Bulk rock lithogeochemistry

Before evaluating the geochemical redox proxies, it is necessary to determine the nature of hydrothermal input. In this regard, the major and trace element content of samples from the vent and un-mineralised mudstones were compared (Fig. 2).

There is clear Fe, Pb and Zn enrichment in the vent complex relative to un-mineralised mudstones (Fig. 2). However, Mo forms an opposing trend, and is most abundant (> 10 ppm) within the un-mineralised samples. In terms of major elements, un-mineralised mudstones broadly overlap with normal marine sediments, and although there is a trend of increasing Fe, there isn’t the extreme enrichment that is preserved in the vent samples.

Figure 2. Major and trace element (inset) data for vent samples (orange) and organic rich mudstones (76-17 = grey; TYK-5 = black). Reference fields given by Böstrom (1973).

4.2 Molybdenum geochemistry

The overall concentration of Mo in mudstone samples (Fig. 2) is well below the 100 ppm threshold used to define strongly euxinic seawater (Scott and Lyons 2012). The δ98Mo value of Macmillan Pass mudstones is also fractionated relative to Late Devonian seawater (Fig. 3), indicating depositional conditions were not strongly euxinic. Hydrothermal Mo input is clearly negligible, as recorded by low Mo within the vent (Fig. 2), and therefore cannot be used to explain the low δ98Mo values (e.g. Fig. 3). Rather, the fractionated δ98Mo values are more consistent with deposition under anoxic to weakly euxinic conditions.
Figure 3. The range of $\delta^{98}$Mo values for organic rich mudstones from Macmillan Pass, together with $\delta^{98}$Mo values for different sources and sinks in the global Mo cycle. The $\delta^{98}$Mo values compiled from references given in Goldberg et al. (2016).

Figure 4. $\delta^{98}$Mo values vs. Fe$_{PY}$/Fe$_{HR}$ for mudstone samples from 76-17 and TYK-5. Samples from TYK-5 have been split into sub-groups according to position above (hw) and below (fw) the mineralised interval. The grey bar denotes the threshold between persistently euxinic (> 0.8) and ferruginous to weakly euxinic (< 0.8), and non-sulphidic (i.e. ferruginous; $\delta^{98}$Mo << 1.5 ‰). This is consistent with low concentrations of seawater sulphate during the Late Devonian, and provides an interesting mass balance constraint on the S supply for SHMS systems.

4.3 Iron speciation

All mudstone samples contain a high proportion of highly reactive Fe (Fe$_{HR}$ = Fe$_{PY}$ + Fe$_{CARB}$ + Fe$_{OX}$ + Fe$_{MAG}$) relative to total Fe (Fe$_{HR}$/Fe$_{T}$ = 0.86), and are above the threshold used to distinguish between deposition under oxic and anoxic waters (Fe$_{HR}$/Fe$_{T}$ = 0.38; Poulton and Canfield 2011). The proportion of Fe$_{HR}$ present as pyrite (Fe$_{PY}$/Fe$_{HR}$) can help distinguish between non-sulphidic (ferruginous) to weakly euxinic (< 0.8), and strongly sulphidic (> 0.8) anoxic waters. In terms of Fe$_{PY}$/Fe$_{HR}$, mudstones from 76-17 and TYK-5 form two groups of data (Fig. 4), which could be interpreted as representing deposition under ferruginous to weakly euxinic conditions (76-17) and strongly euxinic conditions (TYK-5). However, there is no correlation between Fe$_{PY}$/Fe$_{HR}$ and $\delta^{98}$Mo values (Fig. 4), contrary to what may be expected when comparing euxinic and non-euxinic samples (e.g. Gordon et al. 2009).

The footwall mudstones from TYK-5 (red symbols, Fig. 4) are all highly pyritised (Fe$_{PY}$/Fe$_{HR}$ > 0.8) whilst also capturing close to the entire range of $\delta^{98}$Mo values (0.33 to 0.67). The lack of a systematic relationship between $\delta^{98}$Mo values and relative pyrite abundance may have resulted from subsurface pyrite formation (diagenetic, hydrothermal) that occurred during early burial on the periphery of the hydrothermal system.

5 Implications

The majority of SHMS deposits are hosted by pyritic mudstones. However, the origin of the pyrite can be ambiguous, in terms of discerning between diagenetic and hydrothermal processes. At Macmillan Pass, we have demonstrated that the pyritic mudstones hosting the SHMS deposits were not deposited in a persistently euxinic basin; instead, pyrite formed beneath the sediment water interface in a Late Devonian basin that was anoxic (Fe$_{HR}$/Fe$_{T}$ > 0.38), but non-sulphidic (i.e. ferruginous; $\delta^{98}$Mo << 1.5 ‰). This is consistent with low concentrations of seawater sulphate during the Late Devonian, and provides an interesting mass balance constraint on the S supply for SHMS systems.

The results presented here provide evidence that linkages between seawater paloredox and formation of SHMS deposits are likely more nuanced than previously argued. We propose two key factors that warrant further consideration when evaluating the distribution of SHMS deposits in the geologic record; (1) long periods of low seawater sulphate, characteristic of much of the Lower Paleozoic (and Proterozoic) were likely to have been important for the development of sulphide-poor, Pb-Zn-Fe enriched basinal fluids (e.g. Wilkinson 2014); (2) sulphide formation in non-euxinic basins requires optimisation of other processes that concentrate reduced sulphur, originally derived from seawater sulphate, into the host rock. Regarding (2), a number of pathways have been suggested, including replacement of diagenetic barite (Johnson et al. 2004), diagenetic sulphate reduction (Fallick et al. 2001) and thermochemical sulphate reduction (Gadd et al. 2016). These processes all ultimately involve organic carbon as an electron donor, and formation of SHMS deposits in basins characterised by high biological productivity is an emerging theme of recent models for SHMS mineralisation. Notably, in restricted, euxinic basins, maintenance of primary productivity (and deposition of thick sequences of organic rich mudstone) will be inhibited by the drawdown of trace elements and nutrients.

We propose that high productivity and enhanced carbon burial are key pre-requisites for the development of favourable host rocks, and SHMS deposits form where deep basin faults provide a flow path for metal-rich hydrothermal fluids.
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Acid sulphate alteration in the Iberian Pyrite Belt

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Abstract. Acid sulphate alteration was characterized at the Lagoa Salgada, Caveira, Lousal, Aljustrel and S. Domingos VHMS deposits of the Iberian Pyrite Belt, and correlated with the supergene kaolinite-halloysite alteration facies observed. The supergene alteration decreases with depth and distance to the massive sulphide orebodies. Nevertheless, the primary volcanic textures of their host rocks are often partially preserved, despite the common replacement of hydrothermal phyllosilicates by clays. Regardless of the intensity of kaolinitization, several different alunite vein generations were recognized, as follows: I) deformed, syn-tectonic veins, sub-parallel to the main cleavage and to shear zones; IIa) deformed veins, oblique to cleavage, usually with pytymatic folding; IIb) sub-horizontal vein networks; III) sub-vertical veins associated with late strike-slip faults. The vein-filling mineral assemblage includes alunite, natrioalunite, minamiite, natrijarosite, jarosite and wavellite. The alunite veins occur very often associated with the gossans, but can occur also below the oxidation level, cutting the orebodies, and in direct contact with massive sulphides. Jarosite veins of stages I, IIa and III are minor and occur only in the supergene alteration settings. The occurrences of Al-bearing sulphates are consistent with circulation of very acidic and oxidising fluids, at low temperature conditions, under both syn/late-Variscan, and Alpine tectonic regimes.

1 Introduction

The Portuguese sector of the Iberian Pyrite Belt (IPB) encloses giant deposits such as the Neves-Corvo and the Aljustrel active mines, as well as intermediate to small-size deposits represented in this study by the Lousal, Caveira, S. Domingos, Chança and Montinho old mines, and by the Lagoa Salgada and Salgadinho massive sulfide lenses, the later two prospects being both object of exploration programs now running (Oliveira et al. 2013). Lagoa Salgada, Lousal, Caveira (Salvador orebody), Aljustrel (Algares and S. João orebodies) and S. Domingos are sub-vertically stacked massive sulphide orebodies, which upper parts were affected by supergene alteration that accounts for variably developed gossans (Matos et al. 2003). While in all the other cases the gossans outcrop on surface, in the case of the Lagoa Salgada system, a hidden deposit was identified bellow 128 m of Cenozoic sediments (Oliveira, et al. 1998; Oliveira et al. 2011), and capped by a paleo-gossan, probably Oligocene in age (Matos et al. 2000). Felsic volcanic rocks and minor sediments of the IPB Volcano-Sedimentary Complex (Famennian-Upper Visean) constitute the footwall rocks to these deposits. The purpose of this study is the characterization of the acid sulphate alteration patterns recognized in the proximity of these massive sulphide lenses and related proximal stockworks. Research was focused on understanding the possible significance and implications of vein-controlled alteration assemblages containing alunite and jarosite group minerals, namely to distinguish supergene alteration signatures, from very low pH hydrothermal alteration patterns characterized by extreme leaching of volcanic and sedimentary rocks. Acid sulphate alteration not only contributes to enhance our understanding of the IPB ore-forming processes, but also improves the mineral exploration array of tools known.

2 Methodology

The study of the Lousal, Caveira, Algares, S. João and S. Domingos deposits was based on very detailed mapping (1/2000 scale) of the geological units, structural setting, outcropping mineralization, and hydrothermal and supergene alteration. At the Lousal and Aljustrel mines, near surface mine galleries were additionally studied. In the case of the Lagoa Salgada prospect, logging and sampling of the drill holes LS4, LS6, LS9, LS10, LS11, LS14, LS15, LS22, LS43 was performed, in order to produce a subsurface geological map (~70 m level; 20 m below the Paleozoic/Cenozoic paleosurface). Geological mapping was supported by structural and stratigraphic studies, which included volcanic and sedimentary rock dating (e.g., Oliveira et al. 2013, and references therein). Besides optical inspection under the microscope, the mineral identification and mineral chemistry studies relied on EPMA, PIMA II (Portable Infrared Mineral Analyser), and XRD analyses. Short wavelength analysis was carried out on sawed surfaces of dry rock samples. The PIMA VIEW software (Horsfall, 1999) was used to extract parameters for mineral identification (both sulphate and clay minerals), wavelengths and depths of absorption features from hull quotient corrected spectra. The analytical work was run at the laboratory facilities of both the National Laboratory of Energy and Geology (LNEG), and of the Faculty of Sciences of the University of Lisbon. A very tight mineralogical control on a large number of samples (>500), coupled with extensive alteration mapping and textural interpretation at all scales, was crucial to understanding the relationships between the different stages of sulphate vein formation.
3 Alunite veins vs. supergene kaolinite / halloysite alteration

3.1 Lagoa Salgada

The Lagoa Salgada deposit was discovered by the Portuguese Geological Survey (SGF, presently LNEG) in 1992, in the Sado river Cenozoic Basin, a large area where the IPB Paleozoic basement is mostly hidden by sediments, which can be more than 200 m thick (Matos et al. 2000; Oliveira et al. 1998; Oliveira et al. 2011). The deposit is composed of two massive sulphide ore lenses (SW and NE), with proximal stockwork feeder zones in quartz-feldspar porphyritic volcanic rocks. Several exploration drill hole campaigns have defined inferred resources of 3.7 Mt of massive ore, and indicated resources of 2.9 Mt @ 3.40 % Zn, 2.94 % Pb, 0.34 % Cu, 54.72 ppm Ag and 0.82 ppm Au (Daigle, 2012, Tetra Tech Wardrop unpublished report to Portex company). The deposit orientation is N15W, plunging 75º to 65º NE. It was mapped along 536 m, with thickness ranging between 25 and 35 m. Due to erosion and supergene alteration, a 10 to 20 m thick hematitic gossan, with a clay-rich top and a more siliceous base, occurs 128 m below surface, under the Cenozoic sediments (Matos et al. 2000; Oliveira et al. 2011). The Lagoa Salgada gossan is similar to those known in other IPB deposits such as La Lapilla, Tharsis, San Telmo, Lomero, San Miguel, Rio Tinto, Peña de Hierro (Velasco et al. 2013) and Algaras (Matos et al. 2003). Locally, high contents in Au, Pb, Sn, As and Ag do occur and translate into inferred resources as follows: 0.28 Mt @ 0.3% Cu, 5.6% Pb, 0.3% Zn, 60.6 ppm Ag e 1.0 ppm Au. Maximum tin grades of up to 1.4% Sn have been detected. The gossan progressively grades downward into the massive sulphide orebody, through a sub-horizontal, four meters thick (on average) supergene enrichment zone. This supergene alteration horizon is characterized by the occurrence of chalcocite and covellite, and by pronounced metal enrichment (e.g., LS4 - 6 m @ 2.1 % Cu and LS9 - 4 m @ 3.32 ppm Au e 253.6 ppm Ag; Matos et al. 2000). The massive sulphide mineralization has significant contents in Zn and Pb (locally >20%), and low Cu grades (e.g., drill hole PX05: 18.10 m @ 7.33% Zn, 5.54% Pb, 1.30 ppm Au, 72.03 ppm Ag (Daigle 2012); and drill hole LS22: 78.6 m @ 7.52% Zn, 4.79% Pb, 1.34 ppm Au, and 94.65 ppm Ag; Castelo Branco, 1996). The massive sulphide mineral assemblage is composed of sphalerite, arsenopyrite, tetrahedrite (tennantite), galena, lollingite, chalcopyrite, cassiterite, stannite, chalcocite, neodigenite, covellite, enargite, bornite, bouronite, meneghinite, bismuth sulphosalts and pyrrhotite (Oliveira et al. 1998; Matos et al. 2000; Oliveira et al. 2011). Significant indium concentrations have been measured in some zoned crystals of sphalerite. At Lagoa Salgada the hanging wall sequence begins with a chert horizon. The footwall sequence is defined by a Feldspar-Quartzphyric Volcanic Unit (Oliveira et al. 2011). This unit is formed by rhyodacites and minor rhyolites, with predominant coherent facies and intercalations of monomictic breccias, sometimes with jigsaw-fit textures, and autobreccia facies. This volcanic unit was dated 356.4 ± 0.8 Ma (Tournaisian) by Barrie et al. (2002). It grades laterally and downwards to the Quartzphyric Volcanic Unit formed by rhyolites and rhyodacites and dated 356.21 ± 0.73 Ma (Tournaisian; Barrie et al. 2002). A large ore-forming hydrothermal alteration system characterised by chlorite+pyrophyllite, chlorite+sericite+carbonates, quartz+sericite and sericite assemblages has been recognized and mapped (Matos et al. 2000). The occurrence of pyrophyllite (Relvas et al. 1994), coupled with fluid inclusion studies involving the chloritic facies of the stockwork (Jaques and Noronha 2001), collectively suggest very acidic alteration conditions at interaction temperatures in excess of 400ºC. Either of these factors would greatly favour extreme leaching of the footwall rocks, and thus higher metal concentrations in the mineralizing fluid.

The SW and NE orebodies are bounded by major thrust faults, locally accompanied by large-scale kaolinite-halloysite supergene alteration. This alteration is zoned (Matos 2003), being pervasive in the vicinity of the massive sulphide bodies, and less prominent either in the proximal stockwork mineralization hosted by the feldspar-quartzphyric volcanic rocks (e.g., from NW to SE: LS22, LS14, LS11, LS9, LS10, LS4, LS5 and LS6 drill holes), or close to the semi-massive sulphide occurrences hosted by quartzphyric volcanic rocks (e.g., LS23, LS26 and LS28 drill holes). The kaolinitization extends from the paleo-oxidation level down to 90-100 m, decreasing in intensity with depth. This pre-Oligocene acid weathering alteration consists of variably pervasive alteration of the matrix of the volcanic rocks. Their original textures are often partially preserved. Replacement of hydrothermal phyllosilicate minerals by clays is quite common. The kaolinitization process increases in the main fault zones, denouncing underground water circulation along these tectonic structures. A similar model was described for the Las Cruces deposit (Doyle, 1996). XRD data (this study) shows kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and greenalite, $\text{Fe}_3\text{SiO}_5(\text{OH})_4$ in the paragenesis that replaces the matrix of the felsic volcanic rocks. Halloysite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})\text{nH}_2\text{O}$ was identified by PIMA.

Centimetric to millimetric veins filled with alunite were described both at the footwall and at the hanging wall of the massive sulphides (e.g., LS4, LS6, LS9, LS10, LS11, LS14, LS15 and LS43 drill holes; Matos, 2000; Matos et al. 2003). Several different generations of alunite veins have been distinguished, as follows: I) deformed, syntectonic veins, sub parallel to the main cleavage and shear zones; IIa) veins deformed veins, oblique to cleavage, usually with pytymatic folding; IIb) sub-horizontal vein networks (e.g., drill hole LS14); III) veins occupying late fractures. Stage I veins relate with a NNW-SSE structural corridor mapped along over 400 m (drill hole data). Stage I and stage II veins show comb structures and late polygonal structures (with cell shape) between the fold hinges zones. Microprobe data show that Na-rich sulphates occupy the cores of these polygons and of late globular structures.
whereas the sulphates filling the veins are K-rich. The various generations of alunite veins extend at depth down to 90 m below the paleo-weathering level, cutting non-oxidized massive sulphides. XRD analysis of the vein mineralogy enabled the identification of alunite KA1(PO4)2(OH)6, natroalunite NaAl1(PO4)2(OH)6, and minamiite (Na,Ca)1-xAl3(SO4)2(OH)6. Wavellite Al3(PO4)2(OH)3 5H2O was also identified by PIMA.

3.2 Caveira and Lousal

The Caveira and Lousal mines occur in the NW sector of the IPB. In both cases, the cores of their hosting antiform structures expose rocks of the Phyllite-Quartzite Group (Givetian-Strunian), whereas the limbs are formed by felsic and basic volcanic rocks and sediments of the Volcano-Sedimentary Complex (VSC) (Strunian-Upper Visean; Matos et al. 2014). Detailed mapping of the alteration facies in both deposits shows kaolinite alteration zones associated to the outcropping iron hats of the Salvador orebody at Caveira, and of the Central and West orebodies at Lousal (Matos and Relvas, 2006). In the Lousal deposit, the kaolinitization (mainly kaolinite and halloysite) is particularly well developed along fault zones parallel to the mineralization, and affects preferentially the black shales of the VSC.

3.3 Aljustrel (Algares and S. João orebodies)

The giant Aljustrel deposit is one of the largest of the IPB. The mining camp contains six massive sulphide orebodies hosted by volcanic and sedimentary rocks of the VSC (Barriga et al. 1997): Feitais (54 Mt), Moinho (44 Mt), São João (45 Mt), Algares (>20 Mt), Gavião (>20 Mt) and Estação (>20 Mt).

Two sub-vertical orebodies outcrop (Algares and S. João), being mined since Roman times (Matos et al. 2010). The hanging wall sequence on top of the Aljustrel orebody contacts with the massive sulphide mineralization through a metric to decametric interval of cherts, whereas its footwall sequence is composed of felsic volcanic rocks dated 352.4 ± 1.9 Ma (Lower Tournaisian; Barrie et al. 2002). Felsic volcanic rocks, volcaniclastic breccias and black shales host the São João orebody. Detailed mapping of these two gossans shows a clear zonation in the kaolinite alteration facies, particularly obvious in the Algares orebody (Matos et al. 2003). Al-sulphate veins were mapped in both sides of its strongly deformed gossan. The following vein generations were recognised: I) deformed, syn-tectonic veins, sub-parallel to the main cleavage and showing compression micro-fractures; IIa) deformed veins, oblique to cleavage, usually with pytmgmatic folding; III) sub-vertical veins associated with late fractures. Stage I veins occur in a 2-3 m-thick layer enclosing multiple, centimetric white to light pink-brown alunite veins, mainly sub-vertical and sub-concordant with the principal cleavage. These veins are associated with a structural corridor mapped for 550 m. XRD data enable the positive identification of natroalunite NaAl1(SO4)2(OH)6, alunite KA1(PO4)2(OH)6, minamiite (Na,Ca)1-xAl3(SO4)2(OH)6, Wavellite Al3(PO4)2(OH)3 5H2O was also identified by PIMA.

At the S. João open pit, Al- and Fe- sulphate veins were also recognised, sub-parallel to narrow gossans distributed in a particular tectonic setting conditioned by the Messejana Fault, which is a major regional strike-slip fault with displacements that may reach up to 2 km length (Matos et al. 2010). XRD analysis allowed the identification of natrojarosite NaFe3(SO4)2(OH)6 and jarosite KFe3(SO4)2(OH)6, specially in stage III veins. Alunite was identified by PIMA in stage IIa veins.

3.4 S. Domingos

The S. Domingos mine is located near the border with Spain. This deposit was firstly exploited during the Roman era, and afterwards, during modern times, between 1857 and 1966, both in a large open pit, and in underground works that went 420 m deep (Matos et al. 2006). In the old pit, the local sequence is well exposed with a VSC sequence represented by rhyolites and black shales, which host the massive sulphide lense and the proximal stockwork, and voluminous, although late, diabase. The VSC sequence is confined to a sigmoidal structure oriented E-W that contacts by thrusts and left-lateral shearing with the Phyllite-Quartzite Formation, dated Famennian by palinmorphs (Matos et al. 2006).

At the S. Domingos deposit, kaolinitization is observed near the fault zones identified in the northern side of the open pit, affecting the rhyolite unit that hosts the stockwork. In the eastern sector of the pit, kaolinitization is more intense within the fault zones that cut diabases. The following alunite vein generations were recognised: I) deformed, sym-tectonic veins, sub-parallel to the main cleavage and to WNW-ESE shear zones; IIa) deformed veins, oblique to cleavage, usually with pytmgmatic folding (e.g., in late diabase); IIb) sub-horizontal vein networks; III) sub-vertical veins associated with late NE-SW strike-slip faults. The stage I and II veins occur in a large variety of lithologies: chloritized volcanics, black shales, silicified volcanics, diabases and volcanic breccias from the VS Complex; and shales from the Phyllite-Quartzite Group. In addition, PIMA data indicate the presence of barite associated with alunite. In the southern area of the pit, a dense network of stage IIb alunite veins was recognized, hosted by a volcaniclastic polymict breccia poorly affected by kaolinite alteration.

4 Discussion and conclusions

Strong kaolinitization of volcanic rocks and gossans is a well-known characteristic in many deposits of the Iberian Pyrite Belt, being considered a useful exploration guide both for outcropping, and for near surface massive sulphide mineralization. Mapping the kaolinite-halloysite alteration facies in Lagoa Salgada, Caveira, Lousal, S. João, Algares and S. Domingos has put in evidence a clear
alteration zonation that may help defining vectors for mineral exploration. This type of alteration is particularly pervasive near mineralized areas affected by fault zones. For instance, in Lagoa Salgada and Algares pervasive kaolinization of quartz-feldspar porphyritic volcanic rocks are perfectly visible in shear zones affected by stretching along cleavage. Late, sub-vertical geological structures also promote the development of supergene alteration, as observed in Lagoa Salgada down to 90 m below the paleotopography.

Study of the Al-sulphate vein morphology and distribution in the Lagoa Salgada, Algares, S. João and S. Domingos massive sulphide deposits shows several generations of veins as follows: I) deformed, syn-tectonic veins, sub-parallel to the main cleavage and to shear zones; IIa) deformed veins, oblique to cleavage, usually with ptygomatic folding; IIb) sub-horizontal vein networks; III) sub-vertical veins associated with late strike-slip faults. The alunite veins often occur associated to kaolinitization of the host rock. However, at the S. Domingos and Lagoa Salgada deposits, alunite veins have been observed in deep, non-oxidized horizons, where the hosting volcanic rocks were very poorly kaolinized. This evidence, coupled with the strong deformation and structural control of the stage I alunite veins, which occur parallel to the main cleavage and are most likely coeval with the verticalization and folding of the structure, strongly indicate that at least part of the alunite veins should predate the kaolinite-halloysite supergene alteration, having a different origin, certainly hypogenic and probably syn-tectonic. The evolution of the morphology and distribution of the veins from stage I to stage IIb (formation of the vein networks) suggest significant fluid pressure constraints, and favour a progressive deformation model for their build-up history.

The occurrence veins filled by alunite group minerals is coherent with very low pH and high Eh conditions for fluid circulation, at relatively low temperature (between 100°C and 300°C, Scher et al. 2013). The precipitation of alunite, besides K⁺ and Al³⁺, requires high concentrations of H₂SO₄ in the fluid. Alunite deposition can be driven by acidity produced during oxidative weathering of sulphide minerals. The oxidation and hydrolysis of iron from sulphides releases H⁺ and is the source of acidity, which dictates the water chemistry and drives subsequent reactions. In settings where the altered rocks are felsic, kaolinite and alunite can coexist. The VSC massive sulphide and stockwork mineralization hosted by intensely altered felsic volcanic rocks (pyrophyllite, silica, chlorite and sericite), can be the source of metals and acidity for tectonometamorphic fluids. The studied deposits were affected by strong shear deformation. The mode of occurrence, morphology and filling mineral assemblages of the alunite veins, as well as their relationships with the supergene alteration facies observed, are most likely related with sulphate fluid circulation (acid sulphate alteration) during the Late Variscan distensive phases. The occurrence of alunite veins demonstrates a complex geological history after the formation of some of the IPB orebodies. Intense acid fluid circulation correlated with metamorphism, tectonics and acid weathering may account for metal enrichment in several IPB deposits (e.g., Au and Ag at Lagoa Salgada and Algares orebodies).

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Geological controls on grade and tonnage in volcanogenic massive sulphide (VMS) deposits

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Abstract. Volcanogenic massive sulphide (VMS) Cu-Zn-Pb-(Au-Ag) deposits provide critical metals to the global economy. Deposits with exceptional grade and/or tonnage (high value deposits) are critical targets for modern mineral exploration and development. Most VMS deposits formed in extensional tectonic environments (e.g., arc rifts, back-arc basins, rifted continental margins) associated with high temperature magmatism. The largest VMS deposits were associated with sediment-rich continental/peri-continental arc rift/back-arc environments, whereas higher grade deposits are commonly associated with rifted continental/peri-continental arcs. Efficiency of process is another key factor in controlling grade and tonnage. The efficiency of metal extraction from source rocks, precipitation of a greater abundance of metals from upwelling hydrothermal vent fluids, and enhanced and prolonged zone refining during deposit evolution can all lead to greater tonnages and grades of mineralization. Moreover, magmatic fluids are implicated in the generation of many large and/or high grade VMS deposits, particularly those enriched in precious metals. Identification of geological and geochemical features that outline the right tectonostratigraphic setting and efficiency of processes is critical for finding the next generation of high value VMS deposits.

1 Introduction

Volcanogenic massive sulphide (VMS) deposits are important global sources of base metals (Cu-Zn-Pb) and precious metals (Au, Ag). They have been mined for millennia; however, new resources depend on finding high value deposits with greater tonnages and/or higher grades, so as to ensure longevity of mining and the ability to withstand volatility in metal prices in the longer term. In this paper the craton- to nano-scale factors that create high- value VMS deposits are evaluated.

2 Volcanogenic massive sulphides: the target

Volcanogenic massive sulphide (VMS) deposits form in extensional geodynamic setting associated with magmatism (Franklin et al. 2005; Galley et al. 2008; Piercey 2011). They are thermally convective hydrothermal systems whereby magmatic heat drives seafloor hydrothermal convection, where seawater convects through the underlying crust, reacts and alters the rocks extracts metals and other ligands into the hydrothermal, and subsequently moves upwards toward the seafloor along synvolcanic and synsedimentary faults (Franklin et al 2005; Galley et al. 2007). At or near the seafloor the fluids mix with seawater to precipitate massive sulphide on the seafloor (exhalative sulphides) and/or below the seafloor (subseafloor replacement-type sulphides)(Doyle and Allen 2003; Franklin et al 2005; Galley et al. 2007; Piercey 2015). This process is diachronous and often the sulphide mounds undergo zone refining resulting in the well-developed metal zoning observed in VMS deposits (i.e., Cu-rich core, Zn-Pb-(Ba)-rich outer parts)(e.g., Eldridge et al. 1983; Large 1992; Ohimoto 1996).

3 Controls on grade and tonnage

The generation of high value deposits requires the generation of deposits with high tonnages and/or high grades. Efficiency of process, including efficiency of precipitation and zone refining, tectonics and crustal architecture of a given area, and deposit preservation also play a role. Outlined below are the various potential processes that play a role in forming high-value VMS deposits.

3.1 Tectonics and crustal architecture matter

Throughout geological time VMS deposits are associated with extensional tectonic environments and high temperature magmatism (Piercey 2011, and references therein). The cumulative contained base metal in VMS deposits as a function of VMS deposit sub-class is shown in Figure 1. Notably, deposits with greatest tonnages are associated with felsic volcanic rocks, and in belts that are partially to fully underlain by continental crust (e.g., Piercey 2011). Moreover, VMS deposits have a distinctive clustering through geological time with peaks in the Neoproterozoic (~2.7 Ga), Paleoproterozoic (~1.8-1.9 Ga), Cambrian-Ordovician (~0.51-0.46 Ga), Devonian-Mississippian (~0.39-0.35 Ga), and Mesozoic-Cenozoic (~0.2-0.1 Ga)(Fig. 2). The distribution of massive sulphides is partly related to preservation (Cawood and Hawkesworth 2013), but also reflects supercontinent assembly and extensional accretionary orogenesis (e.g., Huston et al. 2010). In general, the largest VMS deposits (e.g., Brunswick #12; deposits of the Iberian Pyrite belt) were associated with sediment-rich, rifted continental margin arcs and back-arc basins, whereas the highest grade deposits were generally associated with rifted continental arcs (e.g., Buchans, Hellyer, Greens Creek).

3.2 Precipitation efficiency

Volcanogenic massive sulphide systems are remarkably inefficient and in modern hydrothermal vents only 1-5%
metal precipitates from the upwelling hydrothermal fluid (Converse et al. 1984). To form the large deposits found in the ancient geological record precipitation efficiency must have been greater with greater. Some of the largest VMS deposits are found in volcaniclastic- and sediment-rich geological environments, and many are associated with shale-rich sequences that have evidence for deposition under anoxic conditions (e.g., Franklin et al. 2005; Goodfellow 2007). Many deposits in volcaniclastic- and sediment-rich environments have evidence for formation via subseafloor replacement, which resulted in deposition of sulphide both on the seafloor and in the shallow subseafloor, resulting in larger deposits (Doyle and Allen 2003; Piercey 2015). In ancient sediment-rich basins with anoxic conditions the sedimentary pile and ambient water column had excess free H2S, which led to the precipitation of greater amounts of sulphide relative to normal oxygenated basins with SO4-rich bottom waters (e.g., Goodfellow 2007). Both replacement and anoxic waters have been important in some environments for increasing precipitation efficiency and generating higher tonnage deposits.

3.3 Increasing grade

One of the main mechanisms to increasing grade in VMS deposits is zone refining (Eldridge et al. 1983; Large 1992; Ohmoto 1996; Schardt and Large 2009). Many high grade VMS deposits had diachronous histories with early low temperature (<300°C) Zn-(Pb-Ba) deposition, followed by a higher temperature (>300°C) phase of Cu-deposition (Fig. 3). During the evolution of a massive sulphide mound dissolution of earlier formed Zn-(Pb)-rich sulphides by later hotter, Cu-rich fluids resulted in dissolution of earlier formed Zn-Pb sulphides with Zn and Pb returned to solution, coupled with deposition of Cu-rich sulphides in their place (Eldridge et al. 1983; Large 1992; Ohmoto 1996; Schardt and Large 2009). In efficient systems, during this process the Zn and Pb that were returned to solution eventually re-precipitated near the mound/deposit edge or into the overlying water column (Fig. 2). If this process is long-lived and efficient, and there is a sufficient semi-permeable cap rock (e.g., barite, anhydrite, volcaniclastic rocks, sediments), it leads to the formation of well-zoned, high-grade Zn-Pb-Cu deposits (Fig. 2).

The semi-permeable cap rock appears to be a critical component for facilitating enhanced re-precipitation and enhancing grade (Schardt and Large 2009; Piercey 2015). There are numerous examples of high-grade mineralization associated with semi-permeable cap rocks, including barite (e.g., Buchans, Hellyer), volcaniclastic rocks (e.g., Matagami), and semi-permeable sedimentary rocks (e.g., Wolverine). Empirically, it appears that semi-permeable cap rocks coupled with zone refining are important for increasing grade in VMS deposits (Schardt and Large 2009; Piercey 2015).

Figure 2. Distribution of tonnage of VMS deposits through geological time. Database utilized from Huston et al. (2015).

3.4 Are magmas important?

It is well known that magmatic heat is critical in driving hydrothermal circulation in VMS systems (e.g., Galley et al. 2007; Piercey 2011, and references therein); however, the role of magmatism in ancient VMS deposits is less well defined. In modern seafloor massive sulfide (SMS) systems, there are numerous arguments to suggest magmatic fluids contributed to the metal and fluid budget of SMS deposits (e.g., Yang and Scott 1996; de Ronde et al. 2011). In the ancient record the evidence is more circumstantial. Nevertheless, many ancient deposits that are exceptionally enriched in metals, including precious metals and/or are large, have varying combinations of: aluminous
alteration assemblages commonly associated with magmatic-hydrothermal ore systems; S isotope systematics indicative of magmatic SO2 disproportionation indicative of magmatic volatile input; O-H isotopes indicative of magmatic fluid input; anomalous mineral assemblages typical of magmatic hydrothermal deposits (e.g., sulfosalts-rich); and enrichments in elements typical of magmatic-hydrothermal ore deposits (e.g., Sn-W-Bi-Te-Sb-As-Au-Ag) (e.g., Sillitoe et al. 1996; Hannington et al. 1999; Relvas et al. 2006; Goodfellow 2007; Huston et al. 2011; Mercier- Langevin et al. 2011; Brueckner et al. 2016). Collectively, these results are consistent with some high grade and/or large and/or precious metal-enriched VMS deposits containing a magmatic fluid/volatile component in their genesis.

4 Summary

Finding high value VMS deposits is critical for the future metal supply of the planet and it requires integrated field to laboratory approaches that consider processes from a craton- to nano-scale. Identification of the right locales on the planet where these processes have taken place are critical to finding the next generation of resources. Extensional accretionary environments along pericontinental and continental margins are particularly productive tectonic settings throughout geological time. Moreover, identification of sub-settings where precipitated efficiency is likely to be enhanced (e.g., volcaniclastic- and sediment-rich belts), and the probability of zone refining is increased, are critical for finding large and/or high grade deposits. Finally, while difficult to prove conclusively, some belts and deposits exhibit evidence for magmatic fluid input into VMS hydrothermal systems – these belts may also yield deposits that are large and/or high grade and/or enriched in precious metals.

Acknowledgements

Discussions with the following people have influenced the ideas presented within: Rod Allen, Maurice Colpron, Bruce Eglington, Jim Franklin, Alan Galley, Bruce Gemmell, Harold Gibson, Wayne Goodfellow, Mark Hannington, Richard Herrington, John Hinchee, David Huston, Ross Large, Dan Layton-Matthews, Patrick Mercier-Langevin, Thomas Monecke, Don Murphy, JoAnne Nelson, Sally Pehrsson, Jan Peter, and Lawrence Winter. Their ideas have shaped the way I see VMS deposits and I thank them for this. Steve Piercey is funded by an NSERC Discovery Grant.

References


Figure 3. Zone refining model for VMS deposits based on the concepts of Eldridge et al. (1983). Figure modified from Large (1992)

Large RR (1992) Australian volcanic-hosted massive sulfide deposits; features, styles, and genetic models. Econ Geol 87: 471-510


Types of sediment-matrix igneous breccias in the VHMS host sequence of the Iberian Pyrite Belt

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Abstract. Sediment-matrix igneous breccias are common in the Iberian Pyrite Belt. These rocks enclose volcanic and sedimentary components and, despite being formed by contrasting processes, therefore assuming different meanings and implications, they often show similar textures. The correct identification of these breccias is decisive for the interpretation of their volcanic and/or sedimentary formation processes, as well as for the interpretation of their host lithostratigraphic sequence. The Volcanic-Sedimentary complex of the Iberian Pyrite Belt hosts one of the most outstanding accumulations of massive sulphide mineralization on earth. Therefore, the interpretation of the volcanic and sedimentary units, their emplacement relations and environment of deposition is critical for understanding the geological evolution of the belt and, consequently, the depositional setting(s) of the massive sulphide ores. The contact between volcanic and sedimentary units assumes special importance in this context specially when it consists of breccias made of volcanic and sedimentary components. Their accurate interpretation is critical for understanding the position of the mineralization in the hosting sequence and its mode and timing of formation, with obvious implications for exploration in this remarkable province.

1 Introduction

The Iberian Pyrite Belt (IPB) is located in southern Portugal and Spain and hosts 1850 Mt of sulfide ore in more than 92 massive sulphide deposits (Leistel et al. 1998). The VHMS deposits are hosted by the Volcanic-Sedimentary Complex (VSC), a submarine bimodal volcanic and sedimentary sequence of Upper Devonian to Carboniferous age that overlies marine siliciclastic sedimentary facies deposited in a continental platform setting (Phyllite-Quartzite Group) and is overlain by a thick marine turbiditic sequence (Baixo Alentejo Flysch Group) (Oliveira 1990).

The VSC can be very thick (600 to 1300 m; Silva 1997; Leistel et al. 1998; Tornos 2006) and is dominated by sedimentary facies, mainly hemipelagic mudstone, locally with discontinuous jasper beds. The volcanic units of the VSC are mainly felsic (rhyolitic and rhyodacitic) comprising coherent and monomictic breccia facies and pyroclastic units (Rosa et al. 2010). Mafic coherent and monomictic breccia facies are relatively minor. The felsic facies consist mainly of thick intervals of monomictic breccia with jigsaw-fit and clast-rotated domains that overlie or surround compositionally similar intervals of coherent facies. The sediment-matrix (felsic) igneous breccia occurs at the contacts with sedimentary facies, typically with overlying mudstone. Some examples of bedded felsic monomictic breccia occur above or beside the intervals of felsic coherent and monomictic breccia facies. Pyroclastic units of felsic composition consist of wispy fiamme (formerly pumice clasts; e.g. Bull and McPhie 2007), dense felsic clasts, quartz and feldspar crystals or crystal fragments, and fine (<1 mm) matrix. However, thick (several to tens of m) pyroclastic units are typically massive or weakly graded and laterally extensive (>5 km). Other pyroclastic units occur in thin or thick beds, some of which have a matrix of non-volcanic mudstone (Rosa et al. 2010).

The VSC formed in a submarine depositional setting. This is indicated by the abundant and diverse marine fossils that occur in the sedimentary units, such as radiolarian, conodonts, dasycladales and ammonoids (Boogaard 1963; Oliveira 1990; Korn 1997; Oliveira et al. 2004; Rosa 2007; Rosa et al. 2010), and also due to the abundance of massive sulfide deposits throughout the province. Thick intervals of black mudstone and turbidites, and the open-marine habitat of some fossils (Boogaard and Schermerhorn 1980; Oliveira 1990; Korn 1997) collectively indicate that the VSC, or most of it, formed below wave base.

2 Types of sediment-matrix igneous breccias

Sediment-matrix igneous breccias were identified and described by Rosa et al. (2016). Five different types of breccias were defined and interpreted, showing that breccias having similar textures may have been formed by significant different processes, which have implications in the interpretation of the stratigraphy of the sequence that contains the breccias. In the IPB, or in most other mineralized volcanic-sedimentary sequences,
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The sediment-matrix igneous breccias defined in the IPB can form in any submarine environment where volcanism and sedimentation are concomitant. Therefore, other volcanic-sedimentary sequences formed in submarine settings can have similar types of breccias, irrespective of their age. It is important to note that the breccias contain coarse (>2 mm), angular or ragged, porphyritic igneous clasts. In each case, the igneous clasts all have the same texture and phenocryst population, suggesting that they have the same composition and came out from the same source.

The five types of breccias identified in the IPB (Rosa et al., 2016) are: 1) peperite; 2) sediment-infill volcanic breccia; 3) mud-matrix resedimented hyaloclastite; 4) mud-rich water-settled fiamme breccia; 5) apparent sediment-matrix igneous breccia.

2.1 Peperite

Peperite results from interaction between hot, molten magma and unconsolidated sediment. This interaction results in the dismembering of both the magma and the host sediment (White et al. 2000; Skilling et al. 2002). Sediment-matrix igneous breccias interpreted to be peperite in the IPB by Rosa et al. (2016) consist of a complex combination of igneous clasts and sedimentary domains. They occur at the base or top of thick intervals of coherent and monomictic breccia facies. The igneous clasts can be felsic or mafic and are texturally and mineralogically identical to associated coherent and monomictic breccia facies of felsic or mafic composition. These clasts may show quenched margins and are blocky with planar or curviplanar margins, or ragged or fluidal in shape. The igneous clasts occur in a sedimentary matrix that grades into the underlying planar and laminated mudstone, indicating that the peperite matrix was originally part of the mudstone. Between the igneous clasts the laminations of the mudstone in the matrix can be contorted and disrupted, or the mudstone can be massive, and mudstone can occur in short and thin fractures in the igneous clasts. The presence of peperite at the base of igneous units indicates that they have emplaced over, or into unconsolidated sediment. The presence of peperite along the top contact of igneous units indicates they are intrusions that have intruded into unconsolidated sediment.

2.2 Sediment-infill volcanic breccia

Sediment-infill volcanic breccias comprise deposition of fine detrital or chemical sediment in the spaces between framework-supported volcanic clasts of a pre-existing breccia. These breccias form in subaqueous environments and occur at the top contact of lavas or domes with a carapace of coarse hyaloclastite. The infiltration of sediment into the clastic rock is presumably a common process in submarine environments, as documented in modern examples at the Mid-Atlantic Ridge (Costa et al. 1997; 2000) since settling of fine particles from suspension will occur almost continuously during quiet periods of acquecence between eruptions. In the IPB examples (Rosa et al. 2016) of the sedimentary matrix is massive or planar laminated and grades into the overlying bedded sedimentary units. Additionally, the laminae in adjacent sedimentary domains of the breccia matrix are, in these domains, conformable with the regional bedding. The sediment settles from suspension in the interstitial water, and/or is deposited from dilute water currents moving through void space between clasts. The conformity of bedding in adjacent domains of the breccia and its presence of bedding, its parallelism with regional bedding, indicates that the sedimentary matrix emplaced after the formation of the clastic framework and the lamination probably formed by settling from suspension of hemipelagic mud in the void spaces of clastic framework.

2.3 Mud-matrix resedimented hyaloclastite

Formation of hyaloclastite is common in lavas and domes that emplace in a subaqueous setting, and its remobilisation is typical due to the collapse and downslope movement of the loose and unstable hyaloclastite (Yamagishi and Dimroth 1985; Yamagishi 1987). Remobilisation of the hyaloclastite clasts may involve transport in density currents that spread past the igneous source, and move over unconsolidated sediment, incorporating it. This breccia occurs in conformable beds that can have irregular erosional contacts and the internal laminae of the rip up sedimentary clasts have random orientation. The breccias grade upward into the overlying sediments. Therefore, the igneous components were sourced from unstable hyaloclastite and the sedimentary components from mud that formed the seafloor.

2.4 Mud-rich water-settled fiamme breccia

Pumice clasts produced near water can cool in air before falling into water and become water-logged relatively slowly, remaining in suspension for long periods (e.g. Whitham and Sparks 1986; Gifkins et al. 2002; McPhie and Allen 2003; Stewart and McPhie 2003). These clasts can travel long distances and deposit away from their sources, sinking at the same time as much finer (mud) pelagic or hemipelagic sediment or ash. This process produce a deposit composed of coarse pumice clasts defining layers or scattered in very fine laminated or massive sediment. In old volcanic-sedimentary successions compaction and diagenesis can change the appearance of the pumice clasts (Bull and McPhie 2007) forming fiamme due to the collapse of the void vesicles. The mudstone matrix is typically thinly laminated or massive. The occurrence of pumice and mud indicates that they were deposited simultaneously by suspension and had similar low densities.
2.5 Apparent sediment-matrix igneous breccia

This category is extremely important in hydrothermally altered volcanic successions that were altered by ore-forming hydrothermal fluids, because hydrothermal alteration can greatly modify original textures and produce apparently clastic textures (Doyle and Allen 2003; Gifkins et al. 2005). An apparent breccia texture can form by hydrothermal alteration along fractures in coherent facies or in monomictic jigsaw-fit igneous breccia. Patchy alteration of igneous texture can create a texture made of porphyritic apparent igneous clasts in a clastic matrix. The textural patterns depend of the primary characteristics of the coherent facies, the water-rock interaction processes and the composition of the fluid(s) involved (Gifkins et al. 2005). In the IPB, the domains that resemble sedimentary matrix consist of fine-grained secondary minerals (chlorite, silica and sericite) that occupy fractures and replace the adjacent igneous domains (Rosa et al. 2016). In some examples, the hydrothermal alteration mineral assemblage includes abundant sulphides (Relvas et al. 2001; Tornos et al. 2005).

3 Conclusions and exploration implications

Sediment-matrix igneous breccias are abundant in the VSC of the IPB (Rosa et al. 2016) but can occur in volcanic sedimentary sequences of any age. They are formed by a combination of typically monomictic, porphyritic or aphyric igneous clasts and a sedimentary matrix of variable composition (volcanic sediment, non-volcanic sediment, or a combination).

Distinguishing lavas or domes from intrusions may depend critically on the correct interpretation of sediment-matrix igneous breccias, as syn-volcanic intrusions and lavas can be compositionally and texturally similar. Sediment-matrix igneous breccias may be present along the upper contacts of both intrusions and lavas or domes; in the former, the sediment-matrix igneous breccia is peperite, whereas in the latter, it is sediment-infill volcanic breccia. The correct interpretation of sediment-matrix igneous breccias is therefore critical, especially when they are present at the top contacts of coherent facies intervals. They help to distinguish lavas from intrusions, in determining the timing of sedimentary, volcanic, intrusive and hydrothermal events, and in the recognition of seafloor positions. Intrusions are younger than the host succession, and do not mark seafloor positions. They typically disrupt and complicate the stratigraphic sequences. Correct identification of intrusions is important, particularly in VHMS successions where recognition of seafloor positions is critical for massive sulphide exploration.

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Source of salinity in the Broken Hill (Australia) Pb-Zn-Ag deposit: insights from halogen ratios in fluid inclusions

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Abstract. Ratios of Na/Br, Br/Cl, and I/Cl were determined on leachates of fluid inclusions from the Broken Hill Pb-Zn-Ag deposit in Australia. Paragenetic relations suggest that whereas all analyzed inclusions formed during or after regional metamorphism, ion ratios are not greatly changed from those of the pre-metamorphic ore-forming fluids. Based on relatively high Br/Cl and I/Cl ratios, and low Na/Br ratios, we suggest that the high salinities that characterize Broken Hill fluid inclusions reflect a source dominated by evaporated seawater and not dissolved evaporites.

1 Introduction

Constraints on the source of salinity in clastic-dominated (CD) stratiform Pb-Zn deposits are important for understanding processes of mineralization. However, only limited data are available for this deposit type, owing to the general paucity of primary fluid inclusions available for study. Here we report halogen ratios and other ion data obtained from fluid inclusions in the Broken Hill (Australia) Pb-Zn-Ag deposit, which has the greatest amount of contained Pb + Zn (51.8 Mt) among all 120 CD Pb-Zn deposits worldwide (Taylor et al. 2009). Although fluid inclusions in the Broken Hill deposit are uniformly secondary, due to pervasive recrystallization during post-ore deformation and metamorphism, our results provide some insights into the source of salinity for this historically important, super-giant ore deposit.

2 Geologic setting

The stratiform Broken Hill Pb-Zn-Ag deposit is contained within a late Paleoproterozoic sequence consisting of siliciclastic metasedimentary and minor metavolcanic rocks (Stevens et al. 2008). Protoliths are interpreted to be shale, sandstone, minor rhyolite and tholeiitic basalt, plus rare limestone and non-marine evaporites (Stevens et al. 2008). The deposit is multiply deformed and highly metamorphosed. U-Pb geochronological studies demonstrate that the felsic volcaniclastic protolith of the Hores Gneiss, which hosts the stratiform ores, formed at 1685 ± 3 Ma (Page et al. 2005). Based on field and geochronological studies (Stevens 1986; Raetz et al. 2002; Page et al. 2005), important later events were granulite-facies metamorphism at ca. 1600 Ma, retrograde schist formation at 1600-1570 Ma, and greenschist-facies metamorphism at ca. 520 Ma; granites and pegmatites were emplaced at 1683 ± 5, 1597 ± 3, 1591 ± 5, ca. 1490, and ca. 500 Ma; tholeiitic basalts—now amphibolites—formed as flows, sills, and/or dykes at 1690-1670 Ma. A major retrograde shear zone cuts the deposit and may have controlled the shape of the orebodies (Rothery 2001).

The main Pb-Zn-Ag deposit forms a set of six stacked lenses (lodes) of semi-massive to massive sulphide 7.3 km long, 250 m wide, and up to 850 m in vertical extent (e.g., Plimer 1984; Groves et al. 2008). From stratigraphic base to top, these are designated C lode, B lode, A lode, No. 1 lens, No. 2 lens, and No. 3 lens. Proportions of ore and gangue minerals vary widely among different lodes. Galena and sphalerite are major ore minerals, accompanied by minor pyrrhotite, chalcopyrite, arsenopyrite, loellingite, and sulphosalts; gangue minerals are dominantly quartz, calcite, fluorapatite, fluoride, bustamite, rhodonite, hedenbergite, and K-feldspar, with minor garnet, garnhite, pyroxmangite, micas, and amphiboles. Distinctive wall rocks contain abundant Fe- and Mn-rich garnets (Spry et al. 2007). Broken Hill is also famous for a diverse suite of secondary minerals including Cl-, Br-, and I-rich phases such as chlorargyrite, bromargyrite, and iodargyrite (Plimer 1984).

3 Previous fluid inclusion studies

Wilkins (1977) first described fluid inclusions from the main Pb-Zn-Ag lodes and documented diverse types occurring in different settings and host minerals. Ten types were recognized, containing varying proportions of aqueous solution, gas (locally CO2 and/or CH4), liquid CO2, and myriad daughter crystals (NaCl ± birefringent ± isotropic). Wilkins and Sverjensky (1977) reported on saline fluid inclusions in bustamite and their relationship to clinopyroxene exsolution. Wilkins and Dubessy (1984) distinguished three families of fluid inclusions and a chronological order based on Raman microprobe gas analyses: approximately equimolar N2-CH4-CO2 in blue lode quartz and pegmatite, approximately equimolar CH4-CO2 in the discordant vein quartz, and N2-CH4 and N2-CO2 both in varying ratios in shear-zone quartz. Williams et al. (2005) presented in situ Pb and Zn data for high-salinity
fluid inclusions. No previous publication has reported Br or I contents, or their ratios, in fluid inclusions from the Broken Hill deposit.

4 Samples and methods

Table 1 lists information on samples analyzed in this study, locations, mineral hosts, and types of fluid inclusions present. Details on the fluid inclusion assemblages and related data are available in Wilkins (1977), Wilkins and Sverjensky (1977), and Wilkins and Dubessy (1984). All fluid inclusions analyzed in this study are syn- to post-metamorphic; those in the bustamite sample are considered to have formed during post-peak prograde metamorphism based on their paragenesis during exsolution of associated clinopyroxene (Wilkins and Sverjensky 1977).

Table 1. Analyzed samples and major fluid inclusion types.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mine location</th>
<th>Host mineral</th>
<th>FI types</th>
</tr>
</thead>
<tbody>
<tr>
<td>37683f</td>
<td>ZC 18 L</td>
<td>Bustamite</td>
<td>Large HS</td>
</tr>
<tr>
<td>37683c</td>
<td>ZC 18 L</td>
<td>Bustamite</td>
<td>Large HS</td>
</tr>
<tr>
<td>37687</td>
<td>Unknown</td>
<td>Quartz</td>
<td>Small LS+HS</td>
</tr>
<tr>
<td>37687</td>
<td>Unknown</td>
<td>Hedenbergite</td>
<td>Small LS+HS</td>
</tr>
<tr>
<td>39713f</td>
<td>North 27 L</td>
<td>Quartz (V)</td>
<td>Large LS+HS</td>
</tr>
<tr>
<td>39713c</td>
<td>North 27 L</td>
<td>Quartz (V)</td>
<td>Large LS+HS</td>
</tr>
<tr>
<td>37693</td>
<td>North 24 L</td>
<td>Knebelite</td>
<td>Large HS</td>
</tr>
<tr>
<td>36431</td>
<td>ZC A Lode</td>
<td>Quartz (B)</td>
<td>Small HS</td>
</tr>
<tr>
<td>39728</td>
<td>NBHC 14 L</td>
<td>Quartz (Peg)</td>
<td>Small Complex*</td>
</tr>
</tbody>
</table>

Abbreviations: f, fine grained, c, coarse grained, L, level, V, vein; B, blue; Peg, pegmatite; HS, high salinity (one or more daughter salts), LS, low salinity (no daughter salts).

Notes: All samples are from the main Pb-Zn-Ag lodes, except 39713 (discordant quartz vein) and 39728 (quartz-feldspar pegmatite internal to B Lode). Large inclusions are > ca. 10 μm.

*Fluid inclusions are both low and high salinity and contain CO₂, N₂, and CH₄ in approximately equal molar proportions.

Analysis was done following Yardley et al. (1993). This procedure involves atomic emission spectroscopy of cations and ion chromatography of anions in leachates from fluid inclusions in crushed mineral separates.

5 Results

Key molar ion ratios discussed in this paper are listed in Table 2. Ranges of other ratios determined include Na/Cl (0.26-0.66) and Na/SO₄ (1.12-195.0).

Table 2. Selected ion ratios in Broken Hill fluid inclusions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Host mineral</th>
<th>Na/Br</th>
<th>Cl/Br</th>
<th>Br/Cl</th>
<th>I/Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>37683f</td>
<td>Bustamite</td>
<td>101.4</td>
<td>153.4</td>
<td>0.0065</td>
<td>1.802E-04</td>
</tr>
<tr>
<td>37683c</td>
<td>Bustamite</td>
<td>85.11</td>
<td>223.5</td>
<td>0.0045</td>
<td>1.635E-04</td>
</tr>
<tr>
<td>37687</td>
<td>Quartz</td>
<td>153.1</td>
<td>599.5</td>
<td>0.0017</td>
<td>4.118E-05</td>
</tr>
<tr>
<td>37687</td>
<td>Hedenbergite</td>
<td>116.5</td>
<td>444.8</td>
<td>0.0022</td>
<td>3.325E-05</td>
</tr>
<tr>
<td>39713f</td>
<td>Quartz (V)</td>
<td>479.2</td>
<td>940.4</td>
<td>0.0011</td>
<td>6.793E-05</td>
</tr>
<tr>
<td>39713c</td>
<td>Quartz (V)</td>
<td>438.4</td>
<td>849.9</td>
<td>0.0012</td>
<td>4.269E-05</td>
</tr>
<tr>
<td>37693</td>
<td>Knebelite</td>
<td>140.2</td>
<td>296.6</td>
<td>0.0034</td>
<td>5.202E-05</td>
</tr>
<tr>
<td>36431</td>
<td>Quartz (Blue)</td>
<td>112.9</td>
<td>422.2</td>
<td>0.0024</td>
<td>1.349E-05</td>
</tr>
<tr>
<td>39728</td>
<td>Quartz (Peg)</td>
<td>100.5</td>
<td>153.0</td>
<td>0.0065</td>
<td>2.776E-05</td>
</tr>
</tbody>
</table>

Molar ratios of I/Cl vs Br/Cl in the Broken Hill samples (Fig. 1) plot nearly wholly within the field for modern formation waters and also mostly within the field for Midcontinent (USA) Mississippi Valley Type (MVT) Zn-Pb deposits. Data for one sample of bustamite (two size fractions) are within the field for sandstone-hosted Pb-Zn deposits. All data have higher I/Cl ratios than that of modern seawater. Excluding results for the quartz vein sample (two size fractions), Cl/Br ratios are uniformly lower than those of magmatic-hydrothermal ore deposits (>750); Na/Cl ratios are lower than those of Phanerozoic orogenic Au deposits (>0.7) (Hofstra et al. 2016).

Figure 1. Molar ratios of I/Cl vs Br/Cl for inclusion fluids from Broken Hill. Other data shown are from Campbell et al. (1995), Kendrick et al. (2011), and Yardley (2013). Retrograde metamorphic fluid trend is adapted from Svensen et al. (2001). SET, seawater evaporation trend.

A plot of molar ratios for Na/Br vs Cl/Br (Fig. 2) shows that all of the Broken Hill data fall within, or close to, the fields for Irish Zn-Pb deposits and world MVT Zn-Pb deposits but generally at ratios much lower than seawater.

Figure 2. Molar ratios of Na/Br vs Cl/Br for inclusion fluids from Broken Hill. Shown for comparison are data for other ore deposits and fluids (Banks et al. 2002; Leach et al. 2004). SET, seawater evaporation trend.
6 Discussion

Evaluating the source of salinity in Broken Hill fluid inclusions requires careful consideration of major constraints and uncertainties. The first issue is the fluid source for the fluid inclusions, given that all such inclusions formed during or after granulate-facies metamorphism at \( \sim 1600 \) Ma, about 85 m.y. after Pb-Zn-Ag mineralization assuming that the ores originated mainly by synsedimentary or diageneric processes (e.g., Parr et al. 2004). Second is the salinity source, in light of diverse mechanisms that can produce high salinities within a highly deformed and metamorphosed hydrothermal ore deposit. Both of these issues are discussed below.

6.1 Potential fluid sources

The development of high fluid flux in metamorphic terranes can reflect one or more fluid sources. Candidates include pre-metamorphic hydrothermal or basinal fluids, syn-metamorphic fluids related to devolutilization reactions, syn- to post-metamorphic fluids linked to retrograde reactions, granite-related hydrothermal fluids (pre-, syn-, or post-metamorphic), and surface-derived fluids (e.g., Kendrick and Burnard 2013). Discriminating among these possible fluid sources in the Broken Hill deposit is difficult owing to the complex deformational and metamorphic history of the area. An important oxygen isotope study by Cartwright (1999) provides some constraints, showing that \( \delta^{18}O \) values progressively decrease with proximity to the main sulphide lodes, thus suggesting a genetic relationship to pre-metamorphic, low-\( ^{18}O \) hydrothermal fluids. These putative fluids could be linked to the primary Pb-Zn-Ag mineralizing event, or to the emplacement of early granites; a localized flux of retrograde fluids cannot be ruled out, however, based on the presence of aqueous fluid inclusions in some granulites (Touret and Nijland 2013). The latter possibility is consistent with the occurrence of high bulk Rb/Sr ratios and abundant sericite in a zone at least 300 m wide that envelopes the Broken Hill deposit (Plimer 1975).

6.2 Ion ratios and salinities

Given the anhydrous nature of the metamorphic minerals that host the fluid inclusions studied here (Table 1), a first-order evaluation must consider possible fractionation of halogens (Cl, Br, I) between the fluid phase and other prograde metamorphic minerals in the Broken Hill deposit and surrounding wall rocks. The only hydrous mineral therein is fluoroapatite (Plimer 1984), which everywhere contains a maximum of ca. 50 ppm Br that during metasomatism is preferentially fractionated into fluids and not apatite (Kusebauch et al. 2015). These data suggest that the Br (and I) inventory of the hypogene Pb-Zn-Ag ores is dominated by fluid inclusions and not by fluoroapatite (or other minerals). The Na inventory is similarly constrained, based on the scarcity and absence of albite and scapolite, respectively, and the lack of any other Na-rich minerals within the deposit (Plimer 1984). Metamorphic fractionation, including gravitational fractionation, of Cl, Br, and I cannot be ruled out, however (see Bons and Gomez-Rivas 2013; Teiber et al. 2015).

Another potential source of high-salinity fluids is felsic igneous rocks. This source is permissive, based on the Br/Cl and I/Cl field for I-type magmatic-hydrothermal fluids that is positioned at one end of the trend for the Broken Hill data (Fig. 1). However, this possible source is considered unlikely because all of the Paleoproterozoic felsic metavolcanic and metagranitgneisses at Broken Hill (e.g., Hores Gneiss, Rasp Ridge Gneiss) have S-type and not I-type geochemical affinities (Raveggi et al. 2008).

A third parameter to consider is a contribution of high-salinity fluids produced during retrograde metamorphism (e.g., Crawford et al. 1979; Yardley and Graham 2002). This is important, owing to strong evidence for such overprinting on the Broken Hill deposit and surrounding wall rocks (Plimer 1975; Cartwright 1999). However, retrogression of granulites yields high Br/Cl but low I/Cl ratios, both related to fluid/muscovite fractionation (Svensen et al. 2001), which is opposite the trend shown by data for the Broken Hill fluid inclusions (Fig. 1). Thus, on balance, we think retrograde processes did not greatly affect the ratios of these halogens. This interpretation is supported by the fact that fluid inclusions in the bustamite are post-peak metamorphic and not significantly younger (e.g., no hydrous daughter minerals are present).

Final consideration is given to the possibility that melting of the Broken Hill orebody affected halogen systematics of the fluid inclusions. Williams et al. (2005) reported that saline fluid inclusions in one sample of blue and surrounding white quartz from the Western A Lode contain extremely high Pb/Zn ratios that could reflect equilibration with a syn-metamorphic sulphide melt (cf. Frost et al. 2011). However, the overall high Pb/Zn ratio (1.2) of the Broken Hill orebody does not require a high-grade metamorphic origin, because Pb/Zn ratios of 1.0 and 3.0 characterize, respectively, the greenschists-facies Sullivan Pb-Zn-Ag deposit in Canada and the sub-greenschists-facies Lih Pb-Zn deposit in Alaska (Taylor et al. 2009). Related is the proposal by Mungall and Brenan (2003) that aqueous fluids evolved from sulphide melts have low Br/Cl ratios, i.e., less than that of seawater. However, the Broken Hill Br/Cl ratios are higher than the seawater value (Fig. 1), a pattern that is inconsistent with control of these ratios by a sulphide melt. Williams et al. (2005) concluded that high-salinity and Pb-rich fluids in inclusions at Broken Hill were externally derived, late- to post-metamorphic fluids. This model may be correct for inclusions in retrograde minerals and late fractures, but our data for inclusions in syn- to post-peak metamorphic bustamite argue against this interpretation.

Slack et al. (1989, 1993) presented isotopically light B values in tourmaline from the Broken Hill block that suggest the former presence of non-marine evaporites in deep footwall strata beneath the deposit. However, if the halogen ratios of the fluid inclusions reported here are broadly similar to those of the pre-metamorphic ore-
forming fluids, especially Cl/Br ratios that are less than that of seawater (Fig. 2), then leaching of evaporates is discounted and a preferred source of the high salinities is seawater that evaporated past the point of halite saturation.

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Structurally controlled fluid flow pathways in the Irish Zn–Pb ore field: Insights from metal distributions at the Lisheen and Silvermines deposits

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Abstract. The world-class Irish Zn-Pb(-Ag) deposits comprise one of the major metallogenic provinces in the world. The location of these orebodies is structurally controlled, but it is not well understood exactly how fluids migrated from source to sink. This study, therefore, investigates metal distribution patterns at the Silvermines and Lisheen deposits to gain insights into these fluid pathways and the structural controls on mineralisation. Distinct points along segmented normal faults are seen to serve as feeders to individual orebodies. These feeders are characterised by highly localised and elevated Ag, Cu, Ni and As concentrations as well as low Zn/Pb ratios which increase away from these feeders. Metal distributions are initially controlled by major and minor normal faults, and affected by later oblique-slip dextral faults and strike-slip faults. High tonnage areas without typical feeder signals are interpreted to be structural trap sites which are distal to fault-controlled feeder points. This study highlights the importance of a well-connected plumbing system for metal-bearing fluids to reach their basinal traps.

1 Introduction

Understanding the structural control and metal distribution in Irish-type Zn-Pb deposits is of key economic importance for exploitation and exploration in the Irish Midlands. This study aims to gain insights into the local controls on mineralisation, locate the position of feeder zones, and track fluid pathways along faults and through host lithologies from proximal to distal areas of the deposit. To this end, metal distribution patterns, and their relation to structural and stratigraphic frameworks, are investigated at two Irish-type deposits, Lisheen and Silvermines.

The term feeder is used in mineral deposits to refer to locations where metal bearing fluids enter the site of mineralisation. Mineralisation occurs by replacement of Lower Carboniferous marine carbonates due to fluid mixing of high temperature, high salinity, reducing metal-bearing fluids and low temperature, medium salinity seawater derived fluids (Wilkinson et al. 2005, 2009; Barrie et al. 2009; Wilkinson 2010). The majority of ore-stage fluid inclusions show homogenisation temperatures of 130-240 °C (Wilkinson 2010) and recent clumped C-O isotope analyses have demonstrated similar temperatures (Hollis et al. 2016). Under these conditions, mobility of Zn and Pb is mainly sensitive to pH, T and fO2 changes, with Zn generally being more mobile than Pb (e.g. Anderson 1987; Cooke et al. 2000). This study develops upon previous work in which metal distributions have been used to roughly identify the feeder zones within Irish-type Zn-Pb deposits (Andrew 1986; Davidheiser-kroll et al. 2002; Fusciardi et al. 2004; Ashton et al. 2015).

2 Methodology

The structural framework and stratigraphy at the Silvermines and Lisheen deposits was investigated using proprietary 3D geomodelling software packages. Vulcan® (Maptek) was used for explicit picking of detailed fault and horizon geometries in areas of high data density and structural complexity. The explicitly picked horizons and faults from Vulcan® were then used as direct input into SKUA-GoCAD® (Paradigm) and Mining Suite plugins of Mira Geoscience. Here, implicit interpolations of several horizons and fault points was carried out using the discrete smooth interpolator (e.g. Caumon et al. 2009). Data validation, exploration and visualisation was carried out with Leapfrog3DGeo® (ARANZ Geo Ltd.). Additional data-entry, data-validation and georeferencing was accomplished using MOVE® (Midland Valley Ltd.), ArcMap® (ESRI) and QGIS (qgis.org FOSS).

The structure and horizon model interpretations are based on the following data sources. The dataset for Silvermines consists of primary legacy data that were digitised and georeferenced for this study. The primary data include paper drillcore logs, assays (Pb, Zn, and sparse Ag), mine plans with geology and structures, geological sections based on drillhole and underground information as well as surface geological maps from GSI and literature. For the Lisheen deposit, all data was available digitally, including a full surface and underground drillhole database, core photos, an extensive suite of assays, detailed 3D digitised face mapping at 4m intervals of the entire mine and surface geological maps. This study has built upon earlier Vulcan models that were developed during mine exploitation.
At Lisheen, a full suite of metals was systematically assayed. Specific gravity and elemental concentrations of Zn, Pb, Fe, Cu, Ni, Ag, Co, As, S, Tl and Sb were measured using ICP-MS. Metal distribution maps were generated in Vulcan using grades and tonnages calculated from a geostatistically determined block model that incorporated >70,000 one-metre-composited assays. The tonnages are displayed as the total tonnage of a specific metal contained within a 4x4m column through the ore body. In the Zn/Pb ratio map columns with <3t of lead are not shown in order to remove anomalously high or low ratio values resulting from trace Zn and Pb grades.

At Silvermines, Pb and Zn were systematically assayed and often Ag was also analysed. Specific gravity and Fe were not available, therefore metal distributions are analysed using length-weighted average grades. Some 22,200 assays that included Zn and Pb grades were composited into 1m segments, as well as 2,800 Ag assays. A length-weighted composite grade for each metal was then generated for each segment. The ratios were calculated and the resultant grade or ratio values inverse distance weighted using a 4-sector search radius of 50m. In the Zn/Pb ratio map points with <3wt% of Zn+Pb are not shown in order to remove anomalously high or low ratio values resulting from trace Zn and Pb grades.

This mineralisation is enveloped by semi-massive, disseminated and vein-hosted sulphides. The Lisduff Oolite Member of the Ballysteen Fm is also occasionally mineralised in the footwall of normal faults (Fusciardi et al. 2004).

Several families of structures were identified at Lisheen (Figure 1). Firstly, the most important structures are an array of E-ENE trending left-stepping normal fault segments. These faults are components of the Rathdowney trend, a regional ENE trending fault system. Four major fault segments define the southern end of individual Waulsortian-hosted orebodies at Lisheen (Fig. 1). Normal fault displacements are on the order of 160-220m, with NW dipping relay ramps transferring the displacement from one segment to another. Many minor normal faults occur with displacements of up to 15m and strikes which are parallel to the major normal faults. These normal faults pre-date the main phase of Zn-Pb mineralisation, with the faults acting as pre-cursory conduits for post-faulting fluid migration and trapping.

Secondly, low-displacement NW-trending normal fault and forced-fold geometries are observed throughout the orebodies. Thirdly, NE-SW dextral oblique-slip reverse faults cross-cut the segmented normal faults. These normal faults are often reactivated, or associated with fault-bend folds and occasional overfolds of the Ballysteen Fm. These structures are interpreted to be related to inversion during the Variscan orogeny. Finally, predominantly dextral NW-trending, subvertical strike-slip faults crosscut all previous structures and are attributed to the more recent Alpine orogeny: these faults are more groundwater prone than any other structures.

At Silvermines, Pb and Zn were systematically assayed and often Ag was also analysed. Specific gravity and Fe were not available, therefore metal distributions are analysed using length-weighted average grades. Some 22,200 assays that included Zn and Pb grades were composited into 1m segments, as well as 2,800 Ag assays. A length-weighted composite grade for each metal was then generated for each segment. The ratios were calculated and the resultant grade or ratio values inverse distance weighted using a 4-sector search radius of 50m. In the Zn/Pb ratio map points with <3wt% of Zn+Pb are not shown in order to remove anomalously high or low ratio values resulting from trace Zn and Pb grades.

3 Lisheen deposit

The Lisheen mine in Co. Tipperary was mined for 17 years from 1999 until December 2015 and produced 22.4 Mt at 11.63% Zn and 1.96% Pb. Mineralisation at Lisheen consists of several massive sulphide lenses near the base of the Waulsortian Fm in reef carbonates and reef breccias.

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hanging wall of both major and minor normal faults. These faults also control the distribution of the thick pyrite caps that sit above Zn-Pb mineralisation in their hanging walls.

Cu, Ni, Co and As show high tonnages proximal to distinct points (feeders) along the main controlling normal fault segments, with high metal tonnages dying out quickly away from these points. These feeders occur both in the Waulsortian Formation in the hanging wall and in the Lisduff Oolite Member in the footwall of the normal faults. Mineral assemblages include tennantite-tetrahedrite, niccolite, chalcopyrite, Ag-sulphosalts and barite, in addition to sphalerite and galena (Fusciardi et al. 2004). The Lisduff Oolite Member hosted ore bodies are spatially restricted. When restored to their original position before Variscan dextral oblique-slip movement on reverse faults, these feeder points within the footwall orebodies line up with hanging wall points of elevated Ni, Co, Cu and As in the Waulsortian Fm across the segmented normal faults. Other minor E-NE trending normal faults occasionally show minor amounts of Ni and Cu as well, but only in the Waulsortian Formation. No elevated Ni, Cu or Co are seen in other parts of the mine.

High tonnages of Zn and Pb occur in the hanging wall of the major normal fault segments proximal to these Ni-Cu-As-Ag-Co rich points (Figure 1). Zn tonnages, however, extend over a much wider area than Pb tonnages. This is reflected in the Zn/Pb ratios, which increase N to NE-wards away from the normal faults and Ni-Co-Cu-Ag-As rich feeders. Zn/Pb evolves from ratios of 3:1 proximally to ratios of 12:1 distally. In addition to this, Zn/Pb ratios also show clear NW trends that correlate with NW trending structures. The Zn/Fe ratio shows a similar control by NW trends. In some places areas of elevated Zn/Fe and Zn/Pb coincide, but this is not always the case.

The Island Pod and Bog Zone East orebodies have very high Zn/Pb ratios and high Zn+Pb tonnages but completely lack elevated Ni, Cu, Co and Ag values. In the Island Pod, EW normal faults with only minor displacements are found in the north and south of the orebody.

No significant grades are found up-dip in the relay ramps between the normal faults. Moreover, the edges of Main Zone and Derryville orebodies align with the lower edge of the relay ramps. In Main Zone, an area of particularly elevated Pb tonnes occurs in the orebody at the edge of the MZ-DV ramp (Figure 1).

Where dextral oblique-slip reverse faults offset the metal sulphides and arsenides, elevated metal tonnages occur along the faults, certainly in Main zone and in Derryville (Figure 1). In both of these zones, the reverse faults intersect (part of) the zones of elevated Ni, Co, Cu and As.

4 Silvermines deposit

The Silvermines deposit in Co. Tipperary has had several centuries of activity with modern mine life lasting from 1963 until its closure in 1982 for the main Pb-Zn mine and in 1993 for the Magcobar barite open cast mine. The main mine area contained 17.7 Mt of ore resource at 6.4 Zn%, 2.5 Pb% and 23.0 g/t Ag (Andrew 1986) of which 11 Mt was mined at 10 Zn+Pb%. The Magcobar barite deposit in the same area produced 5.0 Mt of 85% BaSO₄.

Two major stratiform (‘concordant’) orebodies are present within the deposit, G-zone lower and B-Zone (Figure 2). The ore occurs as mainly sphalerite, galena and pyrite replacing carbonates and carbonate breccias near the base of the Waulsortian Fm (Taylor 1984; Andrew 1986; Reed and Wallace 2004). Another stratiform orebody occurs in the Cooleen zone prospect (cf. Lee and Wilkinson 2002). Besides these, several orebodies exist that are discordant to the stratigraphy, including the G-Zone upper, K-Zone (Knockanroe), C-Zone (Ballygowan South) and P-Zone (Figure 2). At K-Zone and C-zone, ore is associated with brecciated carbonates of the Lisduff Oolite Member or the Old Red Sandstone Formation.
The main structures at Silvermines are a WNW-trending array of left-stepping fault segments with maximum displacements between 130-375m (Figure 2). These faults are colloquially referred to as the Silvermines fault zone. The relay ramps between many of the fault segments are breached. Other minor WNW trending normal faults with throws less than 10m are observed throughout the orebodies. Subvertical veins with barite, galena, carbonates, quartz and tetrahedrite are associated with NW-NNW-trending faults in the region.

At G-zone, low Zn/Pb ratios of 2:1 occur within the fault plane of the normal fault and ratios at the base of the Waulsortian steadily increase towards the NNE away from the fault (Figure 2). Elevated Ag values occur very close to, and along both major and minor normal faults. The highest Ag values correspond to points with highest Pb values. The Zn/Pb ratio is very elevated in P-zone (>20:1) and moderately elevated in K-zone (12:1) and C-zone (10:1).

5 Discussion and conclusions

Distinct points along segmented normal fault arrays are seen to serve as feeders to many of the orebodies. Here, fluids spill out into the hangingwall, generally near the base of the Waulsortian Reef Fm. These feeders control the location of several of the orebodies along the various fault segments. The metal zonations emanating from feeders can be explained in terms of changes in temperature, pH and oxygen fugacity, most likely and primarily by mixing of hot medium-salinity metalliferous fluids and low-temperature high salinity brines.

Besides the controls exerted by feeders on metal zonation, many other structural trends control metal distribution at the scale of the individual orebodies. Importantly, other higher tonnage areas without the typical feeder signal are found in both of the deposits. These are interpreted to represent distal orebodies, possibly representing the farthest extent reached by the ore-forming fluids, or remobilisation of ore from more proximal locations.

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Geochemical evolution of exhalative massive sulfide mounds in the southern Iberian Pyrite Belt

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Abstract. The volcanogenic massive sulfides (VMS) of the southern Iberian Pyrite Belt (IPB) occur as zoned exhalative mounds interbedded with shale. They formed at the Devonian-Carboniferous boundary in anoxic bottom waters. Some deposits include a hanging wall with banded sulfides (banded ore), and a foot wall with a dominant massive pyrite core and siderite-sulfide rocks (carbonate ore), interpreted to be of biogenic origin, and rooted in a stockwork.

High-precision geochemistry of samples from selected representative deposits (e.g. Sotiel-Migollas, Tharsis, Neves Corvo and Lousal), and the host shale, show chemical, textural and isotopic zonations that likely preserved evidence of the evolution of the hydrothermal system from early exhalative-biogenic deposition to diagenetic-hydrothermal maturation inside the mound. We propose an evolution of the system during the mixing between two contrasting fluids; modified seawater accumulated in the seafloor and deep hydrothermal fluids that ascended through the feeder zones. Early sulfides precipitated in the seawater-mound interface caused by the reaction of the metal-rich deep fluids with reduced sulfur derived from the biogenic reduction of seawater sulfate (BSR). Towards the core of the mound there is an increasing influence of the hydrothermal fluids that percolate through the already formed sulfides modifying the original textures and isotopic signatures.

1 Introduction

1.1 Regional geologic setting

The IPB is located in the southwestern most Iberian Massif. It includes more than 80 massive sulfide deposits with 1750 Mt of mineralization and 2500 Mt of mineralized stockwork (Tornos 2006) formed during the late Devonian to the early Carboniferous. Later Variscan deformation largely modified the initial architecture, developing a complex set of thrusts synchronous with low-grade regional metamorphism (Silva et al. 1990).

The oldest recognized rocks are shale and sandstone of the Phyllite-Quartzite (PQ) Group, that form a thick sequence (>2000 m) of Givetian-Famenian age (Schemerhorn 1971) and deposited in a shallow marine continental platform. Conformable above this unit is the Volcanic Sedimentary Complex (VSC), which comprises dominant calc-alkaline andesite to rhyolite and minor tholeiitic to alkaline basalt. These rocks show abundant interbedded volcanioclastic rocks, shale, chert lenses with manganese mineralization, and massive sulfides (Tornos 2006) that likely represent the infilling of a gradually deepening continental basin. The estimated age is Famennian to Visean (Oliveira 1990). The sequence is completed by the Flysch Group, a turbiditic package up to 3000 m of late Visean age.

The massive sulfides are divided in two major groups that reflect contrasting depositional settings and ages (Tornos 2006). The deposits in the northern region, such as Rio Tinto, Aguas Teñidas, La Zarza and Aljustrel, are located in the apical part of felsic domes and interpreted as dominantly formed by the replacement of host volcanic rocks during the early Touraisian. Meanwhile, those in the southern region (Sotiel-Migollas, Tharsis, Neves Corvo, Lousal, Las Cruces, Aznalcóllar-Los Frailes and Masa Valverde) are shale-hosted, older (Strunian) and larger, but more pyrite-rich.

1.2 The southern region and biogenic mounds

The shale-hosted deposits of the southern IPB are interpreted as dominantly exhalative and formed in third order basins in a time span of 3-4 Ma (Tornos 2006). They are related to volcanism associated with paleogeographic changes synchronous with the onset of volcanism close to the Devonian-Carboniferous boundary. They are interpreted to have been deposited in brine pools formed during the accumulation of reduced and saline hydrothermal fluids on the seafloor (Solomon et al. 2002; Tornos et al. 2008). Widespread sulfate reduction was due to the microbial metabolism in which the abundant land-derived organic matter, supplied by the destruction of nearby forests, acted as electron donor for extremophilic microbes that reduced seawater sulfate to \( \text{H}_2\text{S} \) (Menor-Salván et al. 2010). Suboxic to oxic conditions were re-established in the water column immediately after the hydrothermal activity ceased.

The contact between the stockwork zone and the exhalative sulfide-rich mounds is some meters thick and irregular, marked by the stratabound replacements of shale by the massive sulfides. The lower part of the exhalative mineralization includes, in Sotiel-Migollas and Tharsis, a carbonate ore up to 60 m thick. This rock consists of finely laminated siderite-pyrite layers that are later brecciated and cemented with a similar but coarse-grained mineral assemblage. These rocks are interpreted to have formed by the deposition of massive sulfides on the seafloor accompanied by the formation of microbial mats on the surface of the mound during peak times of microbial activity (Tornos et al. 2008). The carbonate ore is capped by up to 100 m of monotonous and structureless massive sulfides and the banded ore. The banded ore is a prominent feature of the Tharsis deposit and includes several meters
of alternating pyrite and shale showing widespread sedimentary structures. There are no evidences of sulfates in these massive sulfides, suggesting that they formed in euxinic conditions.

The shale adjacent to the massive sulfides shows a pervasive hydrothermal chloritic alteration and precipitation of carbonates and pyrite.

2 Methodology

Representative samples of the carbonate ore, banded ore and the host shale were taken at different depths from nine drillcores from the Sotiel-Migollas, Tharsis, Neves Corvo and Lousal deposits. These samples were complemented by those from outcrops in the western part of Tharsis.

The chemical composition of the carbonates was obtained using both a JEOL Superprobe JXA-8900M at the Centro de Microscopía Electrónica de la Universidad Complutense de Madrid (Spain) and a JEOL hyperprobe JXA-8500F at the GeoForschungsZentrum (GFZ) German Research Centre for Geosciences (Potsdam, Germany). In-situ $\delta^{34}S$ (% V-CDT) values on pyrite of varying textural types were determined using a CAMECA 1280-HR Secondary Ion Mass Spectrometer (SIMS) at the GFZ. $\delta^{13}C$ (% V-PDB) and $\delta^{18}O$ (% V-SMOW) values of dolomite and ankerite-siderite were determined using a Finnigan DELTAplus XP mass spectrometer at the Stable Isotope Laboratory of the Instituto Andaluz de Ciencias de la Tierra CSIC-UGR (Granada, Spain). $^{87}$Sr/$^{86}$Sr ratios of carbonates were measured with a Thermal Ionization Mass Spectrometer (TIMS) Phoenix IsotopX at the Centro de Apoyo a la Investigación (CAI) of Geochronology and Isotope Geochemistry at the Universidad Complutense (Madrid, Spain). Initial Sr isotope ratios on shales were calculated at 358 Ma, the assumed age of the rocks using present day $^{87}$Sr/$^{86}$Sr and Rb/Sr ratios, and the $^{87}$Rb decay constant of 1.42*10^{-11} (Steiger and Jäger 1977).

3 Results

Electron microprobe analyses of the carbonates in the carbonate ore and in the hydrothermally altered shale show significant chemical variability. These variations are larger at Sotiel-Migollas than in the other deposits studied. Early dolomite is widely replaced by ferroan dolomite to ankerite and, later, to sideroplesite and siderite.

In-situ $\delta^{34}S$ values on different pyrite textures ranged from -43.3 to +4.4‰ (Table 1). The subhedral pyrite from Neves Corvo is remarkable for its very negative $\delta^{34}S$ values, as low as -43.3‰, some of the most negative ones recorded in VMS deposits (Ohmoto 1986; Wilkin and Arthur 2001; Huston et al. 2010).

Twenty-five samples of carbonates from the hydrothermally altered shale, carbonate ore, and banded ore were measured for their $\delta^{13}C$ and $\delta^{18}O$ isotopic compositions. $\delta^{13}C$ values in dolomite range from -12.2 to -5.2‰ and $\delta^{18}O$ from +14.1 to +25.2‰. Siderite shows a similar variability with $\delta^{13}C$ ranging between -11.1 and -5.2‰. However $\delta^{18}O$ values are, on average, higher than in dolomite, from +18.0 to +27.8‰.

Both isotopes vary according to the type of host rock. The carbonates in the altered shale show more negative $\delta^{13}C$ values than the carbonate and banded ores. $\delta^{18}O$ signatures in the three lithologies are similar, but the shale has a narrower range.

The carbonate ore from Sotiel-Migollas and Tharsis exhibit minor variations and the carbon isotopes of both deposits are very similar; however, oxygen signatures are more depleted in Sotiel-Migollas (3-5‰).

Initial $^{87}$Sr/$^{86}$Sr ratios of the unaltered shale are between 0.71290-0.71354, the hydrothermally altered shale is 0.70911 and the carbonate-banded ores are 0.70846-0.71284. Most of the values obtained are well above from those of seawater near the Devonian-Carboniferous boundary (0.7075-0.7085; Veizer et al. 1999). The carbonates of Sotiel-Migollas are very variable (0.70846-0.71354), whereas at Neves Corvo and Tharsis show values of 0.70911 and 0.70950-0.71276, respectively.

4 Discussion

The mineralogy and geochemistry of the massive sulfide mounds and the adjacent shale in the southern IPB give insights on the mineralizing process. We distinguish two possible sources for the fluids involved in ore formation; the ambient seawater, and the deep hydrothermal fluids that are vented on the seafloor. Our working hypothesis is that during the mineralizing event the seafloor was dominated by saline, anoxic and hot (ca. 60-100°C) water that was the product of the mixing between the deep hydrothermal fluids and seawater, and was the locus of major microbial activity. This water was immiscible with the overlying ambient seawater, more oxidized, less saline and cooler (Tornos et al. 2008). The early sulfides and carbonates formed by fluid mixing at the modified seawater-rock interface in a system dominated by seawater and only small amounts of deep fluids that reached the

Table 1. Summary of the $\delta^{34}S$ (%) values from pyrite of varying textural types.

<table>
<thead>
<tr>
<th>Deposit</th>
<th>$\delta^{34}S$ frambooidal</th>
<th>$\delta^{34}S$ colloform</th>
<th>$\delta^{34}S$ anhedral</th>
<th>$\delta^{34}S$ subhedral</th>
<th>$\delta^{34}S$ euhedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sotiel-Migollas</td>
<td>-42.3 to -4.2</td>
<td>-11.1 to +4.4</td>
<td>-12.6 to +3.0</td>
<td>-16.1 to +1.7</td>
<td></td>
</tr>
<tr>
<td>Tharsis</td>
<td>-25.2 to -11.2</td>
<td>-11.7 to -1.3</td>
<td>-12.2 to -9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neves Corvo</td>
<td>-43.3 to -29.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lousal</td>
<td>-4.5 to +1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
surface. Later maturation inside the mounds occurred at progressively higher temperatures and higher deep fluid/modified seawater ratios. Such an evolution is known as hydrothermal zone refining (e.g. Eldridge et al. 1983; Large et al. 1989; MacLellan et al. 2006) and is widespread in modern systems (Humphris et al. 1995; Herzig and Hannington 1995) and the ancient record (Galley et al. 1993; Hannington et al. 1999; Piercey et al. 2014).

The carbon isotope data reflect mixing between two end members; organically-derived carbon with δ13C < -10‰, likely derived from the oxidation of organic carbon flowing into the basin, and marine carbonate with δ13C ≈ 0‰ (Broadbent et al. 1998).

Oxygen isotopes track the temperature variations of the precipitated carbonates. If early dolomite precipitated from the modified seawater with δ18O close to 0‰ (Ohmoto 1996), the estimated temperature of precipitation is 55-141°C. The isotope composition of the siderite formed in the internal zone of the mounds suggests that the deep hydrothermal fluids had a δ18O near +4‰ (Tornos and Heinrich 2008), yielding estimated temperatures of formation close to that of the earlier dolomite (ca. 72-156°C). These values are broadly consistent with the calculations of Solomon et al. (2002) for the temperature at which the stagnant water in the brine pools reach a steady state equilibrium (60-100°C) and the temperatures guessed by Tornos et al. (1998) in the Tharsis deposit. In general, it seems that the carbonate ore in Sotiel-Migollas precipitated at somewhat higher temperatures (up to 156°C) than in Tharsis (<114°C). The hydrothermal alteration on shale took place at equivalent temperatures (109-151°C).

Strontium isotope ratios of the carbonates in the carbonate ore are slightly less radiogenic than those from the host shale (0.70911-0.71354). The estimated relative proportions of the different Sr sources (Faure 1986) suggest that ambient seawater is the dominant supplier of Sr, with between ca. 88-99‰, with the contribution of the underlying basement almost negligible. However, the radiogenic Sr signatures in the carbonates within the altered shale suggest a higher contribution from the basement.

High-resolution analyses of sulfur isotopes suggest that there is a close relationship between the δ34S values and the maturation in pyrite textures. At temperatures below ca. 150-200°C (Machel 2001) sulfate reduction to reduced sulfur can only be biogenically produced. The fractionation depends on the type of extremophilic organisms involved, the availability of electron donors, and the open/close nature of the system to both SO42- and H2S (Ohmoto 1986; Habicht and Canfield 2001). Thus, the large depletions of δ34S signatures observed in the early pyrite textures of the southern IPB can be interpreted as the product of a combined multi-step process of biogenicallymediated sulfate reduction (BSR), sulfide oxidation, and microbial disproportionation of sulfur intermediate compounds (elemental sulfur, thiosulfate or sulfite; Thamdrup et al. 1993; Canfield and Thamdrup 1994; Habicht and Canfield 2001).

The lowest signatures are found in both the early framboidal pyrite and the fine-grained subhedral grains. The massive and euhedral late pyrite have systematically higher values. This evolution from primary to more evolved textures reflects a gradual but complex change in the δ34S composition of the fluid. Likely, they track the mixing of sulfur from two endmembers, which derived from in-situ microbial reduction of seawater in a system partially to completely open to sulfate and reduced sulfur derived from the deep hydrothermal fluids and likely leached from the underlying rocks. The maturation of the sulfides in the massive sulfide mounds tend to homogenize and increase the δ34S signatures.

The δ34S values of this study (-43.3 to +4.4‰) show a fractionation up to ≈66‰ compared to the original seawater sulfate (Kampschulte and Strauss 2004), which is one of the highest recorded in natural systems (see Canfield and Thamdrup 1994; Rudnicki et al. 2001; Lode et al. 2017).

5 Conclusions

A geochemical study done on the host shale and the carbonate and banded ores from representative VMS deposits of the southern Iberian Pyrite Belt (Sotiel-Migollas, Tharsis, Neves Corvo and Lousal) support the following findings:

1) Microbially-mediated mounds, formed on the seafloor, are abundant in the base of the deposits. They show a complex chemical, textural and isotopic evolution from the original sedimentary-exhalative formation to the late maturation, something that suggests complex fluid mixing between modified seawater and deep upflowing hydrothermal fluids. These data suggest that the carbonates (dolomite to siderite) formed between 55 to 156°C, which is consistent with precipitation in a brine pool close to the steady state equilibrium (<100°C).

2) High-precision SIMS analyses on the different types of pyrite reflect large variations of the δ34S values, with a predominance of negative values. The lowest values are present on pyrite showing the most primitive textures, including one of the most negative values ever described in the IPB (δ34S=-43.3 ‰, in Neves Corvo). This strongly suggests that reduction of seawater sulfate took place by a multi-step process likely involving BSR, sulfide oxidation and/or disproportionation of sulfur intermediate compounds in a system partially open to sulfate, in an scheme similar to that proposed by Lode et al. (2017).

3) Broad covariance between Sr and S isotopes suggests that the evolution of the δ34S values reflects mixing between two fluids in an evolving system from open to partially closed to sulfate conditions. Early sulfides precipitated in the modified seawater-mound interface by reaction of the deep fluids with reduced sulfur mainly derived from BSR. Inside the mound there is an increasing influence of the reduced and hot deep hydrothermal fluids, something that modified the primary textures and isotopic signatures.
Acknowledgements

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References


The Pobeda modern submarine hydrothermal sulfide edifice cluster (Mid-Atlantic Ridge, 17°08’N): mineralogy and chemical composition

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Abstract. The new Pobeda sulfide edifice cluster, associated with peridotites, was discovered in the 37th cruise of the Russian R/V Professor Logachev by the Polar Marine Geosurvey Expedition (PMGE) in collaboration with VNIIOkeangeologia, Saint-Petersburg, Russia. This work presents the results of a mineralogical and chemical investigation of sulfide deposits from the Pobeda-1 and Pobeda-2 hydrothermal fields (Mid-Atlantic Ridge), which is a part of the Pobeda hydrothermal sulfide cluster. Pyrite, marcasite are the major ore minerals; sphalerite, isocubanite and chalcopyrite are less abundant in sulfide bodies of hydrothermal field Pobeda-1. Isocubanite, sphalerite and chalcopyrite are the major ore minerals; pyrite and marcasite are less abundant in sulfide deposits of hydrothermal field Pobeda-2. The microprobe analysis of different sphalerite grains from various mineral aggregates illustrate that the Fe content varies between 2.7 and 25.1 wt.%.

1 Introduction

Oceanic core complexes (OCC) are characteristic tectonic components of the lithosphere of slow-spreading MOR. They are blocks (serpentinitized peridotites, serpentinite and gabbros) transported to the ocean floor along systems of detachment faults penetrating to the base of the oceanic crust (McLeod et al., 2009; Silantyev et al., 2011). A discovery of a new type of massive sulfide deposits associated with peridotites (Bogdanov et al., 1997) caused intense study of northern and central part of the Mid-Atlantic ridge (MAR). To date, all OCCs on the Mid-Atlantic Ridge that have been investigated in detail are known to host active or inactive hydrothermal sulfide deposits. The Logachev hydrothermal field at 14°45’ N (Bogdanov et al., 1997; Petersen et al., 2009; Bortnikov et al., 2011), Rainbow site near 36°14’N (German et al., 1996, 2010; Bogdanov et al., 2002; Kuznetsov et al., 2008), the Semenov cluster at 13°30’N (Beltev et al., 2007, 2009; Pertsve et al., 2012; Bortnikov et al., 2014; Melekestseva et al., 2014), the Irinovsky site at 13°20’N (Bortnikov et al., 2015), the Ashadze at 12°58’N (Beltenev et al., 2003; Bortnikov et al., 2010), and Nibulungen 8°18’S (Melchert et al., 2008; Schmidt et al., 2011) occur along of the central part of the Mid-Atlantic ridge. Several new hydrothermal fields associated with ultrabasic and basic rocks were discovered by the Russian R/V Professor Logachev.

The new Pobeda sulfide edifice cluster, associated with peridotites, discovered in the 37th cruise of the Russian R/V Professor Logachev by the Polar Marine Geosurvey Expedition (PMGE) in collaboration with VNIIOkeangeologia, Saint-Petersburg, Russia.

2 General description

The Mid-Atlantic Ridge between 17°14’N and 16°40’N is characterized by two ridge segments (17°30’-16°58’N (the Northern segment) and 16°58’-16°40’N (the Southern segment)) interrupted by non-transform discontinuities. This section of the Mid-Atlantic Ridge has a unique tectonic structure. The largest (among the known for the equatorial part of MAR) oceanic massif is situated on the eastern flank of the MAR rift valley of the Northern segment. The other massif with complex tectonic steps is situated on the western flank of the MAR rift valley of the Southern segment. Both massifs are oceanic core complexes. They are composed of serpentinitized peridotites, serpentinite, gabbros. The rift valley floor consists of basalts (tubular and pillow lavas), dolerite and dolerite-basalt dikes (unpublished report of PMGE, 2016; Cherkashov et al, 2016, in press).

The Pobeda hydrothermal sulfide cluster is located on the eastern flank of the MAR rift valley on the western slope of the OCC massif at a depth between 1950 and 3100 m. The hydrothermal sulfide cluster consists of the Pobeda-1 and the Pobeda-2 hydrothermal fields, and the Pobeda-3 sulfide site.

The active hydrothermal field Pobeda-1 (17°08.7’ N, 46°23.44’ W) is located in water depths between 1950 m and 2400 m. It is consists of four sulfide bodies, some ferriferous deposits, ferriferous crusts, and metalliferous sediments. Sulfide bodies are sulfide mounds about 10 m in height, some of them with sulfides chimneys, and fragments of sulfide sites and chimneys. The active Pobeda-2 hydrothermal field (17°07.45’ N, 46°24.5’ W) is situated in 4 km South-West from the Poweda-1 in water depths between 2800 m and 3100 m. As well as the Pobeda-1, the Pobeda-2 is associated with peridotites and gabbroenites. The Pobeda-3 sulfide site (17°08.3’ N, 46°25.2’ W) is located at the depth of 2500 to 2700 m and largely covered by metalliferous sediments with Fe-Mn crusts, pyrite and barite grains (unpublished report of PMGE, 2016).

3 Samples studied

Samples 37L195a-2, 37L196a and 37L204d-OB were taken from the sulfide body II from the hydrothermal field...
Pobeda-1. Samples 37L107d Fe-Cu and 37L107d Py-Wur were taken from the hydrothermal field Pobeda-2. All samples collected during the 37th (2014-2015) cruise of the R/V Professor Logachev.

4 Analytical procedure

Mineral analyses were performed with JXA-8200 electron microprobe (JEOL Ltd., Japan) with five wavelength-dispersive spectrometers at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry RAS (IGEM RAS). The operating conditions were as follows: a voltage of 20 kV and a probe current of 20 nA and a beam diameter of 1 mkm. In each situation, background counts were measured in half the time for peak measurement on both sides of the peak.

For pyrite and pyrrhotite counting intervals were 10 sec for S (Ka, PETH), Fe (Ka, LIF), Ni (Ka, LIF), Sb (La, PETH) and 30 sec for Co (Ka, LIF) and As (La, TAP). Standards were FeS2 (for Fe and S in pyrite), FeS (for Fe and S in pyrrhotite), GaAs (for As), Ni (for Ni), NiSbS (for Sb) and Co (for Co).

For sphalerite counting intervals were 10 sec for S (Ka, PETH), Zn (Ka, LIF), In (La, PETJ), Ag (La, PETH), 20 sec for Fe (Ka, LIF), Mn (Ka, LIF), Cu (Ka, LIF), Hg (Ma, PETH), Sn (La, PETH) and 30 sec for Cd (La, PETJ). Standards were ZnS (for Zn and S), CdS (for Cd), CuFeS2 (for Fe), InSb (for In), Mn (for Mn), Ag (for Ag), Cu (for Cu), HgS (for Hg) and Cu2FeSnS4 (for Sn).

For chalcopyrite counting intervals were 10 sec for S (Ka, PETH), Zn (Ka, LIF), Fe (Ka, LIF), Cd (La, PETH), Ni (Ka, LIF), Mn (Ka, LIF), 20 sec for Co (Ka, LIF), 30 sec for As (La, TAP). Standards were CuFeS2 (for Cu, Fe and S), GaAs (for As), ZnS (for Zn), CdS (for Cd), Ni (for Ni), Mn (for Mn) and Co (for Co).

5 Mineralogy

5.1 The hydrothermal field Pobeda-1, the sulfide body II

The sample 37L195a-2 is porous, fine-grained pyrite-marcanite seafloor massive sulfides with Fe oxides, pyrrhotite, and anhydrite. Pyrite occurs as fine-grained and colloform aggregates. Marcasite occurs as spear-like and tabular grains, which replace relics of tabular pyrrhotite, anhydrite or barite. Marcasite overgrows anhydrite and forms sheath-like aggregates. Sphalerite occurs as elongated fine-grained aggregates in central part of pyrite aggregates (Fig. 2). Isocubanite+chalcopyrite occurs as emulsion-like inclusions in sphalerite that are diverse in morphology and distribution. The isocubanite+chalcopyrite inclusions are, as a rule, arranged regularly in the form of bands parallel to the zones of growth and displaying the internal structure of sphalerite crystals. Isocubanite+chalcopyrite also occur as xenomorphic segregations in pyrite and sphalerite aggregates.
monomineralic pyrite or marcasite fragments (1-2 mm) (Fig. 3). Sulfide fragments consist of colloform concentrically-zoned pyrite-marcasite aggregates, frambooids, grains and aggregates of pyrite, isometric grains of isocubanite, chalcopyrite, secondary Cu sulfides and Fe oxides in pyrite aggregates.

5.2 The hydrothermal field Pobeda-2

The sample 37L107d Fe-Cu is porous, fine-grained isocubanite+chalcopyrite-pyrite-sphalerite seafloor massive sulfides. Isocubanite with chalcopyrite lamellas occurs as grains and aggregates of isometric grains. A grain size is from 1-2 to 100-200 μm. Pyrite occurs as relics isometric grains. Late pyrite fills pores and cavities in isocubanite+chalcopyrite-pyrite-sphalerite aggregates. Sphalerite occurs in four morphologically distinct forms. Sphalerite-I forms thin vein (~ 100 μm). Concentrically-zoned sphalerite-II and crystals of sphalerite-III form zonal veins (1-2 mm). The size of single sphalerite-II grain is 50-150 μm. Sphalerite-IV overgrows isocubanite+chalcopyrite grains (Fig. 4). Elongated or xenomorphic grains develops along ultrafine veinlets (<5-7 μm) in porous pyrite segregations. Also this mineral occurs as fine-grained aggregates 5-15 μm in pyrite. The tentatively identified chemically as glaucodot - (Co,Fe)AsS (?). Small single grains are included into pyrite aggregates. The chemical composition of these grains suggest it is clausthalite (?).

The sample 37L107d Py-Wur is porous, fine-grained isocubanite+chalcopyrite-secondary Cu sulfides-pyrite-sphalerite seafloor massive sulfides. Isocubanite with chalcopyrite lamellas occurs as grains and aggregates of isometric grains. Secondary Cu sulfides (chalcocite, covellite) replace isocubanite. Pyrite occurs in two morphologically distinct forms. Pyrite-I occurs as relics isometric grains and their aggregates. Pyrite-II occurs as euhedral crystals 5–20 μm in size. Crystals of pyrite-II are combined into chains and pocket-like segregations (Fig. 5).

6 Mineral chemistry

The microprobe analysis of pyrite, marcasite and pyrrhotite has shown that all generations of Fe-sulfides is nearly stoichiometric and is characterized by very low As and Co contents (≤0.06 wt.% and ≤0.5 wt.% respectively).

The microprobe analysis of different sphalerite grains from various mineral aggregates illustrate that the Fe content varies between 2.7 and 25.1 wt.%. Mn, Hg and Sn admixtures are below the limit of detection. The Cd and In contents are ≤0.02 wt.% and ≤0.13 wt.% respectively. The Fe content of zonal sphalerite in pocket segregations (37L196a) varies from 19.7–25.1 wt.% in the inner zones of the grain to 14.6–18.9wt % in the outer zones of the grain.

The microprobe analysis of sphalerite-I (37L107d Fe-Cu) has shown that the Fe content varies from 11.6 to 12.9 wt %. The Fe content (37L107d Fe-Cu) are 2.7–4.4 wt % for the sphalerite-II and 7.5–11.8 wt % for the sphalerite-III. The microprobe analysis of sphalerite-IV (37L107d Fe-Cu) has shown that the Fe is 21.9 wt %.

The microprobe analysis of isocubanite has shown that all morphologicall forms are nearly stoichiometric.
7 Conclusions

Pyrite, marcasite, isocubanite are the major ore minerals; sphalerite and chalcopyrite are less abundant. Pyrrhotite, glaucodot (?) and clausthalite (?) are rare minerals. Gange minerals are Fe oxides, barite and anhydrite. Porous, colloform, fine-grained seafloor massive sulfides of hydrothermal fields Pobeda-1 and Pobeda-2 are classified as pyrite-marcasite, pyrite-marcasite-sphalerite-chalcopyrite and isocubanite+chalcopyrite and isocubanite+chalcopyrite-pyrite-sphalerite types.

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References

A new volcanic map for VMS exploration in the Oman ophiolite based on field, geochemical and aeromagnetic data

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Abstract. The volcanostratigraphy of the Oman ophiolite records a continual increase of subduction-zone influence during late Cretaceous seafloor volcanism. The tholeiitic lavas host numerous Cyprus-type volcanogenic massive sulphide deposits, and the transition from MORB-like to boninitic footwall lavas correlates with increasing gold grades in the deposits. The three major upper volcanic units, including the gold-prospective boninites, can be difficult to discriminate based on field observations alone, and are consequently not differentiated on existing regional volcanic maps. We have collated geochemical analyses and maps from the literature and collected and analysed a further 160 samples from the ophiolite to better define the field, geochemical and magnetic characteristics of the four volcanic units. These characteristics were then used during field and aeromagnetically assisted mapping of the four lava units both in outcrop and under sedimentary cover throughout the ophiolite. The resulting map provides a new framework for VMS exploration in the Oman ophiolite, identifying buried fault-repeated blocks, syn-volcanic faults, new prospective horizons and extensive areas of boninites with potential for gold-bearing deposits. From a broader perspective, this study demonstrates the capability of our multidisciplinary approach to the geological mapping of VMS-prospective tholeiitic volcanic suites under cover.

1 Introduction

The Cretaceous Semail ophiolite in Oman provides the world’s largest exposures of undeformed oceanic crust, and its lavas host numerous Cu-dominant Cyprus-type volcanogenic massive sulphide (VMS) deposits (Fig. 1).

The majority of these deposits were discovered in surface outcrops during the 1970s-1990s. However, the application of modern geophysical methods in the 2000s facilitated the discovery of seven new buried deposits. Since that wave of discoveries, no major finds have been made and a renewed approach is necessary if further deposits are to be located under cover.

This approach will likely consist of improvements to geophysical methods, investigation and remote sensing of hydrothermal alteration, and an improved geological map of the different volcanic units which host the deposits. This work addresses the latter issue – mapping the spatial distribution and extent of the different VMS-prospective volcanic units.

Three of the major lava units have long been recognised (Alabaster et al. 1982) and a fourth boninitic unit (Ishikawa et al. 2002) was recently shown by Gilgen et al. (2014) to occur regionally. However, owing to similarities in the field appearance of the upper units, the regional geological maps currently discriminate only two units: SE1 (also termed Geotimes) and SE2 (the three upper lavas grouped together). Further motivation for a new map arises from the recent finding that VMS mineralisation in the ophiolite is volcano-stratigraphically controlled: the majority of known VMS deposits have either a Geotimes (MORB-like) or Boninitic Alley footwall (Fig. 1; Gilgen et al. 2014). Moreover, Gilgen et al. (2014) showed that deposits with Boninitic Alley footwalls have elevated gold grades (Fig. 1). In order to exploit these findings, maps used for exploration need to discriminate all four prospective volcanic units both in outcrop and under alluvial cover, where further undiscovered deposits may be hidden.

By collating maps from the literature, carrying out our own field mapping and sampling, and correlating the
units with systematic aeromagnetic responses, we were able to assign field-discrimination criteria to the units, identify seafloor faults and prospective seafloor horizons, and efficiently produce the first regional map of the four major volcanic units. Moreover, the reduced-to-pole aeromagnetic map allowed us to infer the presence of lava units and faults over broad gravel-covered areas and to map out extensive fault-repeated blocks east of the main prospective areas. Here we present our mapping methodology as well as representative examples of the finished map.

2 Methods

As the volcanic units are often indistinguishable in the field, efficiently mapping them and inferring their presence under cover at the scale of the ophiolite requires a multidisciplinary approach. We obtained field, geochemical and rock magnetic data to assist interpretation of the aeromagnetic map (Fig. 2).

In outcrops where the identity of the unit was not clear from field observations, samples were taken for geochemical assignment. Thus, some 160 newly collected samples were assigned to units according to the methodology of Gilgen et al. (2014) with minor modifications to the discrimination fields.

Whole-rock elemental compositions were determined by X-ray fluorescence (XRF). The samples were powdered in a tungsten carbide mill and fused into pellets at a ratio of 1:5 with Li2B4O7:LiBO2 (66:34 wt.% ratio) flux.

The compositions of relict igneous clinopyroxene crystals were measured by electron microprobe. From these data we calculated median Ti contents and corresponding Mg/(Mg + Fe) ratios (Mg#) of both crystal core and rim spots within individual samples.

Rock magnetic analyses were used to better characterize the magnetic mineralogy of the different units and to help interpret their aeromagnetic signatures (Clark 1997). We made preliminary measurements of hand samples with a handheld Exploranium™ KT5 susceptibility meter and performed test measurements on ten samples at the Institute for Rock Magnetism, University of Minnesota, with preparation underway for measurement of a much larger sample set. We determined magnetic susceptibility and natural remanent magnetization (NRM), and performed hysteresis loops, alternating field demagnetization, and high- and low-temperature magnetic measurements to investigate the mineralogy. Koenigsberger ratios, describing the relative contributions of remanent and induced magnetization, were calculated based on the susceptibility and NRM data, and a local magnetic field intensity of 38 000 nT. Susceptibility also provides a first estimate of the amount of magnetic minerals in each sample. Saturation magnetizations, coercivities and magnetic ordering temperatures were used to further identify the type and grain size of the ferromagnetic grains, and to improve the estimates of their concentrations.

Our mapping is augmented by an airborne magnetic survey performed in 1992 by World Geoscience Cooperation Ltd with a line spacing of 500 m at 100 m above ground level. The acquired data were processed by reduction-to-pole (RTP) transformation, which makes induced magnetic anomalies appear as if their sources were located in a vertically oriented magnetic field, so that they are centred above their source, simplifying geological interpretation.

3 Results

3.1 Geochemical analyses

The majority of collected samples were readily assigned to one of the volcanic units by a combination of whole-rock geochemistry and clinopyroxene compositions.

The most effective discriminant diagram based on whole-rock XRF composition is the Ti vs. V plot (Fig. 2) modified after Shervais (1982) and as used by Gilgen et al. (2014). The plot shows a general decrease in Ti content upwards through the volcanoclastrostratigraphy. Additionally, in comparison to Ti, the compatibility of V is strongly dependent on redox conditions in the mantle source (Shervais 1982). Consequently, magma sources that have been oxidised by fluid or melt input from a subducting slab produce lavas with higher V/Ti ratios, e.g. island arc tholeiites (IAT) and boninites.

Figure 2. Whole-rock Ti vs. V discrimination diagram after Shervais (1982) with fields of volcanic units drawn using data from Alabaster et al. (1982); Ernewein et al. (1988); Einaudi et al. (2003); Godard et al. (2003, 2006); Kusano et al. (2012, 2014); Gilgen et al. (2014, 2016)

For samples with whole-rock compositions that fall in overlapping fields in figure 2, the composition and compositional zonation of relict magmatic clinopyroxenes has proved to be a reliable discriminant (Fig. 3; Alabaster et al. 1982; Gilgen et al. 2014, 2016). The Ti contents and Mg# of clinopyroxenes generally correlate with the whole-rock compositions (Fig. 3). Moreover, core-to-rim zonation of these parameters provides insight into the pre-eruptive fractionation history of the sample, which serves as an
additional discriminant. Geotimes, Alley and Boninitic Alley all show a decrease of Mg# with increasing Ti content, suggesting well-developed open-system fractionation. Contrastingly, Lasail clinopyroxenes show steep zonation trends in figure 3, with minimal Mg# decrease for a given Ti increase, suggesting closed-system, limited fractionation (Alabaster et al. 1982).

3.2 Rock magnetism

The magnetic susceptibility of our samples as measured by handheld susceptibility meter shows a broad range but clear groupings of the individual units (Fig. 4). These groupings, with high susceptibilities in Geotimes and Alley and low susceptibilities in Lasail and Boninitic Alley, match the aeromagnetic RTP anomalies of the units in independently mapped areas (e.g. Figs 5, 6).

As most hydrothermal alteration processes in the upper oceanic crust are oxidative, and the primary carrier of susceptibility in oceanic basalts is magmatic titanomagnetite, the upper values of each unit are most likely to be representative of primary susceptibility, with lower values in all units resulting from oxidation of titanomagnetite to less magnetic phases such as Ti-maghemite and hematite (Ozima and Larson 1970; Rona 1978).

Initial laboratory measurements of rock magnetism show that the magnetic mineralogy of our samples consists of a combination of magnetite, maghemite and hematite with various Ti-substitution. Additionally, goethite, pyrrhotite and greigite may be present in some samples. Sample susceptibilities vary from 6x10^{-4} to 0.1 (SI), and NRM ranges from 0.02 to 9 A/m. Resultant Koenigsberger ratios between 0.7 and ~90 indicate that both induced and remanent magnetizations contribute to magnetic anomalies in some locations, whereas others are strongly dominated by remanent magnetization. The significant contribution of remanence suggests that the NRM directions of the lavas influences their aeromagnetic response, and accordingly their NRM directions (e.g. Godard et al. 2003) should be considered when interpreting the RTP aeromagnetic map (Clark 1997).

4 Interpretation

4.1 Aeromagnetic-assisted mapping of Lasail Unit

In the Wadi Rajmi area (Fig. 5), the weakly magnetic Lasail Unit is clearly recognized by its pale grey appearance and its low aeromagnetic response compared to the adjacent Geotimes and Alley Units. This configuration was confirmed by field observation and sampling (Fig. 5). Lasail lavas consistently display weak RTP anomalies throughout the ophiolite, this is consistent with their low magnetic susceptibility in hand specimen (Fig. 4), high bulk-rock Mg#, and lack of hematite in outcrop suggesting Fe is mostly situated in non-magnetic silicate minerals.

Figure 3. Zonation of molar Ti vs. Mg# (= molar Mg/(Mg+Fe)) in clinopyroxenes. Fields of volcanic units after Alabaster et al. (1982); Kusano et al. (2012); Kusano et al. (2014); Gilgen et al. (2014, 2016). Vectors show zonation between median core values and rim values. Lines without arrowheads represent crystals where growth direction was unclear.

Figure 4. Magnetic susceptibilities of the four major volcanic units as measured by handheld magnetic susceptibility meter. N for Geotimes=20; Lasail=15; Alley=21; B. Alley=8.

Figure 5. Aeromagnetically-assisted mapping of Lasail in the Wadi Rajmi area.
4.2 Aeromagnetic-assisted mapping of boninites

In the area of the Safwa VMS deposit (Fig. 6), the Boninitic Alley unit is readily identified in the field, confirmed by sampling, separated from underlying Alley lavas by a set of discontinuous umbers. These field observations are corroborated by analyses of the footwall and hangingwall of the nearby Safwa deposit (Gilgen et al. 2014). The weak RTP aeromagnetic signal correlates well with the boninites, visible as pale lavas on the satellite image. The generally low magnetic susceptibility of Boninitic Alley in comparison to Alley (Fig. 4) means that gold-prospective boninites can be inferred wherever weakly magnetic lavas overlie highly magnetic Alley lavas.

![RTP Aeromagnetic survey and New geological map](image)

**Figure 6.** Aeromagnetically-assisted mapping of Boninitic Alley in the Safwa area.

5 Conclusions

By augmenting field observations and aeromagnetic map interpretations with geochemical and rock magnetic characterisations, we have been able to map the four major volcanic units of the ophiolite over ca. 600 km² of surface exposure and 250 km strike length. Moreover, the aeromagnetic map has allowed us to infer the presence, and in many cases the unit affiliation of a further ~1400 km² lavas concealed under sedimentary cover. The methods outlined in this study are potentially a viable approach to mapping VMS-prospective tholeiitic volcanic suites in other ophiolites or greenstone belts (e.g. Kerrich et al. 1998).

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Metamorphic overprint on the Ashele Cu-Zn deposit in Altay, Xinjiang: evidences from geology and inclusions

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Abstract. The Ashele Cu-Zn deposit is located in the Ashele Devonian volcanic-sedimentary basin to the south of Altay orogenic belt. Deformation and metamorphic textures are well developed in wall rock and ore, such as pyrite pressure shadows. Three kinds of quartz veins can be distinguished, i.e., the quartz veins in the volcanic layers (Q1), lentoid quartz veins (Q2) in metamorphosed volcanic rocks and sulfide-quartz veins (Q3) cutting across mylonitized tuff. The $H_2O-CO_2$ fluid inclusions in Q1 have $T_{min}$ from 130–247°C, with salinities between 2.8–5.8wt% NaCl equiv. The carbonic inclusions in Q1 have the $T_{min}$ of -58.7–58.3°C, and the $T_{h,cO2}$ of 6.0–8.6°C. The primary $H_2O-CO_2$ inclusions in Q3 have $T_{h,bsf}$ of 220–296°C, with salinities between 3.6–8.8wt% NaCl equiv. The CO₂-rich and low salinity inclusions are typical of metamorphic fluids. The δ¹⁸O values of the parent fluids of Q1, Q2 and Q3, respectively, range from 4.1‰–6.8‰, 6.2‰, and 5.5‰–7.4‰ (SMOW), and the δD values range from -97.3‰~104.5‰, -92.8‰, and -98.7‰~109.6‰ (SMOW), respectively. All these data suggest that metamorphic fluids were involved in deformation and metamorphism of the VMS deposit.

1 Introduction

The Ashele Cu-Zn deposit, located at the northwest of Altay Orogenic Belt, is one of the largest VMS deposit in China. Abundant geological literature regarding the tectonic setting, ore geology, geochemistry, chronology and metallogenic mechanism has been recently published (Wan et al. 2010; Yang et al. 2014). The deposit is considered a typical volcanicogenic massive sulfide (VMS) deposit, which was related to Early Devonian marine volcano-sedimentary events. Some geologists believed that the deposit had been modified by late metamorphic and hydrothermal metasomatism (Zheng et al. 2015). Cu-bearing vein mineralization is associated with silicified tuff. Moreover, that mineralization associated with silicified tuff is deformed. In this study, we report new data obtained from field investigation and comprehensive laboratory study using petrography, mineralogy and fluid inclusions to evaluate the metamorphic overprint on the Ashele Cu-Zn deposit.

2 Geological setting

The Ashele Cu-Zn deposit located at the 30km northwestern of Habahhe. The exposed strata in the Ashele area are the early-middle Devonian Ashele Formation and the late Devonian Qiy Formation (Fig. 1). The Ashele Formation, composed of tuff, rhyolite, basalt, limestone and barite, host the Cu-Zn ore bodies. Yang et al. (2013) report the U-Pb ages are 387±4.2Ma, 388.2±3.3Ma for tuff and basalt, respectively. The Ashele area underwent several phases of folding, with axial planes dipping east and striking NS. The mining area was adjacent to the Erquis deep fault, and its secondary faults including Maerkakuli fault and Biesisala fault.

Fourteen mineralized zones are found in the mine district, and the No.1 mineralized zone includes four ore bodies. The ore bodies that occur between the basalt and tuff are bedded and lenticular. The ore bodies extend along a 900m north-south strike length. The deposit is Cu-Zn rich minor Ag, Au and Pb with an average grade of 2.46% Cu, 2.93% Zn, 0.41% Pb, 18.37×10⁻⁶ Ag, 0.36×10⁻⁶ Au, 22.66% S.

3 Metamorphism and deformation of ore structures and textures

Some geologists suggest that the Ashele deposit had regional metamorphism, and later hydrothermal alterations, which are intensive and dominated by sericite and chlorite; the rocks have also been mylonitized. Wu et al. (2015) reported 251±4.2 Ma $^{40}Ar/^{39}Ar$ isochron age on sericite that is interpreted to reflect the age of brittle-ductile shearing in the district.

Petrographic observations shows that wall rocks have
strong deformation and metasomatic textures, and show
ductile shearing (Fig. 2). Asymmetric and symmetric
pyrite pressure shadows are well developed in
metamorphic tuff, and the quartz formed “pressure
shadows” displays apparent undulatory extinction (Figs.
2a, b). The metamorphosed rhyolitic porphyry has
blastoporphyritic texture and lepidoblastic textures, and
minerals in the matrix are mainly composed of quartz
and secondary minerals such as white mica and sericite.
The quartz grains show widespread recrystallization,
and the scaly sericite distribute directionally in
metamorphic rhyolitic porphyry (Figs. 2a, b). Some
elongated quartz phenocrysts display apparent
undulatory extinction (Fig. 2c). Most of quartz
phenocryst are featured frequently with melting
corrosion structure and secondary fibrous mineral
developing (Fig. 2d). The exsolution of pyrite from
sericite which is in the form of veins and directionally
(Fig. 2e). We also found that tiny sericite veinlets cuts
across the vein quartz in the metamorphic rhyolitic
porphyry (Fig. 2f).

heating and cooling. They are H₂O–CO₂ fluid inclusions
(WC-type; liquid H₂O+liquid CO₂ or liquid H₂O + vapor CO₂; Figs. 3a, b), aqueous inclusions (W-
type; liquid H₂O + vapor H₂O; Fig. 3c) and carbonic
fluid inclusions (C-type; liquid CO₂; Fig. 3d).

Figure 2. Microstructure feature of metamorphism and
deforestation textures in the Ashele Cu-Zn deposit

4 Fluid inclusion

4.1 Fluid inclusions petrography

Three occurrences of vein quartz can be distinguished in
the Ashele Cu-Zn deposit. They are quartz veins in the
volcanic layers (Q1) including rhyolite and basalt,
leptoid quartz veins (Q2) in the schistosity of the
metamorphosed tuff and chlorite schist and quartz veins
(Q3) cutting across the mylonitized tuff with
disseminated pyrite and chalcopyrite.

Three types of fluid inclusions were recognized in
vein quartz (Q1, Q2 and Q3) on the basis of phases
present at room temperature and phase changes during

Figure 3. Photomicrographs of fluid inclusions from the
Ashele deposit. a- The isolated H₂O-CO₂ inclusion; b-
The scattered fluid inclusions; c- The aqueous fluid
inclusions; d- Carbonic fluid inclusions.

4.2 Microthermometry results

(1) The main fluid inclusions in Q1 are W-type which
appears as isolated or scattered within individual quartz
grains. The primary W-type fluid inclusions in Q1 have
ice-melting temperatures (T_{m,ice}) from -6.6 to -1.1 °C, and
homogenization temperatures (T_{h,co}) from 117 to 214 °C,
with salinities between 0.18–9.98 wt% NaCl equiv and
densities between 0.86–1.00 g/cm³. The fluid inclusion
assemblages (FIA) of W-type in Q1 have T_{m,ice} from -3.7
to -2.3 °C, and T_{h,co} from 109 to 113 °C. The minor WC-
type fluid inclusions scattered in Q1 have CO₂ melting
temperatures (T_{m,CO₂}) from -57.6 to -56.8 °C, clathrate
melting temperatures (T_{m,clath}) from 7.2 to 8.6 °C, and
homogenization temperatures of CO₂ phases (T_{h,CO₂})
from 8.9 to 29.8 °C (to liquid CO₂) and T_{h,co} are in the
range of 130 to 247 °C, with salinities between 2.8–5.8 wt% NaCl equiv. The C-type inclusions in Q1 have
the T_{m,CO₂} of -58.7–58.3 °C, and the T_{h,CO₂} of 6.0–8.6 °C
(to liquid CO₂) (Fig. 4).

(2) The primary scattered and isolated W-type fluid
inclusions in Q2 have T_{m,ice} from -6.8 to -4.0 °C, and T_{h,co}
from 91 to 272 °C with salinities between 0.18–10.2 wt%
NaCl equiv and densities between 0.83–1.00 g/cm³,
whereas the FIAs of W-type fluid inclusions in Q2 have
T_{m,ice} from -1.0 to -1.9 °C, and T_{h,co} from 105 to 112 °C
with salinities between 0.18–3.23 wt% NaCl equiv and
densities between 0.95–0.97 g/cm³.

(3) The primary WC-type inclusions in Q3 have T_{m,CO₂}
from -59.1 to -57.5 °C, T_{m,clath} from 5.2 to 7.8 °C, and
T_{h,CO₂} from 9.6 to 23.2 °C (to liquid CO₂), with salinities
between 3.6–8.8 wt% NaCl equiv. The T_{h,co} of WC-type
inclusions range from 220 to 296 °C (Fig. 4), but a lot of
them were decrpetitated before homogenization during
heating. The W-type fluid inclusions can be divided into
two groups: one group has T_{h,co} from 100 to 305 °C, and
$T_{m,\text{ice}}$ from -8.1 to -1.2 °C with salinities between 2.07–11.8wt% NaCl eqv and densities between 0.78–0.99g/cm$^3$, and another group has $T_{h,\text{H}_2\text{O}}$ from 217 to 247 °C, and lower $T_{m,\text{ice}}$ from -21.0 to -9.8 °C with salinities between 13.7–23.0wt% NaCl eqv and densities between 0.87–0.97g/cm$^3$. The FIA of W-type inclusions has $T_{m,\text{ice}}$ of -2.7 °C, and $T_{h,\text{H}_2\text{O}}$ of 123 °C.

![Image](image_url)

Figure 4. Histograms of microthermometric data of primary WC-type fluid inclusions from the Ashele Cu-Zn deposit

4.3 Laser Raman spectroscopy

Laser Raman spectroscopic analysis reveals that the volatiles of WC-type fluid inclusions are dominated by CO$_2$ and H$_2$O, with minor N$_2$ in the CO$_2$ phases (Figs. 5a,b,c). This agrees with the observation that the melting temperatures of CO$_2$ solid are lower than -56.6 °C. The W-type inclusions are dominated by H$_2$O (Fig. 5d).

![Image](image_url)

Figure 5. Representative Raman spectra of fluid inclusions from the Ashele Cu-Zn deposit

5 Hydrogen and oxygen isotopes

The $\delta^2$D values of fluid inclusions and $\delta^{18}$O values of quartz from the Ashele deposit are listed in Table 2. The $\delta^{18}$O$_{H_2O}$ was calculated according to the $\delta^{18}$O Quartz and homogenization temperatures of the fluid inclusions using the equation $1000\ln\frac{\text{O}_{\text{H}_2\text{O}}}{\text{H}_2\text{O}}=3.38\times10^6 T^2 - 3.40$ (Clayton et al. 1972).

The calculated $\delta^{18}$O$_{H_2O}$ values of parent fluids of Q1, Q2 and Q3 quartz veins respectively range from 4.1‰ to 6.8‰ (SMOW), 6.2‰, and 5.5‰ to 7.4‰ (SMOW), and the measured $\delta^2$D values of fluid inclusions range from -97.3‰ to -104.5‰ (SMOW), -92.8‰, -98.7‰ to -109.6‰ (SMOW) respectively (Table 1).

<table>
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<th>Sample</th>
<th>Temperature</th>
<th>$\delta^{18}$O (‰)</th>
<th>$\delta^{18}$O$_{H_2O}$ (‰)</th>
<th>$\delta^2$D (‰)</th>
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<td>ASL150</td>
<td>Q2</td>
<td>272</td>
<td>14.2</td>
<td>6.2</td>
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6 Discussions

Petrographic observations show that the wall rocks and ores of Ashele deposit have deformation and metasomatic textures. For example, asymmetric and symmetry pyrite pressure shadows, zonal extinction of quartz, undulatory extinction of quartz, and altered of quartz edge. These features indicate that the deposit was overprinted by metamorphism and late hydrothermal events. The microthermometric and laser Raman spectroscopic data of fluid inclusions documented in this study indicate that there are some carbonic and H$_2$O-CO$_2$ fluid inclusions in the veins-type quartz in the volcanic layers (Q1) and the sulfide quartz veins (Q3). The fluids are characterised by CO$_2$-rich, medium-low temperatures and low salinities. The fluid inclusion homogenization temperatures and salinities in Q1 and Q3 are consistent with a metamorphic fluid source (Fig. 6). The $T_{m,\text{CO}_2}$ and $T_{h,\text{CO}_2}$ of fluid inclusions in Q1 are higher than those in Q3, and the $T_{h,\text{H}_2\text{O}}$ are lower. The minimum trapping pressures of WC-type inclusions can be estimated by using the H$_2$O-CO$_2$-NaCl system phase diagram of Brown and Lamb (1989). Based on the densities of CO$_2$-phases, $T_{h,\text{H}_2\text{O}}$ and the salinities of WC-type inclusions, the minimum trapping pressures of WC-type inclusions of Q1 and Q3 are 230-280MPa and 290-350MPa, respectively. Those characteristics are typical of metamorphic fluids as reported in many previous studies (Robert et al. 1995; Fu et al. 2000). There is a group of primary aqueous fluid inclusions having a higher salinities (13.7–23.0wt% NaCl eqv) than another group (2.07–11.8wt% NaCl eqv). It may be because the CO$_2$ diffuse out as the temperature decreasing (217 to 247 °C) during the H$_2$O-CO$_2$ fluid evolution, and the salinities of remain fluids rise to 10–50 wt% NaCl eqv (Hegemann and Luders, 2003).

The calculated $\delta^{18}$O$_{H_2O}$ and measured $\delta^2$D values of fluid inclusions in Q1, Q2 and Q3 fall in the field of metamorphic fluids and magmatic water (Fig. 7). This may be due to involvement of metamorphic fluids overprinting of original VMS fluids.
7 Conclusions

The deformed and metasomatic textures of wall rocks and ores in the Ashele deposit and abundant H₂O-CO₂ fluid inclusions in quartz veins suggest that metamorphic fluids have involved in deformation and metamorphism of the VMS deposit, and also in late hydrothermal events. The calculated δ¹⁸Oëë and measured δD values may also indicate that the primary VMS fluids were overprinted by the metamorphic fluids.

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References

Deep flow paths in VMS systems: Porosity and permeability of epidote alteration in the Semail ophiolite, Oman

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Abstract. The classic model of hydrothermal alteration of the upper oceanic crust identifies epidotes (basalts altered to epidote + quartz + titanite ± Fe-oxides) as markers of discharging hydrothermal fluid. Epidotes are depleted in metals and therefore they have been proposed as sources for the metals in volcanogenic massive sulfide deposits. However, this model is challenged by recent observations in ophiolites. One way to test the model is by reactive-transport simulations of the alteration. In preparation for this we report new observations of flow paths and of the porosity and permeability of epidotes and their precursor rocks in the Semail ophiolite, Oman. We have found that discharge through the layer of pillow lavas is not controlled by fractures or faults but rather occurs via pervasive rock-matrix flow. Interpillow hyaloclastite is first altered to epidote, followed by the cores of pillows and then by the rims of pillows. Our measurements show that the metasomatism leading to epidotisation of pillow lavas increases their connected porosity by 4–10 vol.% and it increases their permeability by 1–3 orders of magnitude. Thus, enhancement of permeability by epidotisation enables self-propagation of the discharging fluid through the extrusive oceanic crust.

1 Introduction

Metasomatic alteration of the oceanic crust is dominantly caused by circulation of seawater in temperature- and density-driven convection cells (Richardson et al. 1987; Alt 1995). A genetic link between the hydrothermal fluids which form metal-depleted epidotes in the discharge path and those fluids which form volcanogenic massive sulphide (VMS) deposits has been suggested (Richardson et al. 1987; Schiffman et al. 1987; Humphris and Cann 2000). There are numerous examples of epidotes at the base of the sheeted dikes which could feasibly be source rocks for VMS. However, some unexplained observations in ophiolites challenge the assertion that epidotes are the metal-depleted source rocks for VMS-forming hydrothermal fluids. Firstly, whereas Jowett et al. (2012) confirmed that epidotes in the Troodos ophiolite are depleted in Cu and Ni versus fresh diabase dikes, they found that these epidotes are not significantly more depleted than the adjacent spilitised dikes. Therefore, spilites, epidotes or both alteration types could feasibly be source rocks for the VMS deposits. Secondly, recent studies of the Semail Ophiolite (Gilgen et al. 2016) have
demonstrated that epidotes dominantly occur in the extrusive lavas, rather than being restricted to the base of the sheeted-dike complex (SDC), and that most of these epidotes post-date MOR-type spreading and the associated VMS deposits.

Cann et al. (2014) suggested epidotisation overprints fresh diabase dikes, however, we have found petrographic evidence in the pillow lavas that epidotisation overprints previously spilitised basalts (i.e. basalts altered to chlorite + albite + quartz + epidote). Bettison-Varga et al. (1995) reached the same conclusion by fluid-rock interaction modelling.

The sheeted dikes and extrusive lavas in the Semail ophiolite display pervasive epidotisation at various
in the ~1 km thick stack of pillow lavas, seafloor faults are spaced at 10^2–10^3 m intervals and chilling fractures are notably rare. Such discrete fracture systems cannot explain the huge volumes of pervasive epidotisation alteration, and therefore fluid flow during epidotisation must have been dominantly through the rock matrix (i.e. porous-medium flow). Field evidence shows that progressive alteration begins with epidotisation of the inter-pillow hyaloclastite, then it proceeds to replace pillow cores (Fig. 1a,b), and finally it replaces the pillow rims as well (Gilgen et al. 2016).

Earlier workers have presented some data on porosities and permeabilities of the oceanic crust. Einaudi et al. (2003) measured porosity excluding macro-fractures and they found spilite pillow porosities of 0.7–10.8 vol.%. Similar values were found by Christensen and Smewing (1981) by measuring p-wave velocities in plugs, although some macro-fractures could have been included in their samples. Studies which used crack distribution analysis on drill cores or fracture apertures in outcrops obtained higher values, up to 18 vol.% bulk porosity (Johnson 1979 and references therein; Gillis and Sapp 1997). To our knowledge, measurements of the porosity of epidotised pillows have not yet been presented in the literature.

The permeability of dikes from the sheeted dike complex in Oman has recently been measured by Coelho et al. (2015). They found that metadiabase and strongly chloritised metadiabase dikes have similar permeabilities of ~7x10^{-20} m^2 whereas epidotised dikes have permeabilities of ~1x10^{-18} m^2. In the present study we present the first determinations of rock-matrix permeabilities of spilitised and epidotised pillow lavas.

Here we report porosities and permeabilities of epidotises and their spilite precursors from the crustal layers of pillow lavas and the sheeted dike complex (SDC) in the Semail ophiolite.

2 Methodology

Test measurements showed that the porosity and permeability of pillow lavas varies considerably. Meaningful comparisons of spilitised and epidotised pillows can therefore be obtained only if the samples originate from within the same textural zone of an individual pillow or dike; herein such samples are called conjugate pairs. The textural zones within pillow lavas are its rim, core and crust. These zones can also be recognised in partially epidotised pillows (Fig. 1a,b). Within dikes, chilled margins are treated as distinct textural zones from the coarser-grained dike cores. Consequently, our representative elementary volume (REV) for sampling is restricted to a particular textural zone within an individual pillow or dike and it excludes macro-fractures.

Porosity was measured using two techniques, one on plugs and the other on thin sections. These values were then compared for each hand specimen. Permeabilities of plugs were measured using a CMS-300 unsteady-state helium permeameter at room temperature and at 55 MPa confining pressure.

2.1 Porosity methodology

The two chosen methodologies to measure porosity differ in the way the intercrystalline porosity is measured. One uses helium pycnometry of rock plugs measured at room temperature and pressure hence it is termed "pycnometric". The other is based on back-scattered electron (SEM-BSE) images of 2D petrographic thin-sections processed by digital image analysis (DIA) protocols, hence it is termed "DIA". The pycnometric methodology applies to a sample volume between 4 cm^3 and 17 cm^3, whereas the DIA methodology is in practice applicable only to individual thin sections, i.e. to sample areas of ~1.25 cm^2, which translate (given that the mineral texture is isotropic) to a volume of ~1.4 cm^3. Unfortunately, microporosity < 20 μm^3 cannot be measured reliably using DIA due to the presence of mechanical plucking pits induced during sample polishing. For the same reason, intracrystalline cannot be measured using DIA and neither is it accessible by pycnometry measurements.

2.2 Post-obduction clogging minerals in epidotised pillows

Calcite and chlorite were preliminarily identified as post-obduction clogging minerals in epidotises. Calcite is present in intercrystalline pores and occasionally vesicles. Chlorite is in intercrystalline pores and also replaces quartz and epidote. Some of the chlorite may be a relict from the precursor spilite assemblage. However, commonly its overgrowth textures indicate that it formed after epidotisation, potentially within the alteration haloes of late quartz–hematite–pyrite veins (Gilgen 2014). The volume of calcite was estimated by acid-leaching after the porosity determinations by pycnometry. However, neither calcite nor chlorite could be reliably quantified during DIA. Furthermore, neither mineral could be removed prior to the permeability measurements, mainly because unclogging of post-obduction calcite microveinlets by acid treatment would artificially elevate the measured permeability. Due to all these complications, only a subset of the analysed samples is ideal for the chosen analytical methods.

3 Spilite and epidotise porosity

Our pycnometry measurements demonstrated that the coarse-grained cores of spilite pillows have systematically higher porosity (by 1.3–5.2 vol.%) than their fine-grained rims. This is due to inheritance of primary igneous grain-size variation (Fig. 2a,b). However, pillow cores from adjacent pillows show strong variations in absolute porosity, as do rims from adjacent pillows.

A conjugate (spilite-epidosite) pair free of clogging
minerals and macrofractures showed that the spilite has ~3 vol.\% connected porosity whereas the epidosite has ~13 vol.\% connected porosity. Thus, the increase in porosity upon epidotisation is ~10.0 vol.\%. The difference between pore sizes and pore abundance in spilites and epidotises is clearly visible in BSE images of pillow cores (Fig. 2b,c).

In contrast, spilitised dikes from the SDC have systematically lower porosities (<2 vol.\%) and their conjugate epidotises are only ~2 vol.\% more porous.

Figure 2. BSE-SEM images at the same scale. a Spilitised pillow rim. b Spilitised pillow core from the same pillow as in a. c Epidotised pillow core from a different pillow. Abbreviations: Alb = albite, Qtz = quartz, Epi = epidote, Chl = chlorite, Fe-ox = Fe-oxides.

4 Permeability

Our permeability results follow the same trend as the porosity in spilite pillows, i.e. the pillow cores are more permeable than the pillow rims. Similarly, whereas spilitised pillows have very low rock-matrix permeabilities of 9x10^{-20} to 4x10^{-18} m^2, the epidotised pillows (with low to moderate amounts of post-epidotisation clogging minerals) have much higher values of 1x10^{-18} to 3x10^{-15} m^2. Spilite dikes have low permeabilities on the order of ~1x10^{-19} m^2.

5 Discussion and conclusions

5.1 DIA and pycnometric technique comparison

The pycnometric technique overestimates porosity only for fractured samples, but it measures both micro- and macro-intercrystalline porosity well. The effect of calcite clogging on the porosity can be corrected readily by acid leaching, whereas the effect of chlorite cannot be corrected. The DIA technique is limited in that it cannot measure micro-porosity (due to confusion of true micro-pores and mechanical plucking pits on the thin-sections) and that calcite and chlorite cannot be removed by DIA. The presence of post-epidotisation chlorite complicates both techniques and needs to be screened and accounted for. Furthermore, DIA of an area of only ~1.25 cm^2 (~1/3 of a thin-section) may accidentally sample localised zones of high or low porosity, which are not representative of the hand sample, nor of a particular zone in a pillow or dike. Pycnometry of standard plug samples (2.5 cm diam., 5 cm long) is thus more representative, and it has yielded our preferred dataset.

5.2 Flow paths

The weakly consolidated, chloritised and permeable hyaloclastites mantling the spilitised pillow lavas are the initial pathway of the epidotising fluid though a pillow stack (Gilgen 2014). This is consistent with hyaloclastite being the first zone of pillow stacks to be epidotised. The difference in porosity (1.3–5.2 vol.\%) and permeability between the core and rim of spilite pillows clearly explains why epidotisation first occurs in pillow cores (Fig. 1a,b). Even small differences in pre-epidotisation porosity and permeability evidently controlled the flow paths of epidotising fluids. The coarser interiors of dikes similarly provide more permeable channels for fluid flow than their fine-grained chilled margins.

5.3 Reaction permeability

Harper (1988) suggested that epidotises should have higher porosity and permeability than their precursors based on the 10.8 vol.\% decrease when albite is altered to epidote. The self-propagating nature of epidotisation has been indicated by several sources; Bettison-Varga et al. (1995) suggested this based on their fluid-rock interaction
models, Gilgen (2014) based on the $\Delta V_{\text{solids}}$ associated with the measured reaction stoichiometry for epidotisation and Cann et al. (2014) based on petrographic evidence.

The $\sim 1$–$3$ order of magnitude difference between mean permeability values of spilites and epidotes confirms that epidotisation is a self-propagating process during which the hydrothermal fluid creates its own permeability by replacing spilitic precursors with the lower-volume epidote mineral assemblage. This supports the field observations that a permeable fracture network is not required for pervasive fluid flow through spilite rocks.

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A study of inversion within the Irish Orefield from regional to mine scale

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Abstract. The Lower Carboniferous Limestones in Ireland are host to the highest concentration of Zn and Pb per km² in the world. Here, early Carboniferous N-S extension led to the formation of a broadly ENE trending array of normal faults which subsequently acted as the controlling structures for mineralisation. Post-ore compression during the Variscan Orogeny led to inversion of these normal faults and the deformation of many of the original orebody geometries in the Irish Orefield. In a preliminary study we use newly compiled, open-access and industry datasets to explore four main topics relating to inversion: 1) how inversion is manifested regionally throughout the Irish Orefield, 2) how ore-controlling normal faults and lithologies have responded to inversion at the mine scale, 3) the links between various breccia’s and inversion-related deformation and 4) potential inversion-related remobilisation of the mineralisation. This study will provide insights into the principal spatial, rheological and temporal controls on the inversion of Carboniferous normal faults and associated mineral deposits. Ultimately, a more comprehensive understanding of how inversion is manifested will allow for better data interpretation for research, exploration targeting and mine evaluation.

1 Introduction

The Lower Carboniferous limestones in Ireland are host to the Irish Zn-Pb orefield, one of the most significant sources of Zn in the world and the location of several major ore deposits. Two of the largest deposits include the Navan (>100mt @ 8.2%Zn and 2%Pb), and Lisheen (23mt @13.3%Zn and 2.3%Pb) orebodies. All the deposits are stratabound and associated with normal faults that in some cases are seen to influence carbonate sedimentation. Much of the thickest and highest grade mineralisation is adjacent to these faults that appear to have acted as the main conduits for mineralising fluids accessing the carbonate host-rock.

In this study we outline the results of preliminary analysis of Lisheen Mine data, a deposit which is genetically related to the Galmoy and Rapla deposits and located along the broadly ENE-orientated Rathdowney Trend. The gross regional outcrop pattern is largely controlled by broad, ENE-trending folds that mirror the Caledonian strike of the basement seen throughout the SE Irish Midlands (Fusciardi et al. 2003). At Lisheen the outcrop pattern is complicated by a series of E-W to ENE-trending normal faults with throws of 150-200m to the north. They form a series of left-stepping, northerly dipping, en-echelon fault segments that exhibit a classic ramp-relay geometry (Hitzman et al. 1992, 2002; Shearley et al. 1995, 1996; Carboni et al. 2003; Fusciardi et al. 2003). These faults formed as a result of N-S extension during the early Carboniferous and subsequently acted as the key controlling structures for mineralisation which is late- to post-faulting and yet still of Lower Carboniferous age (Fusciardi et al. 2003; Hitzman et al. 2002).

Figure 1. Simplified geological map of Ireland showing the location of the main deposits of focus for this study.

The mineralisation consists of a number of broadly stratiform, stratabound, massive and semi-massive sulphide lenses together with vein and disseminated sulphides. Four economic massive sulphide bodies are known: Main Zone, Derryville Zone, Bog Zone and Island Pod each controlled to the south by a bounding normal fault segment.

The Variscan orogenic episode, which is generally considered to post-date mineralisation, occurred between the Late Carboniferous and Early Permian as a result of the collision between the large southern continent, Gondwana, with a combination of the northern landmasses Laurentia, Baltica and Avalonia which had been assembled into a single
large continent during the Caledonian orogenic cycle (Graham, J.R 2009). In SW Ireland it manifests itself as a series of tight isoclinal folds which formed as a result of dextral transpression due to a roughly N-S oriented $\sigma_1$. This Variscan-related deformation has been well documented in the SW of Ireland where mountainous terrains and long coastal sections allow for excellent exposure. However, this is not the case for the central part of Ireland where outcrop is limited due to glacial sediments and peat cover particularly in areas dominated by the limestone/shale sequences of the Zn-Pb orefield. As a result, the effects of the Variscan and any subsequent deformation is not well defined or understood. This study therefore uses all of the available legacy data from exploration programmes or pre-existing mines, including drillhole logs, assays, underground maps and geophysical data.

These data show that ore deposits throughout central Ireland have been subject to significant inversion, and the purpose of this study is to investigate the structural and potentially mineralogical consequences of this inversion.

2 Aims

This study uses newly compiled open-access and industry datasets, field mapping, 3D modelling, drill core sampling, petrographic analysis and published literature to explore four main topics relating to inversion:

1. How inversion is manifested regionally throughout the Irish Orefield.
2. How ore-controlling normal faults and lithologies have responded to inversion at the mine scale,
3. The links between various breccias and inversion-related deformation.
4. The effects of inversion on potential remobilisation of the mineralisation.

This project will use regional and deposit data from across the orefield but thus far only the inversion along the Rathdowney Trend in the southern part of central Ireland has been examined.

3 Methodology

Preliminary work has focussed on the compilation and digitization of large volumes of data from borehole logs, geophysics and field-mapping, both surface and underground. Surfaces, representing structures and lithologies, were generated using a variety of 3D geomodelling software packages. Vulcan® (Maptek) was used for explicit modelling in areas of high data density where it was possible to
elucidate detailed structural complexity. Data validation, exploration and visualization was carried out with Leapfrog3DGeo® (ARANZ Geo Ltd.). Additional data-entry, data-visualization and georeferencing was carried out using ArcMap® (ESRI). It is planned to conduct structural logging and breccia sampling from select core form the Rathdowney Trend to complement this work.

4 Results

At Lisheen, a compressional event attributed to the Variscan Orogeny, has inverted many of the ore-controlling extensional faults. This has led to:

(i) Development of ENE, dextral-transpressive faults with displacements typically in the order of 50-100m most of which is lateral. These faults offset the larger ore-controlling normal faults along the Rathdowney Trend. Another form of associated deformation is seen in the Derryville Zone and Bog Zone East (see fig.2 for location) where over-thrusting of both orebodies is nicely developed (Fig. 3). Similar strain vectors have been recorded elsewhere along the Rathdowney Trend at Galmoy (R-Zone) and Rapla.

(ii) Buttressing against the footwall block of the normal faults resulting in large scale, north-facing, folds, over-folds and back-thrusts in the proximal hanging-wall. These are usually sited on pre-existing smaller-scale, normal faults related to the larger extensional structures (Fig. 4 & 5).

(iii) The inversion of smaller-scale normal faults within the hanging-wall of the bigger structures, deformation which is generally expressed as folding in the orebody, to form gentle roles, tight pinches or even over-folds (Fig. 6).

(iv) The coincidence of pale, Fe-poor, Zn-rich ore in inversion-related fold hinges, suggesting that additional mineralisation or remobilisation of ore
accompanied inversion. This topic will be the focus of future work.

(v) The occasional development of footwall shortcut thrusts, a style of deformation highlighted by the 3D modelling of the Rapla prospect, some 20km to the northeast of Lisheen along the Rathdowney Trend. This is different to the style of inversion seen at Lisheen despite being on the same fault trend and emphasises the importance of extending this study to a more regional scale.

5 Conclusion

This study provides key insights into the principal spatial, rheological and temporal controls on the inversion of Carboniferous normal faults and associated mineral deposits in the Irish Orefield. We quantitatively identify how inversion has effected orebody geometries at different scales by means of detailed 3D modelling using new and legacy data from various deposits, including Lisheen, Silvermines, Tynagh, Gortdrum and Navan.

Preliminary data from the Rathdowney Trend which includes the Lisheen, Galmoy and Rapla deposits suggests that inversion has resulted in a predominantly ENE-WSW orientated dextral-transpressional slip. This has reactivated and complicated the original E-W orientated, left-stepping, en-echelon ore-controlling faults. Locally, this has significantly deformed the original orebody geometry and preliminary investigation of ore textures suggest that associated fluid flow may have remobilised metals.

Vectors of compression are known to vary across the orefield and further work will characterise how this is manifested. Many of the deposits in the Irish Orefield exhibit significant inversion and therefore a more comprehensive understanding of how inversion is expressed will allow for better interpretation of data for exploration targeting and mine evaluation.

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References


Geochemical stratigraphy of the Karakaya non-sulphide Zn-Pb deposit, Hakkari, SE Turkey

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Abstract. The Karakaya non-sulphide Zn-Pb deposit occurs within a sequence of Middle-Upper Triassic-Jurassic carbonates. The deposit consists of three main parallel ore zones each with an average thickness of 2.5 m. The ore consists of smithsonite, hemimorphite, zincite/hydrozincite, goethite, hematite, cerussite and anglesite. This study details trace element behaviour throughout the 30 m thick sequence of the third ore zone. The average Tl, As, Hg, Sb, Mo, Mn and Ba content of the associated carbonates are 13, 49, 0.25, 2, 4, 2970 and 1454 ppm, respectively. These values are much higher than the average of marine carbonates (0.14, 2.6, 0.04, 1.5, 2, 0.055, and 10 ppm). The average content of the Tl, As, Hg, Sb, Se, Mo and Ba in the 13 ore levels of the third ore zone are 301, 3938, 15, 114, 3, 90, 5629, and 1189 ppm, respectively. The enrichment of the same trace elements in the both ore and associated carbonates suggests a repeated hydrothermal discharge into a sedimentary basin. Trace element-rich ore and carbonates imply a metal-rich pool where the Tl, As, Hg, Sb and Mo precipitated at a basin scale. These trace element associations are more indicative of SEDEX-type mineralization not MVT or Irish-type Zn-Pb deposits.

1 Geology of the Karakaya deposit

The Karakaya non-sulphide Zn-Pb deposit is located in in the south of Hakkari, SE Turkey (Figure 1). The geology regional geology comprises Permian aged thick, organic-rich limestone, Lower Triassic (Skytian) aged mudstones showing red, brown, burgundy and green colours, Middle- to Upper Triassic limestone, dolomitic limestone with interbedded shales and Jurassic limestone and dolomitic limestone (Periçek 1990). The deposit occurs within the Middle-Upper Triassic and Jurassic carbonate sequence.

The deposits are located in the northeast and southwest limbs of an anticline plunging to the northwest (Figure 2). The mineralization consists of parallel ore levels with varying thicknesses from cm to meters. Three of these ore levels have a thickness of more than 1 m and are called Ore Zone-I, Ore Zone-II and Ore Zone-III (Figure 2). The Karakaya ore zones have a lateral continuation of approximately 2.5 km. The direction of the ore zone varies between N35W and N70W.

The ore in the south-western part of the anticline is inclined at 65-85° SSW, while in the north-east ore is inclined at a lower angle of 16-28° NNE. The average thickness of Ore Zones I, II and III is 2.5 m, 3 m and 6 m, respectively with 13 ore levels in Ore Zone 3. Due to faulting and intense oxidation the ore thickness varies and reaches up to 13 m at some locations.

The Karakaya deposit is a non-sulphide zinc-lead deposit developed by oxidation of the primary sulphidic ore which was composed mainly of pyrite/marcasite, sphalerite and galena, described as remnant whiting of the non-sulphide ore zones. The supergene ore mainly consists of smithsonite, hemimorphite, zincite/hydrozincite, goethite, hematite with cerussite and anglesite.

Figure 1. The geology of the Hakkari region (Arabian Plate simplified from the Periçek 1990) and the position of Zn-Pb ores in carbonate rocks (modified after Hanilci and Öztürk 2008).

Figure 2. Geological cross-section showing the Karakaya Ore Zones that parallel to each other and located wings of northwest depressed anticline.
2 Geochemical stratigraphy of ore zone-III

The mineralization is contained in a 30 m thick carbonate-dominated, but shale bearing zone, with at least 13 ore levels (Figure 3). This zone has been sampled with the aim of using the trace element concentrations and their behaviour in carbonates to understand possible scenarios for the origin of the mineralization. The carbonates are represented by the dark grey, well-bedded, locally laminated limestone without fossils. The interbedded dark shales are only a few cm thick in the carbonate-dominated sequence. Ore levels have a very regular thickness and lateral extension and have a sharp contact with carbonates. The ore levels are brownish-purple coloured, earthy at the surface and are locally enriched with zinc-oxide/carbonate, especially next to the wall rock contacts.

Figure 3: Alternation of ore levels (blue arrows) with carbonates at the bottom of the third ore zone.

The carbonate-dominated wall rocks (Figure 4) have a mean concentration of 3.9 ppm Mo (0.5-10 ppm), 3.4 ppm Ni (0.7-7 ppm), 49 ppm As (1-305 ppm), 20 ppm Cd (0.3-103 ppm), 2.1 ppm Sb (0.7-6 ppm), 12.5 ppm Tl (0.4-45 ppm), 0.25 ppm Hg (0.08-2.14 ppm) and 1454 ppm Ba (17-22529 ppm). The thirteen ore levels (Figure 3 and Figure 4) have an average Mo content of 90 ppm (4-420 ppm), the Ni content of 17 ppm (1-52 ppm), the As content of 3938 ppm (38-11904 ppm), the Cd content is 258 ppm (7-1503 ppm), the Sb content is 114 ppm (1-532 ppm), the Tl content is 301 ppm (6-1143 ppm), Hg content is 15 ppm (0.4-207 ppm), Mn content is 5629 ppm and the Ba content is 1189 ppm (between 31-7519 ppm). In figure 4, the pattern of metal enrichment compared to the adjacent carbonates is evident throughout the stratigraphic section. However, even during periods of non-ore deposition the host carbonates are enriched in metals above the values than the average carbonates (Ebens and Shacklette 1982; Ure and Berrow 1982; Wedepohl 1969-1978).

Figure 4. Trace element distribution of the carbonates and ore levels of the Karakaya Ore Zone-III. Dashed lines indicates the average compositions of the carbonates (data taken from Ebens and Shacklette 1982; Ure and Berrow 1982; Wedepohl 1969-1978).

3 Conclusion

The Karakaya non-sulphide Zn-Pb deposit occur within Middle-Upper Triassic-Jurassic limestones deposited in a shallow marine conditions. The continuity of ore levels without changing thickness along their length, and the thin and alternating structure of ore layers indicates that the ore was deposited as a syn-sedimentary sulphidic precipitate in the basin. The sharp contacts between ore and carbonates indicates a depth of deposition below the influence of waves or tides. The massive nature of the ore, without any carbonate, is also indicative of rapid deposition. The trace metal enrichment of associated carbonates and the ore zones is clearly evident for elements such as Tl, As, Hg, Sb and Mo indicating both precipitated in the same basin and that there was repeated pulses of metal-rich fluids exhaled into the basin. The higher trace element (Tl, As, Hg, Sb, Se and Mo) contents of 13 ore levels are also characteristics of the SEDEX-type of deposits rather than other sediment-hosted Zn-Pb deposits such as MVT or Irish-type.
Acknowledgements

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References


The sediment-hosted polymetallic target in SW Poland

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Abstract. Recently Poland has been subject of intense exploration by several exploration companies, with exploration focused on the prospective areas adjacent to reach Cu-Ag deposits of Lubin-Sieroszowice ore district. Recent exploration tested the continuation of low grade copper ore mineralization adjacent to inactive Cu-Ag mines in the Old Copper District. Reconnaissance diamond drilling intersected interesting polymetallic Cu-Ag-Pb-Zn-U mineralization in the lower Zechstein sedimentary rocks of the Old Copper District (North-Sudetic Trough). The high uranium content in mineralized profile opens up potential new research potential for this area.

1 Introduction

In Poland, before discovery of a Cu-Ag deposit in the southern part of the Fore-Sudetic Monocline in 1957 (Wyzkowski 1958), copper production was predominantly from ores from a copper district located within the Grodziecka Trough – the Konrad, Lubichow, Upadowa Grodziec mines, and the Leszczyniecka Trough – the Nowy Koscioł and Lena mines (Romaniec and Janiec 1957). These mines were active since the 1950s until the end of the 1980s, extracting a total of over 60 mln Mg of ore with an average Cu grade ranging between 0.55 % and 1.06 % Cu (Table 1). Due to the growing output of Cu-Ag ore containing over 2 % Cu in the New Copper District in the southern part of the Fore-Sudetic monocline, the extraction from the Old Copper District was gradually abandoned. Despite being an inactive mine, in the Nowy Koscioł mine the geological resources still amount to 13.5 mln Mg of ore with an average Cu grade of 0.6%. The undeveloped Wartowice deposit located west of the Konrad mine have resources of 56 Mt with an average grade of 1.23% Cu and 38 g/t Ag. Recent detailed chemical analyses or rocks from the Old Copper District has shown elevated gold and platinum group minerals in the strata underlying the copper ores (Speczik and Wojciechowski 1997; Wojciechowski 2001; 2011). The area west of the Nowy Kościół mine as previously geologically explored by four drill holes that yielded positive results. These positive results were the justification for new drilling that tested the possibility of a new Cu-Ag deposit in the western part of the Leszczyniecka Trough (Fig. 1). Presented herein are results from recent geological exploration in this area. (Fig. 1).

2 Geological setting

The ore-bearing series in the North Sudetic-Trough comprises from the bottom the Zechstein conglomerate, the basal limestone and the Zechstein limestone. The conglomerate (4.9 m) is composed of carbonate and magmatic rocks with ferrous-carbonate cement. The profile of the basal limestone (2.75 m) is bipartite. The bottom part comprises micritic limestones with organic detritus, locally with horizontal clayey-organic streaks and fractures filled with calcitic sparite and metal sulphides. The upper part of basal limestone consists of limy biolithites with fragmented shells of bivalves, brachiopods, ostracods, as well as algal pellets and fine oncoids. Furthermore, there are local styloлитes and thin diagonal and vertical fractures filled with calcitic sparite and iron oxides.

Table 1. The operation of the individual mines compared to their output and the average copper content of the ore (Konstantynowicz 1971)

<table>
<thead>
<tr>
<th>Mine</th>
<th>Operating period</th>
<th>Average Cu tenor of the ore</th>
<th>Total production of ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Konrad</td>
<td>1953-1989</td>
<td>0.78%</td>
<td>38 mln Mg</td>
</tr>
<tr>
<td>Lubichow</td>
<td>1962-1976</td>
<td>1.06%</td>
<td>2 mln Mg</td>
</tr>
<tr>
<td>Upadowa Grodziec</td>
<td>1953-1963</td>
<td>0.70%</td>
<td>1.6 mln Mg</td>
</tr>
<tr>
<td>Lena</td>
<td>1950-1973</td>
<td>0.55%</td>
<td>14.47 mln Mg</td>
</tr>
<tr>
<td>Nowy Kościół</td>
<td>1955-1968</td>
<td>0.55%</td>
<td>4.02 mln Mg</td>
</tr>
</tbody>
</table>

Above the Zechstein limestone there are dark grey limy marls with numerous fragmented remains of bivalve and brachiopod shells and foraminifers (2.43 m). The middle part of the Zechstein limestone is represented by light grey marly limestones with fragmented shells of bivalves and brachiopods (5.47 m) that limits the ore-bearing series. Barren yellow limy-clayey dolostones with manganese dendrites (17.97 m) rest above.

2.1 Mineralisation

The lowermost part of the geological profile is characterized by iron oxides. The ore mineralization appears 0.8 m below the top of the Rotliegend, with predominant chalcocite, locally accompanied by native silver and stromeyerite. Along the contact of the Rotliegend with basal limestone mineralisation is represented by an association of bornite, chalcopyrite and covellite. There are some local iron oxides concentrated into cloud-like or streak-like forms. Bornite and chalcocite mineralization is predominant in the lower part of the basal limestone. Locally the chalcocite form large, lens-like...
blebs, in which the individual microlites exhibit worm-like textures; moreover, chalcocite cements the nests of frambooidal pyrite dispersed within the rock. Additionally, in the massive nests of chalcocite there are very small oval inclusions of uranium minerals. Locally there are some fine xenomorphic grains of bornite, intergrown with chalcopyrite and silica-uranium minerals. In the middle part of the profile dominate bornite, with its microlites forming nests as well as individual microlites with worm-like texture. Galena and sphalerite with chalcopyrite and pyrite are main ore minerals in the upper part of the basal limestone. These sulphides form intergrowths and replace organic detritus, with large microlites of galena and sphalerite present in fractures filled with calcite. Chalcopyrite replaces fine carbonate grains. Locally there are large nests composed of galena, sphalerite, pyrite and sulfosalt minerals (tennantite-tetrahedrite).

The lower part of the Zechstein limestone complex represented by marly limestones is dominated by occurrence of sphalerite and galena, locally accompanied by pyrite. Pyrite forms frambooids dispersed in the rock and encrusts organic remains along with sphalerite and galena, while locally sphalerite constitutes cement for pyritic frambooids. No sulphide ore has been observed in dolomitic limestones, however, the voids between dolomite crystals are filled by limonite, with minor of hematite. In the vertical profile metal sulphides are arranged in zones. Copper sulphides are predominant in a zone proximal to the sediments affected by strong oxidation, with chalcocite and covellite, followed by bornite and chalcopyrite. The copper zone is gradually replaced by a zone with galena and sphalerite. The zone with copper minerals and the lower part of the lead-zinc zone are overlapped by an interval with uranium minerals and sulfosalt minerals of the tennantite-tetrahedrite group (Fig. 2).

Figure 1. Geological map with the location of documented Cu-Ag deposits, abandoned mines and deposits areas

Figure 2. The ore-bearing interval with lithostratigraphy and mineralisation in the reconnaissance borehole (depth in meters below ground level; gal – galena; sph – sphalerite; bor – bornite; cpr – chalcopyrite; cov – covellite; cc – chalcocite; hem – hematite; t-t – tennantite-tetraedrite; u – uranium minerals).

Figure 3. Selected photomicrographs; A – chalcocite (cc) with covellite (cov) as xenomorphic impregnation in Zechstein conglomerate; B – galena (gal) as replacement of organic detritus grains; C – bornite (bor), chalcocite (cc) and covellite (cov) intergrown with pyrite (py); D – sphalerite (sph) replacing organic detritus.
2.2 Geochemistry

Metal sulphides analyses in a micro-area have confirmed the presence of chalcocite, covellite, bornite, chalcopyrite, sphalerite, galena, tennantite, tetrahedrite, native silver, stromeyerite, jalpaite, as well as uranium minerals (Tab. 2, Fig. 4). The ore-bearing interval is relative vast and embrace 13.5 m, with smooth transitions between the individual zones of rich mineralisation: the copper zone, the uranium zone as well as the zinc and lead zone. The highest copper content is 0.73 wt% with 23 g/t of silver, while the average equivalent copper content of the richest ore-bearing 1.08 m interval equals 0.56 %. The highest lead content is 0.63 %, the highest zinc content is 0.45 %, with the highest uranium content 351 ppm. The thickness of the uranium-bearing interval is 4.08 m and the average uranium content is 0.0162 %.

Figure 4. Uranium minerals (u) as very small inclusions in chalcocite (cc) (BSE).

3 Discussion and conclusions

The distribution of mineralization in the newly drilled borehole is zonal with predominantly Cu-Zn-Pb sulphides with distributions similar to low temperature mineralization associated with the Rote Faule, which contains abundant Cu-Ag reserves (Oszczepalski and Rydzewski 1997; Pieczonka et al. 2007; Oszczepalski and Speczik 2011). Uranium mineralization correlates with tennantite-tetrahedrite group minerals present in the Cu-sulphides, as well as in the Zn-Pb zone. The uranium minerals coexist with the above-mentioned sulphides and form inclusions mainly in copper and lead sulphides, their origin can be explained in two different ways. In the Lubin-Sieroszowice District the high content of uranium is correlated with the rich presence of organic matter in Kupferschiefer (Oszczepalski 1999). This horizon uranium primarily constitutes a component of thucholite (Kucha and Przybyłłowicz 1999). In the case of elaborated borehole, uranium is present as its own minerals with sulfosalts in the basal limestone level, both in the micritic limestone part and in the biolithite. Therefore, the uranium mineralisation must have occurred coincident with the inflow of sedimentary brines that formed the sulfosalts minerals. Moreover, there is no visible correlation between uranium mineralisation and amount of organic matter accumulated in the rock, since the high amount of uranium have been recorded both in the micritic limestone and in the biolithite. The second hypothesis is that uranium has been accumulated in the organic matter during sedimentation and the early diagenesis of lower Zechstein sediments. The organic matter accumulated in the rock was gradually replaced by precipitating copper, lead and zinc sulphides, (Speczik and Püttmann 1987), This process resulted in uranium minerals occurring as small mineral inclusions enclosed in metal sulphides. In the case of the first hypothesis, uranium was supplied to the area of precipitation from outside the system eg. the crust, in the second, uranium remained in the system associated with organic matter, and during the creation of the Cu-Ag-Pb-Zn deposit it precipitated as its own minerals.

While comparing detailed results with the adjacent areas with documented Cu-Ag reserves in Old Copper District, the average copper content is similar. The neighbouring Cu-Ag deposits extracted from 1950 - 1989 featured low copper and silver tenor, amounting to approximately several hundred thousand tonnes of production annually. Additionally, the elevated Zn, Pb, and U contents suggest a potentially prospective deposit at shallow levels in the crust (300-500 m) within the area of Leszczyniecka-Trough. The reconnaissance borehole confirmed the presence of a polymetallic low grade mineralization with a range that can exceed 100 km² merging when the documented deposit located approximately 10 km northwest and the abandoned deposit approximately 7 km to the east. Furthermore, there is still an unexplored area in the west, where the presence of the low grade Cu-Ag-Pb-Zn-U mineralization and the same strata is also expected.

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Investigating regional Pb-Zn mineralization in the Paleoproterozoic Karrat Group, Greenland

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Abstract. Prospective Pb-Zn mineralization is hosted in two formations of the Karrat Group in arctic West Greenland: the Mârmorilik Formation, home to the historical Black Angel Mine, and the recently defined Qaarsukassak Formation. These formations are not observed in direct contact with each other and are separated by a basement topographic high, making it difficult to establish a link between the two formations with respect to their mineralization. Preliminary petrographic work on Mârmorilik and Qaarsukassak mineralization exhibit textures that suggest a late stage remobilization/deformation event after the emplacement of ore mineralization. Two or more phases of sphalerite crosscut massive sphalerite and pyrrhotite in Qaarsukassak mineralization, suggesting multiple stages of ore emplacement. Initial pyrite sulfur isotope analyses by traditional isotope-ratio mass spectrometry show a range of $\delta^{34}$S values between +0.2‰ and +7.2‰. Future work by SIMS analysis is expected to show a larger range of $\delta^{34}$S values if the ore sulfur has a sedimentary origin. Observations in the field show Pb-Zn mineralization concentrated along antiformal hinge lines in the Qaarsukassak Formation trending to the southeast, comparable to mineralization in the Mârmorilik Formation.

1 Introduction

Recent reconnaissance work in the Paleoproterozoic Karrat Group (~2.0-1.9 Ga) is focused on understanding the context of regional Pb-Zn mineralization. Ore sulfide minerals are found in the carbonate-hosted Mârmorilik Formation, where the prolific, but currently inactive, Black Angel Mine is located. Continuing exploration led to discovering Pb-Zn anomalies ~20 km north from Marmorilik (Coppard et al. 1992), known as the “Discovery area”. Here, sedimentary rocks of the Qaarsukassak Formation were recently described as a discrete sedimentary unit within the Karrat Group that occurs stratigraphically below the Nûkavsak Formation (Guarnieri et al. 2016). The Qaarsukassak and Mârmorilik formations were deposited directly on crystalline basement and might be of similar age, but since these two units are not in contact with one another and are separated by a basement topographic high, their stratigraphic correlation is unconfirmed. If it can be shown that the mineralization is epigenetic or structurally controlled, then the two units might host the same mineralization event, regardless of their relative depositional age. The aim of this study is to analyse regional ore sulfide samples to better characterize the isotopic geochemical characteristics of Pb-Zn mineralization in both formations and determine a deposit model for this mineralization. Methods include sulfur isotope analysis of pyrite and ore sulfide minerals, and lead isotopic analysis of galena to determine possible sources of fluids and potential similarities in fluid source(s) for the two host formations.

2 Karrat Group

Previous work suggests the Paleoproterozoic Karrat Group was deposited in an epicontinental rift to foreland basin within the larger Rinkian mobile belt, which is hypothesized to link up with the Foxe fold belt in Canada (Grocott and Pulvertaft 1990). Deposition of the Qeqertarsuup Formation (Lower Karrat Group) occurs unconformably above the Archean basement rocks (Umanak gneiss), possibly in a rift setting (Grocott and Pulvertaft 1990). A regional unconformity separates the lower and upper Karrat Group (Guarnieri et al. 2016) such that mafic volcanic rocks, greywackes, and carbonate rocks lie directly on Archean basement rocks or on the lower Karrat Group. The Mârmorilik Formation (Upper Karrat Group) was likely deposited in a sub-basin since stratigraphy there differs from exposures of the Karrat Group to the north, where the Qaarsukassak Formation occurs (Figure 1).

Figure 1. Simplified geological map of the Karrat Group area showing the Discovery area and Marmorilik.
2.1 Qaarsukassak Formation

The Qaarsukassak Formation has previously been suggested to represent a structurally displaced basal component to the Mârmorilik Formation (Coppard et al. 1992) given the carbonate lithologies and Pb-Zn present in both formations. This description has been updated by Guarnieri et al. (2016), who indicate the Qaarsukassak Formation consists of quartzites and calcite marbles overlain by graphitic quartzites and metamudstones with overall thicknesses ranging from a few meters to <50 m. Intercalated calcite marble and siliciclastics contain a thin layer hosting Pb-Zn mineralization containing grades of 41 wt.% Zn and 9.3 wt.% Pb (Coppard et al. 1992).

2.2 Mârmorilik Formation

The Mârmorilik Formation is host to the main Pb-Zn mineralization discovered in the Karrat Group, which has been suggested as a MVT deposit since it is carbonate-hosted and ore sulfides show evidence of remobilization (Pederson 1980). The historical Black Angel Mine had a life span of almost 20 years, though on-going exploration occurs in the area. The mine is comprised of ten ore bodies totalling 13.6 Mt with grades of 12.3%, 4.0%, and 29 ppm in lead, zinc, and silver respectively (Thomassen 1991; Pedersen 1980).

The Mârmorilik Formation has an estimated structural thickness of ~1600 m (Henderson and Pulvertaft 1967; Grocott and Pulvertaft 1990). The formation is composed of a basal clastic unit, comprising white to green quartzites, locally hosting magnetite. This is overlain by dolomitic marbles that pass upwards to calcitic marbles in the upper part of the formation (Garde and others 1978). Semi-pelite layers can be found in the marbles as well as covering the Mârmorilik Formation. The dominant Pb-Zn mineralization zone is located in the upper calcite marble unit, however mineralization can be found in the lower dolomitic marble unit as well.

3 S isotopes in SEDEX and MVT deposits

Sulfur isotopes can provide insight into the main source of sulfur or if sulfur was fractionated while forming a given deposit (e.g., during sulfate reduction). Sedimentary exhalative deposits (SEDEX) form from sulfide and metal-rich oxidized fluids (Leach et al. 2010). These sulfides form by reaction with H2S in the reduced water column, which results in sulfide precipitation along the seafloor. Therefore, it is likely that the sulfur source originates from seawater sulfate, which is reduced by bacterial sulfate reduction (BSR) under anoxic conditions (Emsbo 2009). Mississippi-Valley type (MVT) deposits world-wide suggest a variety of sulfur sources with the main source still being derived from seawater sulfate (Leach et al. 1993).

Previous work from Farquhar et al. (2010) shows a compilation of ore sulfide δ34S values from both SEDEX and MVT deposits in the Proterozoic Eon. SEDEX deposits show a wide range of δ34S values with a larger Δ34S sulfate-sulfur value of 15.7‰, indicating BSR processes. MVT deposits in the Proterozoic have more positive δ34S values with a smaller Δ34S sulfate-sulfur value of 8.4‰, suggesting both TSR and BSR processes occur.

For this study, fourteen porphyroclastic pyrite grains were selected from seven distinct ore bodies in the Black Angel Mine (Figure 2). Pyrite grains were microdrilled with a diamond tipped drill bit. Sulfur analyses were carried out at the University of Manitoba using protocol procedures described in (Hu et al. 2003) and analysed in a Thermo Delta V mass spectrometer.

Figure 2. Simplified map of Marmorilik area with δ34S values from seven different ore bodies (highlighted in yellow) on porphyroclastic pyrite in the Black Angel Mine.

4 Results and discussion

4.1 Preliminary petrographic analysis

Polished thin sections from the Black Angel Mine ore zones and field samples of the Qaarsukassak Formation reveal differences in mineralogy and texture between the two units. Mârmorilik mineralization shows porphyroclastic pyrite with sphalerite and galena inclusions in a matrix of sphalerite ± minor chalcopyrite infilling around pyrite and gangue minerals. Cataclastic, partial annealing, and durchberwegung textures are present in pyrite grains as well as remobilization textures in sphalerite and galena, suggesting a late stage remobilization/deformation event after initial sphalerite and galena emplacement. These observations concur with previous work on Mârmorilik mineralization (Carmichael 1985, PhD dissertation; Pederson 1980,1981). However, given the deformation, it is still unclear whether more than
An ore phase occurred in the Mârmorilik Formation.

Qaarsukassak sulfide samples are mainly composed of pyrite and pyrrhotite with minor sphalerite crosscutting the gangue sulfides, yet, one locality showed massive sphalerite (+ minor pyrite and chalcopyrite) emplacement after pyrrhotite, altering the grains (Figure 3). Smaller veins show at least two more phases of sphalerite crosscutting the first emplacement of sphalerite and pyrrhotite, suggesting the possibility of multiple ore phases in the Qaarsukassak Formation. A preliminary paragenetic sequence for the Qaarsukassak mineralization has been constructed (Figure 4). This preliminary sequence will be further clarified with continuing petrographic analysis on collected field samples.

**Figure 3.** Petrographic examples of Qaarsukassak mineralization. Top: Younger sphalerite stages cross-cutting original emplacement of sphalerite and pyrrhotite. Bottom: Zoomed out view of massive sphalerite emplacement after pyrrhotite, altering the pyrrhotite grains. Smaller sphalerite veins shown crosscutting both minerals.

4.2 Preliminary $\delta^{34}$S analysis on Black Angel

Preliminary results (Figure 2) from Black Angel pyrite show a range of $\delta^{34}$S sulfide values between $+0.2\%$ to $+7.2\%$ (±0.2%) (VCDT). These results suggest that the sulfur source in the pyrite is probably sedimentary or at least non-magmatic, which would show values closer to 0%. Preliminary results are insufficient to distinguish whether the source aligns to a specific sedimentary-hosted deposit model (SEDEX or MVT). Further sulfur analyses on pyrite and ore sulfides will be conducted using secondary ionisation mass spectrometry (SIMS) at the University of Manitoba.

4.3 Field observations

During the 2016 field season, structural measurements were taken on exposed fold limbs throughout the Qaarsukassak Formation. Fold measurements indicated a moderate plunge with a trend towards ~135-155º (using Bingham analysis). This is consistent with a compressional event, D4, which is roughly NW-SE (Rosa et al. 2017). Remobilized massive sulfides appear to be concentrated within these folds, which is similar to that recorded in the Mârmorilik deformation (Pederson 1980). These observations suggest that the mineralization for both units is structurally-controlled and can be found within folds related to the D4 compressional event.

4.4 Deposit model interpretation

The mineral deposit model for Black Angel Mine and the mineralization hosted in the Qaarsukassak Formation are not well-defined. While the Mârmorilik has been classified as MVT (Pederson 1980) based on the mineralization being carbonate-hosted, SEDEX deposits can be hosted in carbonates as well (Leach et al. 2005) making this an inadequate argument for a MVT model. Typical
characteristics of MVT and SEDEX deposits such as epigenetic vs. syngenetic mineralization and ore body textures are difficult to differentiate as age of the Pb-Zn mineralization relative to its host rocks is poorly constrained (currently being explored using Re-Os geochronology, see “Future Work”) in the Karrat Group and deformation/remobilization events erased primary ore textures.

Based on Leach et al. (2005), comparisons of primary characteristics of SEDEX and MVT deposits, sulfur and lead isotopes can be useful in deposit model classification. SEDEX deposits in the Proterozoic show a wider range of $\delta^{34}S$ values than MVT deposits as well as a greater $\Delta^{34}S_{\text{sulfate-sulfur}}$ value (Farquhar et al. 2010). Lead isotope signatures can show within deposit homogeneity or heterogeneity, which are distinctive for SEDEX and MVT deposits, respectively.

5 Future work

Re-Os geochronology is ongoing at the University of Alberta, analysing pyrites from both formations linked to the Pb-Zn mineralization. Pyrite grains thus far have only shown low concentrations of Re, which are insufficient to determine reliable ages.

A preliminary paragenetic sequence will be refined with further petrographic work in order to characterize Qaarsukassak mineralization.

Pb-Pb isotope analysis on galena samples from each formation are in the queue to be analyzed by Thermal Ionisation Mass spectrometry (TIMS). The data can verify if the Pb-Zn mineralization came from the same source, indicating a co-genetic relationship between mineralization of the two formations.

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References

Modern prospecting for zinc and lead MVT ores near Siewierz in the Upper Silesia Zn-Pb Ore district in southern Poland

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Abstract. In the last decade in Poland the exploitation of Zn-Pb sulfide ores of the MVT in the Upper Silesia Ore District decreased due the exhaustion of Zn-Pb ore resources in the Olkusz region, being now the only active mining area in the district. However, in the northern part of the district, between Siewierz and Zawiercie have been documented several Zn-Pb sulfide deposits which are still undeveloped. They host almost 65% of total documented resources of MVT deposits in Poland. These deposits are of pseudo-bed or nest-like forms and are hosted mainly by dolomitized carbonate rocks of Triassic Muschelkalk. New geophysical surveys, including resistivity and IP, coupled with 3D modeling from older boreholes, allowed the generation of new geological, tectonic, and ore mineralization models in the Siewierz area. These results suggest potential for further Zn-Pb ore resources and new targets for exploration drilling. Furthermore, microprobe (EMPA) studies of Zn-Pb sulfide ores documented interesting trace elements admixture in sphalerite (Ag, Cd) and galena (Au, Sb).

1 Introduction

In the Upper Silesian Ore District (southern Poland) occur Zn-Pb deposits that have a long history of mining exploitation. They occur over an area of 1 000 km² and grouped in the four following regions: Olkusz, Chrzanów, Bytom and Siewierz-Zawiercie. Presently, only exploitation is carried out in the Olkusz region. The deposits from the Chrzanów and Bytom regions are abandoned. The most economically interesting area currently is the Zawiercie region, which has several documented Zn-Pb MVT-type deposits (Fig. 1) that were explored by exploration drilling between the 1970s and 1990s. The estimated Zn-Pb resources of the Zawiercie region are ca. 53.982 Mt of sulfide ores containing 2.344 Mt of Zn and 8.813 Mt of Pb (Szuflicki et al. 2016). In this paper we present the results of modern geological work carried out in co-operation between the Polish Geological Institute-National Research Institute and Mazovia Energy Resources Ltd. The studied area is located to the east from Siewierz and occupies ca. 120 km² of the concession block.

2 Geological background

The Siewierz area is located on the Upper Silesia Block near the contact with the Malopolska Block along the Hamburg-Berlin-Odra-Lublinie-Cracow tectonic zone. This fault has been active since the Precambrian and responsible for voluminous magmatism during the Carboniferous and between Lublinie-Cracow are associated with Cu-Mo-W(±Sn) porphyry-type mineralization (e.g. Myszków deposit; Stein et al. 2005) hosted by Precambrian and/or Paleozoic rocks.

The Zn-Pb deposits in southern Poland are younger originated during the Alpine Orogeny. They are classified as Mississippi Valley-type deposits (Leach et al. 2003). The main economic value has the Ore-bearing Dolomite (OBD) of Muschelkalk (Middle Triassic). It was estimated that from this dolomites comes ca. 95% of total metals production and the rest from the Roeth and the Devonian dolostones (Szuwarzyński 1996). Zn-Pb ore bodies mined from this region are mainly pseudo-bed, nest-like or karst breccias and occur from 40 to 240 m below surface (Górecka 1993; Mikulski et al. 2010). The average content of metals in sulfide ores is usually from 2 to 4% Zn and from 1 to 2% Pb (Gruszczyk and Wielgomas 1990). The current economic resources of zinc and lead ores in Poland are calculated for 83.817 Mt of sulfide ores containing 3.566 Mt of Zn and 1.417 Mt of Pb (Szuflicki et al. 2016). In the operating mines occur ca. 25 % of total sulfide ores and the rest in abandoned and undeveloped deposits. Beside, some prospective and hypothetical Zn-Pb resources of MVT occur also directly to the north of the Siewierz-Zawiercie region (Mikulski and Strzelska-Smakowska 2014).

In the considering concession block near Siewierz occur undeveloped the Zn-Pb Goluchowice deposit and parts of the Siewierz and Poręba deposits. The verified resources for the Goluchowice deposit are ca. 16.916 Mt...
sulfide ores containing 0.562 Mt of zinc and 0.149 Mt of lead (Mikulski et al. 2013). Average content of Zn is 3.4% and of Pb 1.1%. The other two deposits have prognostic resources estimated for ca. 1 million Mg of Zn-Pb ores.

The Gołuchowice deposit lies in the southern upraised part of the Siewierz through. The rocks hosting sphalerite and galena ores are dipping in a north-eastern direction. Zn-Pb sulfide ores in form of nests and lens-like are found mainly in the Ore-bearing Dolomite (OBD) that include here the upper parts of the Gogolin Beds limestone and can be traced down to Diplopora Dolomites (Przeniosło 1974). The thickness of OBD is variable from 10.7 m to 54.2 m (an average ca. 35 m). The big difference in the OBD thickness was due to irregular developments of epigenetic dolomitization and erosion. The highest thickness of OBD was documented in the central part of the deposit. In the NE of the Concession Block ore mineralizations occur much deeper in the Early Triassic (Upper Roeth and Lower Bunter).

In the Poręba and Siewierz deposits mineralization have been found in the Triassic and Devonian carbonate rocks. These deposits are characterized by quite similar parameters, e.g. an average thickness 2.2 m and Zn contents 4.3%. The Pb content is variable, and in the Poręba deposit is 2.4%, and in the Siewierz deposit reach 4.9% (Blajda et al. 2006). In the considering deposits sphalerite-galena ore dominates. They form isolated and small bodies at depth intervals from 40 to 173 m (Siewierz) and from 80 to 219 m b.s. (Poręba).

3 Modern ore prospecting for increase Zn-Pb resources

According to the Geological Work Programme in the concession block near Siewierz at first were carried out geophysical prospecting works and next 3D modelling of geological and ore structures were made.

3.1 Geophysical prospecting with application of the resistivity and induced polarization (IP) methods

Geophysical survey was carried in 2015. The survey was done with resistivity and induced (IP) polarization methods. More than 50 km of electrical measurements were acquired along 16 acquisition lines of 1 to nearly 5 km long, covering virtually entire concession block. Early during the survey it was decided application of 2D resistivity imaging combined with simultaneous IP imaging that might yield much more valuable information concerning lithology, tectonics and content of sulfides, especially dispersed ones, despite of smaller penetration obtained by imaging in comparison to simple IP profiling. Acquisition was performed using ABEM SAS1000 system with active electrode spread of 400 m and electrode spacing of 10 m. Dipol-dipol array applied for the survey allowed for prospection down to 150 m below ground level. Both resistivity and IP datasets were inverted with use of Res2DInv software and presented as geophysical 2D sections both for resistivity and chargeability (Fig. 2).

On the basis of the geophysical sections geological interpretation was performed. Lithological and structural information obtained was interpolated between sections and resultant series of maps of structural features (e.g. faults, bedrock location, lithology of the bedrock) and intensity of chargeability and depth to the chargeability maximum were prepared. We assumed that the maximum chargeability effect is caused by increased sulfide content.

Extensive geophysical survey allowed to better understand geology of the ore-bearing strata, especially complicated structural context of the deposit and allowed to plan drilling campaign.

Figure 2. Prospecting for Zn-Pb sulfide ores with application of resistivity imaging and induced polarization (IP) method in the Siewierz concession block. Upper cross-section shows the chargeability (IP) section along the acquisition line # 6. The lower cross-section shows the resistivity section. High values of chargeability (intensive colours on upper section) are assumed to represent high sulfide content

3.2 Geological modelling in 3D

Computer modelling was based on the developed data from the old prospecting boreholes drilled during documentation of the Gołuchowice, Poręba and Siewierz deposits and on the new results of the geophysical work performed in the concession block (Fig. 2). Access data set contains information about stratigraphy, lithology, ore grade and mineral composition from 701 boreholes. For the purpose of the 3D modelling was used the gOcad 2009 p3 (PARADIGM) software with a set of GeoToolbox plugins in which was created the structural model of the entire concession area. The several lithological units were designated for mineralized and barren the Triassic and Jurassic rocks (Fig. 3). On the basis of the collected information the structural surfaces were distinguished by using DSI algorithm (Discrete Smooth Interpolation). Based on the structural model were generated GRIDS with irregular grid cells in accordance with the structural surface. It was decided to create three separate blocks for: (1) the Diplopora Dolomites (DP) where was observed ore mineralization; (2) the Ore-bearing Dolomite (DK) and (3) Ore mineralization in the deeper part (the Lower Muschelkalk and Bunter; PP_R_WAG).

3D modeling of geological structure revealed that the Triassic sediments are tectonically disrupted and generally deep to the North. The northern surroundings of the Gołuchowice deposit are built on the surface of the Jurassic and the Keuper sediments, which represents the dropped layers limited by faults.
Figure 3. The distribution of Zn-Pb sulfide mineralization together with the induced polarization profiles. The Ore-bearing Dolomite block is transparent.

4 Ore mineralization in the light of the microscopic studies

In the Gółuchowice deposit in sulfide ore dominates a fine-grained sphalerite and medium-grained galena, which impregnated mainly the Ore-bearing Dolomite. In the upper parts of the deposit also appears zinc blende with galena and fine-grained impregnations of galena. Disseminated sulfide ores are solid but those which infill empty spaces and fractures are of vein character (Fig. 5). Brecciated ores appears rarely. In the zones of intensive ankeritization, zinc sulfide occurs as intergrowths with ankerite as well as microscopic inserts in ankerite. Microscopic studies show sphalerite as fine grains (from 2 to 200 μm in diameter (mainly 10-50 μm) and galena grains often from 10 μm to 3 mm in diameter. Sulfide minerals are associated by barite, calcite, dolomite, ankerite and silica. Among the minerals from the weathered zone were recognized smithsonite, hemimorphite, hydrozincite, cerussite and hydrated Fe-oxides. In the impregnate-metasomatic ore type the following ore succession occur: sphalerite – galena – Fe-sulfides (marcasite/pyrite). The similar crystallization succession appears in the veinlet-type ore (coarse-grained or crust-like Zn sulfides, next crust-like galena and Fe-sulfides).

Figure 4. Simplified 3D model of geology and Zn-Pb ores in the Siewiers concession block in the northern part of the Upper Silesia Ore District. Abbreviation: DP+OBD – Diplopora Dolomites + Ore-bearing Dolomite (Triassic Muschelkalk); WAG – Gogolin Beds (Triassic Lower Muschelkalk); RET+PP – Roeth dolomite and dolomitic marl (Triassic Upper Bunter) + sandstone and clay (Triassic Lower Bunter)

Figure 5. Sphalerite-galena vein-type assemblage in the Ore-bearing Dolomite from the Gółuchowice Zn-Pb deposit. BSEI. Abbreviation: gn – galena; sp – sphalerite. Red circle EPMA analysis location
Further modern prospecting is required to recognize new Zn-Pb ore resources in the Siewierz-Zawiercie region which may become the new mining area in the old Upper Silesian Zn-Pb Ore District.

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5 Conclusion

Results of geophysical prospecting carried out using application of the resistivity and induced polarization (IP) methods and 3D geological modeling demonstrate the possibility of a significant increase in resources of Zn-Pb ores of the type MVT in the Siewierz area. Our estimates suggest the potential for ca. 7 Mt of Zn-Pb ores in the Gołuchowice deposit and potential occurrences of mineralization to the NE and SW of the current deposit indicates the ability to increase resources at least. The resources outlined to 110 m below sea level suggest the potential for open pit mining in the northern part of the deposit. There has been limited drilling in the case of the Zawiercie region. Biuletyn Instytutu Geologicznego, 278:115-186 (English Summary)


Microprobe (EPMA) investigation of Zn-Pb-Fe sulfides from the Upper Silesia Ore District revealed that they contains variable admixtures of trace elements. In the Gołuchowice deposit make notice admixtures of silver (<0.05 wt.%) and cadmium (<1 wt.%) in sphalerite (Figs. 5a-b) and of gold (up to 0.12 wt.%; Fig. 5c), cobalt (up to 0.16 wt.%) and copper (up to 0.14 wt.%) in galena. In the galena from the Gołuchowice deposit Sb does not occur, while in the other MVT deposits, may constitute up to 2 wt.% (Fig. 5d).
Microstructural features and trace element contents of the sulphide generations in the Hadal Awatib East Cu-Au(±Zn-Ag) VMS deposit (Red Sea Hills, NE Sudan)

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Abstract: Auriferous volcanogenic massive sulphide (VMS) deposits have been explored and mined since 1991 in the Ariab mining district (Red Sea Hills, NE Sudan). This district is located in the 0.85-0.55 Ga Arabian-Nubian Shield (ANS). This part of the East African orogeny hosts several type of deposits (VMS, orogenic gold, porphyry-type deposits), and underwent numerous deformation stages that have affected both the geometry and the metal stock of the mineralized orebodies. Different generations of sulphides, notably chalcopyrite, have been microstructurally and texturally recognized in the Hadal Awatib East Cu-Au(±Zn-Ag) VMS deposit and have been correlated to the regional deformation events, from syn-orogenic D1/2 deformation stage for Ccp1 to late orogenic D3 deformation stage for Ccp2 and Ccp3.

Trace element signatures in these different generations of Ccp allow the discrimination between the VMS lenses (Zn, Sb, Sn, In and As) and the stringer zone (Bi and Se). However, trace element contents remain the same for the different Ccp generations, which suggests that younger mineralization was remobilized from preexisting mineralization.

1 Introduction

1.1 Lithostructural framework of the ANS (Red Sea Hills, NE Sudan)

The Arabian-Nubian Shield (1.4 10^6 km²; Plyley et al. 2009), which corresponds to the northern part of the East African orogeny (Fig. 1; Johnson et al. 2011), is currently considered to be the next promising gold exploration target for orogenic and VMS deposits (Trench and Groves 2015; Barrie et al. 2016). For these latter, known deposits are clustered in districts such as the Ariab VMS-oxide gold district (Barrie et al. 2016) located in the northern part of the Haya terrane (extent of Fig. 2; Fig. 1). It hosts more than 20 auriferous deposits mined since 1991 such as the large Hadal Awatib East VMS deposit.

As described by Johnson et al. (2011), the ANS originates from a “Supercontinent Cycle” which occurred during Neoproterozoic and is composed of (1) the break-up of Rodinia supercontinent (870-800 Ma), (2) the opening and closing of Mozambique paleo-ocean (Stern 2004) associated with juvenile crust formation (800-670 Ma), (3) the collision of continental crust fragments leading to Gondwana supercontinent formation (650-600 Ma) and finally (4) convergence associated with transpressive tectonics and extrusion of the northern part of the ANS northwards (600-550 Ma). The later history involves ANS break-up during the Miocene Red Sea opening (Vail 1983; Deschamps and Lescuyer 2002).

Figure 1. Arabian-Nubian Shield lithostructural framework, modified after Johnson et al. (2011) and Fritz et al. (2013). CED = Central Eastern Desert, SED = South Eastern Desert.

1.2 Structural evolution of the Ariab mining area (Red Sea Hills, NE Sudan)

Several deformation events have affected the Ariab mining district through time (Abu Fatima 2006; Fig. 2). D1 deformation is characterized by ENE-trending structures resulting from regional transpression-related shearing coeval with greenschist facies metamorphism that
affected volcanic arc terranes during their burial. Ductile deformation has led to folding and S0/1 foliation development before progressive change in compression direction from NW-SE (D1) to E-W (D2) associated with brittle ductile-transition; D2 deformation stage is coeval to early terrane accretion and collision and remobilizes both S0/1 foliation and 1st generation folds. As the transition from D1 to D2 deformation seems to be progressive, a composite D1/2 deformation is commonly considered. The D3 stage of deformation is characterized by NW-trending sinistral shearing and S3 crenulation foliation development coeval with retrograde metamorphism during terrane exhumation and E-W compression leading to the final ANS consolidation. Finally, a late-Pan African minor D4 deformation stage (not represented on Fig. 3), probably coeval with early Red Sea rifting, can be expressed locally within the Ariab mining area by NE-trending faulting and NW- and ENE-trending shear zones reactivation.

Figure 2. Ariab mining district structural framework, modified after Abu Fatima (2006).

Mineralizing events in the Ariab mining district are poorly constrained regarding these deformation stages. Therefore, this study will (1) document the different regional deformation events and their impact on mineralization utilizing microstructural and textural observations, and (2) characterize the geochemical signatures of each sulphide generation through LA-ICP-MS analysis.

2 Methodology and sampling

The Hadal Awatib East deposit is located in the northern part of the Ariab mining district (Fig. 2). Resources are estimated at 68.8 Mt at 1.22 wt% Cu, 0.74 wt% Zn and 1.1 g/t Au (Bosc et al. 2012). The orebody is composed of two main reverse lenses following a deep dipping, NE-trending S0/1 foliation affected by S3 crenulation foliation (Fig. 3).

The different samples used for this study come from drill holes crosscutting Hadal Awatib East sulphide lenses (Fig. 3). All the different ore zones visible on the cross sections realized after Surpac 3D-model of the deposit have been sampled: (1) the high-grade Cu ore, (2) the stringer zone ore transposed in the S0/1 foliation that is not separated from high-grade Cu zone in Fig. 3, (3) the disseminated ore zone and (4) the two volcanogenic massive sulphide lenses composing most of the orebody.

Petrographic analyses were carried out using an optical microscope as well as a scanning electron microprobe at the CRPG (Nancy, France). The major and trace elements geochemistry of sulphides (chalcopyrite, pyrite, and sphalerite) were obtained by electron microprobe (previous study) and LA-ICP-MS analyses performed at the GeoRessources laboratory (Nancy, France) respectively.

Figure 3. Sampling within the Hadal Awatib East VMS deposit for this study. Cross sections have been realised on Surpac software from a 3D-model of Hadal Awatib East VMS deposit. Cross sections lines are represented on the schematic map of the deposit (top of the figure), as well as drill heads corresponding to sampled drill holes. Samples are labelled D + drill hole number – apparent depth along the drill hole.

3 Characterization of the different generations of sulphides observed at Hadal Awatib East deposit

3.1 Textural characterization of the different generations of sulphides observed at Hadal Awatib East deposit

Several pyrite (Py), sphalerite (Sp) and chalcopyrite (Ccp) generations have been discriminated thanks to their microstructural and microtextural features at Hadal Awatib East deposit. The interpretation of microtectonics helped to
place the mineralization events in relation to regional deformation events (Abu Fatima 2006) (Fig. 4).

Figure 4. Paragenetic sequence of the Hadal Awatib East orebody main sulphides, completed after Abu Fatima (2006).

Three generations of Ccp are identified (Fig. 5): (1) pre- to syn-D1/2 Ccp1 is only observed within the disseminated ore and expressed as inclusions in Py2 porphyroblasts; (2) Ccp2 generation is expressed as chalcopyrite interstitial to annealed Py3 and coeval with interstitial Sp2 and minor galena which means that Ccp2 is syn- to post-D2, D3-related annealing of pyrite as described by Abu Fatima (2006); (3) late Ccp3 is massive and occurs only at the edge of the massive sulphide lenses composing Hadal Awatib East orebody, in the so-called “high-grade Cu ore” (Fig. 3). Ccp1 is replacing both pyrite, sphalerite and host rock and would have been formed during late Cu-rich fluid injection within the ore ante- to syn-D1 deformation event as the high-grade Cu zone is apparently not discordant with D3-related structures.

3.2 Trace elements incorporation of the different generations of chalcopyrite observed at Hadal Awatib East deposit

The main trace elements incorporated in Ccp are Ni (up to 80 ppm), Zn (50 ppm), Se (250 ppm), As (16 ppm) and Pb (50 ppm). However, their contents vary according to the orebody zone that is considered. Principal component (statistical) analysis was carried out considering 11 trace elements of interest (Zn, Sb, As, Sn, In, Fe, Mn, Ag, Pb, Bi, Se and Ag) to better characterize Ccp trace element incorporation (Fig. 6).

The two first principal components (PC) carry 59% of the explained variance of the initial data which is enough to consider the results obtained reliable. PC1 is dominated by Zn, Sb, Sn, In and As while PC2 is representative of Pb, Bi, Ag and Se behaviour. Even if the interpretation of PC1 and PC2 in terms of element mobility remains difficult, the projection of the dataset in PC1 vs PC2 plane allows to fairly discriminate the different ore zones: Ccp from the center of the VMS lenses are correlated with PC1, Ccp from high-grade Cu and stringer zone ores with PC2 and the edge of the VMS lenses located between these two previous zones has an intermediate signature. However, the different generations of Ccp can’t be discriminated when they coexist in the same ore zone like Ccp2 and Ccp3 at the edge of the VMS lenses. Ccp1 was only observed within the disseminated ore and only one analysis was carried out as interstitial chalcopyrite is often too little to be analysed independently.

Figure 5. Microtextural features of the different generations of chalcopyrite observed within the Hadal Awatib East orebody. All the photographs are realized in polarised, non-analysed reflected light.

Figure 6. Principal component analysis results for chalcopyrite trace elements incorporation (n = 63).
4 Discussion and new insights for further auriferous VMS deposits exploration in the Red Sea Hills region (NE Sudan)

4.1 Chemical zonation of chalcopyrite within the Hadal Awatib East VMS deposit

The zoning of most VMS deposits is accounted by a cooling path for both the main sulphide phases and their accompanying trace elements. Thus, the high-temperature (HT) Cu-rich stringer zones of many deposits are dominated by pyrrhotite-magnetite assemblages with Cu, Co, Bi, Se, In, Ni and Mo, whereas lower temperature (LT) Zn-rich massive sulphide zones are dominated by pyrite-sphalerite-galena Zn, Pb, Ag, Cd, Sn, Sb, As, Hg, Tl and W poly-metallic signature, whereas some elements, such as Ag and Sn, may be enriched in both HT, Cu-rich and LT, Zn-rich mineral assemblages (Hannington, 2014).

This pattern is observed in the Hadal Awatib East deposit with Bi, and Se in the stringer zone, and Zn, As, Sb, In, and Sn in the VMS and periphery of the system. In the same way, even if not demonstrated in this communication, the Co and Se content of both pyrite and sphalerite represent good vectors for the orebody zonation.

4.2 Hydrothermal reworking of the VMS from D1/2 (Ccp1) to D3 (Ccp2/Ccp3)

As multiple generations of Ccp expressing replacements or overprinting events have been described (Fig. 4 and 5), it is unlikely that the variation in trace elements incorporation in Ccp only results from the physicochemical variation of a single fluid event in a cooling path. The distinct trace elements incorporation in Ccp may be explained by hydrothermal reworking, with each new chalcopyrite generation being associated with remobilization of metals from a previous mineralization remobilization without any new metal income. This process of ore refining involves the continuous dissolution and re-precipitation of earlier formed minerals by the flow of high-temperature fluids through the deposit, as already proposed in previous studies (e.g., Eldridge et al. 1983; Lydon 1988; Large 1992; Hannington 2014).

5 Conclusion

The Hadal Awatib East VMS deposit results from a polyphased hydrothermal event, during at least from the volcano-sedimentary series burial (D1, 800-670 Ma) to the late consolidation of the ANS (D3, 600-550 Ma) (Johnson et al. 2011). Geochronological limits on these different hydrothermal pulses should better constrain the duration of this whole hydrothermal system. As the different generations of Ccp have kept the same geochemical features through time but express strictly the same variation regarding their position in the orebody (stringer zone, VMS, etc…), they may be considered as a potential exploration guide at the deposit scale.

Acknowledgements

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References

Trace-element variation in pyrites within the Derryville ore body, Lisheen mine, Ireland

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Abstract. Chalcophile and siderophile elements present within Irish-type carbonate-hosted Zn-Pb deposits are contained within iron sulphide phases found throughout the ore zones supported by systematic spatial variations in mine-scale assays. The current pilot study utilises laser ablation ICP-MS raster mapping analysis (Fe, S, Mn, Co, Ni, Sn, Ag, Sb, Hg, Pb, Cu, Zn, As, Cd, Ti) to characterise sulphide phases within a set of texturally and spatially-constrained samples from the Derryville ore zone at the Lisheen mine. Concentrations of Mn, Co and Ni are found in early diagenetic pyrite, which display corrosion textures likely due to interaction with a sulphur-deficient (crustally derived) mineralising fluid. Enrichments in As, Cu, Tl and Ag are observed in late-evolved and hydrothermally derived pyrite and marcasite phases that postdate Zn-Pb mineralisation.

1 Introduction

Targeting Zn-Pb deposits in the mature Irish midlands district has historically been restricted by inconsistent geophysical signatures, yet, bulk lithogeochemical exploration techniques are generally limited to the economic elements of interest (Zn-Pb±Cd) and a select group of trace elements (Fusciardi et al 2003). Recent work along the Rathdowney Trend has found that trace-element signatures exhibit systematic variations with proximity to mineralisation (Torremans et al 2017). New exploration tools may be developed as a result of understanding the paragenetical distribution of trace elements relative to main-stage mineralisation at the Lisheen Mine.

Zn-Pb deposits within Ireland are found within a Lower Carboniferous marine transgressive sequence of Dinantian-aged limestones. Deposits in the north of the Irish midlands along the east-west Navan trend are hosted by a series of micritic, oolitic and bioclastic grainstones (with minor argillaceous laminations) known as the Navan Pale Beds (Wilkinson and Hitzman, 2014). Whilst deposits along the northeast-southwest Rathdowney Trend, form within biomicritic reef packstones of the Waulsortian Formation, which sit above the projected trace of the basement Iapetus suture. The Waulsortian Formation is stratigraphically younger than the Navan Pale Beds (Fusciardi et al. 2003). Both formations lie conformably, through a transitional sequence, above the Devonian Old Red Sandstone, which in turn is unconformably underlain by Silurian metavolcanic rocks (Philcox, 1984). Both have been discussed as potential metal sources for Irish type Zn-Pb deposits (Wilkinson 2010).

1.1 Irish-type deposit model

Irish-type carbonate-hosted Zn-Pb deposits sit as an intermediate class of sedimentary-hosted Zn-Pb deposits, with hybrid features between the Mississippi-Valley (MVT) and sedimentary-exhalative (SEDEX) type end members. These multiphase stratiform massive sphalerite-galena-pyrite mineralised bodies are controlled by the mixing of a sea-water derived brine (8-19 wt% NaCl, 50-130°C) and a deep hydrothermally-derived brine (>20 wt% NaCl 130-240°C; Wilkinson 2010). The hydrothermally-derived brine requires deep-seated structures to provide a conduit for fluid migration (Hitzman, 2002). Mineral deposit
formation occurs in the hanging-wall of normal faults that developed as relay-ramp systems during Tournaisian and Visean extensional tectonism (Kyne et al., 2017). The host stratigraphy, a 150 m-thick, flat-lying, clean biomicrite is thought to have formed a palaeoaquifer at the time of mineralisation (Fusciardi et al., 2003). Dolomite forms much of the alteration assemblages associated with mineralisation in various pervasive and breccia-fill forms. Silica and illite are also associated with intense chemical dissolution of the reef during sphalerite-galena precipitation.

Stratiform carbonate replacement Zn-Pb mineralisation of the Irish Midlands is relatively devoid of non-economic sulphide minerals, in comparison to other types with Zn-Pb mineralisation (see Leach et al., 2010). The notable exception is pyrite, which occurs temporally and spatially throughout the deposit. Pyrite-dominant zones overlie the Main Zone sphalerite-galena ore body and forms a distal halo in the hanging-wall of fluid-controlling structures appearing stratabound in nature along ore horizon; paragenetically, pyrite occurs at all stages of the ore system.

2 Methodology

Samples were taken from 10 vertical diamond drillholes along a section perpendicular to a major fault (feeder conduit) transecting the Derryville ore body. Bulk lithogeochemistry of parent samples was undertaken at ALS Loughrea by inductively-coupled plasma mass-spectrometry (ICP-MS) using a 4-acid digestion. Polished thin sections of samples from the lowermost reef-bearing sulphides (n=4) were examined by reflected-light microscopy, scanning electron microscopy (SEM) and dispersive x-ray analysis (EDS) for optical and backscatter electron (BSE) imagery along with non-destructive quantitative chemical analysis.

Sulphide textures and their grain relationships were characterised, with a number of target minerals identified for element mapping. Laser ablation ICP-MS analyses were performed using a Teledyne PhotonMachines G2 193 nm Excimer ArF laser with a HeEx II 2-volume cell coupled to a Thermo Elemental iCapQs mass spectrometer at the Geochemistry Laboratories of Trinity College Dublin. The ablation cell was retrofitted with a Teledyne Cetac Aerosol Rapid Introduction System (ARIS), which connected the ablation cell to the ICP-MS torch. The elements analysed include $^{32}\text{S}$, $^{55}\text{Mn}$, $^{58}\text{Fe}$ - $^{59}\text{Co}$, $^{60}\text{Ni}$, $^{63}\text{Cu}$, $^{70}\text{Zn}$, $^{75}\text{As}$, $^{109}\text{Ag}$, $^{114}\text{Cd}$, $^{118}\text{Sn}$, $^{121}\text{Sb}$, $^{202}\text{Hg}$, $^{205}\text{TI}$, and $^{208}\text{Pb}$. Analyses were performed by ablating lines using a 5 $\mu$m beam with a 1 $\mu$m overlap, proceeding as a continuous profile at 35 $\mu$m/sec with a repetition rate of 55 Hz, and a fluence of 1.0 J/cm$^2$ to avoid melting of sulphides. Analyses of NIST-610 and BCR-2G glass standards and the MASS-1 sulphide standard flanked sample analysis. Data reduction, using Iolite 2.7 (Patron et al., 2011), utilised the Trace-Element data reduction scheme Woodhead et al. (2007) and internal element standardisation with $^{59}\text{Fe}$.

3 Results

Previous work at the Lisheen mine has shown several broad metal correlations (Torremans et al. 2017), including Co-Ni-Mn-As-Cu-Tl, which exhibits a >90% correlation with an Fe-S ratio of 1.

Petrographic observations follow the established sulphide paragenesis (Figure 3) for the deposit with textures supporting multiple stages of dissolution and crystallisation involving pyrite±marcasite, sphalerite and galena. Early pyrite (Py$_1$) has a spongy appearance and was defined as disseminated aggregated framboids (Figure 2, left, centre zone); framboidal pyrite was subsequently recrystallised into disseminated botryoidal pyrite (Py$_2$). These phases are mostly recrystallised by latter hydrothermal phases, however, distal to feeder structures
Figure 4. Laser Ablation ICP-MS Mass-1-normalised concentration maps (ppm) of sulphides samples representing sites distal to controlling structures (left), centrally within the ore body (centre) and proximal to controlling structures (right). Later and more proximal pyrite phases exhibit lower contents of Co, Ni and Mn relative to early diagenetic pyrite.
LA-ICP-MS data shows these are deficient in elements associated with ore stage mineralisation (Zn-Cd-Cu-As-Tl) within the core, yet has elevated Co, Ni, Mn, Pb and Sb (Figure 4, left) and a further central zone (preserved framboids) identified by increased Sn. The distal, early-stage crystal shows evidence of a later rim (Py4) with distinctively higher As-Tl concentrations associated with minor crystals of sphalerite. Within the ore zone, preserved early pyrite occurs as radiating agglomerated botryoidal forms (Figure 2, centre), which is subsequently recrystallised into euhedral crystals (Py3) with additional, fine, massive pyrite (Py3) replacing the accompanying carbonate phases. As and Co are concentrated in the rims of, early, hydrothermally altered diagenetic pyrite (Figure 4, centre) similar to the distal sample; large euhedral recrystallised pyrite concentrates Mn-Cu preferentially.

Massive finely-crystalline Pyx in the proximal sample is As-rich, (Figure 4, right), yet poor in many other trace elements analysed. Bladed marcasite overgrows both pyrite and sphalerite phases. Trace-element variations are less certain, with Tl broadly defining the pyrite core albeit with considerable internal variation. Nickel is preferably concentrated in pyrite over marcasite; Co and Mn contents are variable with no discernible features.

Sphalerite contained within more proximal samples generally displays lower concentrations of Mn-Co-Ni-Cu-Tl and can be found as rims around early ore-stage pyrite (Figure 4, right). These elements increase within additional growth zones of the sphalerite further from the pyrite/marcasite crystal boundary.

4 Conclusions

Bulk assay data suggests that Co, Ni, Mn, As, Cu and Tl are substituting into iron sulphides, with their contents varying both temporally and spatially (proximity to feeder conduits). Mineral chemistry largely confirms this, however, a more extensive characterisation of all sulphide minerals (including sphalerite, galena, arsenopyrite) is required to fully understand trace-element distribution within Irish-type Zn-Pb deposits and altered host rocks.

Early pyrite phases are enriched in Mn, Co and Ni relative to the later pyrite stages associated with sphalerite. This likely reflects a bacteriogenic or diagenetic origin as previously described and constrained δS^34 signatures (Wilkinson, 2004). Hydrothermally-derived pyrite is rich in zoned chalcophiles over siderophiles with high Cu concentrations being accommodate by sphalerite where chalcopyrite is not forming as a discrete phase.

This research is part of a larger trace-element geochemical vectoring study, exploring and identifying potential geochemical vectors for Irish-type Zn-Pb deposits. Further LA-ICP-MS data collected for other occurrences from the Irish Midlands, both within ore zones and regionally will be compared to the results obtained from the Derryville ore body. This methodology is to be expanded to include all carbonate and silicate alteration phases associated with sulphides.

Understanding trace-element variations at the mineral scale may allow for the reinterpretation of subtle trace-metal correlations for the available regional lithogeochemical data, discerning between residual sulphur correlated with Mn-Co over As-Tl-Cu, and hence discriminating geochemical anomalies.

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References


Controls on the distribution of the deleterious elements bismuth, cobalt and cadmium in the base metal sulphide deposits of the Mesoproterozoic Aggeneys-Gamsberg Ore District, South Africa

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Abstract. The presence of deleterious elements in sulphide ore mineral assemblages has dire economic and environmental implications. Specifically, we study the distribution of bismuth (Bi), cadmium (Cd) and cobalt (Co) in the Upper- (UOB) and Lower Ore Bodies (LOB) of the four sedimentary exhalative base metal sulphide deposits in the Aggeneys-Gamsberg Ore District (South Africa). Whole rock geochemical data from all four deposits, using elemental ratios, reveal broad trends in the distribution of these deleterious elements, with the highest concentrations observed in the Swartberg ore deposit. Further investigation using scanning electron microscopy (SEM) focusses on the distribution and partitioning of these elements within individual co-genetic sulphide mineral parageneses identified in the Swartberg ore deposit. In this ore body, cobalt partitions preferentially into pyrite (average concentration: ~4000 ppm), Bi is concentrated predominantly in galena (concentrations can exceed 2 wt. %), and Cd is hosted predominantly in sphalerite (up to 5324 ppm). The distribution of deleterious elements between the different ore bodies (i.e., LOB versus UOB) and across different ore deposits is discussed in terms of hydrothermal ore forming processes and distance from the proposed exhalative source. Furthermore, the implications for this distribution will be discussed in a context of minerals exploration and geo-metallurgy.

1 Introduction

The Aggeneys-Gamsberg Ore District (A-GOD) is located near Aggeneys in central Bushmanland some 100 km east of Okiep and 45 km west of Pofadder (Fig. 1). The District consists of four separate but largely similar stratabound Cu-Pb-Zn-Ag-Ba-Fe-Mn deposits, hosted within a medium-to-high grade metamorphosed volcano-sedimentary sequence that has experienced poly-phase deformation (Rozendaal et al., in press). Of the four deposits (Fig. 1, listed from west to east: Swartberg, Broken Hill (with down plunge extension Deeps), Big Syncline and Gamsberg), only Swartberg and Broken Hill/Deeps are currently being mined (0.36 and 1.44 Mt of ore per annum respectively). The average grade attained from these two ore bodies is 0.40 % Cu; 2.5 % Pb; 2.2 % Zn; 20 g/t Ag. Big Syncline is a large, very low grade zinc deposit, although exploration potential exists for areas of significantly higher grades. The Gamsberg deposit is a supergiant zinc resource, which has been intermittently mined on very small scale to supplement the Deeps production. On 28 July 2015, more than 40 years after its discovery and after many feasibility studies by its several owners, mining of the deposit by open cast was initiated. It will produce 250 000 tons of zinc metal from 4 Mt of ore per year as from 2018. This will make it one of the largest future producers of zinc in the world.

Deleterious elements in the ores are those that invoke a penalty from the buyers of the mineral concentrates if it exceeds a particular concentration. These elements include, amongst others, bismuth (Bi), cobalt (Co) and cadmium (Cd), and their presence results in elevated smelter costs, a decreased product quality and increased environmental disposal costs (e.g., Zanatell 2007; Lane et al. 2016). Exploration drilling and grade control during mining have shown that the sulphide ores of the Swartberg deposit contain elevated concentration of such elements, particularly if compared to the other deposits in the District. The purpose of this study is to quantify the concentration and mineral association of Cd, Co and Bi in the various ore types of the Swartberg deposit. The results are further interpreted by considering whole-rock deleterious element geochemical trends between Swartberg and other ore deposits in the District, notably the nearby Broken Hill/Deeps and Gamsberg deposits. The variations will be explained from a deposit genesis perspective and the implications for the geo-metallurgy of the Swartberg ore body will also be discussed.

Figure 1. Location of the Aggeneys-Gamsberg Ore District (A-GOD) with inset map showing the individual ore deposits (Swartberg, Big Syncline, Broken Hill/Deeps and Gamsberg).

2 Methodology

For this study, at total of 40 grab samples were collected from underground mining areas of the Upper Ore Body
(UOB, 687 Level) and the Lower Ore Body (LOB, 715 Level (Fig. 2)) in the Swartberg ore deposit. Sample selection ensured good spatial resolution along strike of the respective ore bodies, and ensured that representative material was collected from all major lithologies present in each of the mineralised stratigraphic sections (i.e., UOB and LOB).

Polished blocks were prepared for thirteen UOB samples and nineteen LOB samples. Textural and mineralogical characterisation was conducted using reflected light microscopy (Nikon Eclipse E200) and Scanning Electron Microscopy (Zeiss EVO MA 15 SEM, Central Analytical Facility, Stellenbosch). Major elements were analysed using quantitative energy dispersive X-ray spectroscopy (EDS), whereas trace elements (notably Bi, Cd, and Co) were quantified using wavelength dispersive spectroscopy (WDS, Oxford Instruments) with a detection limit of 10 – 100 ppm. Up to 25 spot analyses were obtained from each sulphide mineral present in the respective samples resulting in over 750 data points that were used in this study.

The whole rock geochemical data for these samples were obtained from X-Ray Fluorescence (XRF) analysis (ALS Chemex, Johannesburg). These data were compared to an extensive whole rock XRF (ALS Chemex, Johannesburg) dataset (>300 data points) collected by Black Mountain Mining for the upper- and lower ore bodies of Swartberg, Broken Hill/Deeps and Gamsberg.

3 Results

3.1 Mineral hosts of deleterious elements: Swartberg ore deposit

Because of its high deleterious element concentration, the Swartberg deposit was selected for in-depth analysis of its deleterious element partitioning between major co-genetic sulphide minerals (sphalerite, galena, pyrite, chalcopyrite; Table 1). Textural evidence, from reflected light microscopy and SEM, was used to confirm the co-genetic nature of the mineral parageneses evaluated. The concentration of Cd within individual sulphide minerals was generally low for pyrite, chalcopyrite and galena; however, in sphalerite Cd concentrations could exceed 0.5 wt. %. The dominant host for Co was pyrite where concentration levels ranged from below the detection limit to 3.9 wt. % in the LOB. Although no pyrite data was obtained from the UOB, some high Co concentration measurements were recorded in sphalerite (average ~ 965 ppm). Bismuth concentrations were highest of all the deleterious elements evaluated (up to 4 wt. %) and this element was found to occur preferentially within galena. The average concentration of Bi in chalcopyrite exceeds the client specifications (penalty level: 1000 ppm) in the LOB and shows a weak spatial trend (Fig. 2) with distance from the hinge zone (interpreted to coincide with the original vent complex (Stedman 1980)). In the UOB, Bi concentration levels exceed the penalty level in all three sulphide minerals, and for each of these minerals, Bi concentrations are consistently higher in the UOB relative to the LOB.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Bi concentration (ppm)</th>
<th>Cd concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite</td>
<td>50 (10)</td>
<td>0.5 (10)</td>
</tr>
<tr>
<td>Galena</td>
<td>500 (100)</td>
<td>10 (1)</td>
</tr>
<tr>
<td>Pyrite</td>
<td>50 (1)</td>
<td>5 (1)</td>
</tr>
</tbody>
</table>

Table 1. Average deleterious element concentrations within various sulphide mineral hosts in the Swartberg ore deposit (values reported in ppm and standard deviation given in parentheses).

3.2 Whole rock geochemical trends in deleterious element distributions across A-GOD deposits

Enhanced geological context for the high concentration and partitioning behavior of deleterious elements in the Swartberg deposit was provided by considering whole-rock geochemical trends in the A-GOD area. Specifically, various trace element to major element ratios were used in comparing the Swartberg deposit to the Brokenhill/Deeps deposits and to the Gamsberg deposit.

Gamsberg: This supergiant zinc resource is rich in sulphide, however, contains very little galena (<0.5 wt. %) and is devoid of economic copper minerals (e.g., chalcopyrite). In addition, the trace metals concentrations in this deposit are exceedingly low. Within the primarily sphalerite mineralisation, Cd levels are much lower than the other deposits evaluated (i.e., 20 ppm Cd / 1% Zn). Similarly, the Bi levels are significantly reduced relative to the other deposits and average 10 ppm Bi / 1% Pb.

Brokenhill/Deeps: The ratios for the deleterious trace elements are variable dependent on the lithological unit within the orebody. Relative to Gamsberg, there is significant enrichment in both cadmium (40 ppm Cd / 1% Zn) and bismuth (30 ppm Bi / 1% Pb). Cobalt is variable and correlates with the sulphur content.

Swartberg: The orebody has an internal variation with Cd, Bi and Co increasing in concentration towards the postulated hydrothermal metal source (Rudnick 2017, Fig. 2). The trace element to major metal ratios are significantly elevated relative to the other two deposits evaluated in this study (100 ppm Cd / 1% Zn; 100 ppm Bi / 1% Pb; 800 ppm Co / 1% Cu).

4 Discussion

The partitioning of trace metals between different co-crystallized hydrothermal sulphide minerals in the Swartberg deposit follow well established trends that can be explained by trace metal geochemistry (e.g., ionic size and charge), the crystal chemistry, and its maximum trace element budget (George et al. 2016). For example, Cd2+ can easily substitute for Zn2+ in the sphalerite mineral structure due similarities in size (0.78 Å and 0.60 Å respectively; Ye et al., 2011). In comparison, galena is known to substitute significant quantities of Bi3+ for Pb2+.
Despite the difference in valence state, in this reaction, charge balance is maintained through coupled substitution with single valence cations (e.g., Ag1+; Renock and Becker 2011). George and co-workers (2016) have previously found that such geochemical and mineralogical understandings preclude the need to invoke temperature, pressure and redox controls on trace and deleterious element partitioning between different co-mineralised sulphide minerals.

However, physico-chemical controls such as temperature and redox state may need to be invoked to explain differences in mineral chemistry as a function of spatial distribution (e.g., along strike within ore horizons (Fig. 2), or between adjacent ore deposits, (Fig. 1)) and between different ore horizons (e.g., UOB versus LOB). For example the high Bi concentration in galena in the UOB relative to the LOB (Table 1) may reflect the effects of temperature conditions of the respective ambient hydrothermal brines, since Bi(OH)3 solubility in aqueous solution is positively correlated with temperature (Tooth et al. 2013). Similarly, spatial trends in mineral’s trace-metal inventory may be affected by such physico-chemical parameters (e.g., Bi in chalcopyrite, Fig. 2).

In depth analysis of the mineral parageneses in the Swartberg deposit show that deleterious element concentrations are most strongly linked to the prevalence and trace metal budget of their preferred host mineral (e.g., Bi controlled by presence and trace element budget of galena). Here we posit that observed trends in relevant trace to major element ratios (in the current example; Bi:Pb) can be used to infer spatial differences in physico-chemical conditions of ore formation. Specifically, our comprehensive dataset shows distinctive trends in such ratios between different ore deposits in the studied ore district, and these trends can be used to support the presence of physico-chemical gradients away from a previously-interpreted hydrothermal feeder fault (Rudnick et al. 2013, 2015).

5 Conclusions

1. Sections of the Swartberg ore have concentrations of deleterious elements that could be problematic and could exceed the client specifications (1000 ppm) in the concentrates. The geo-metallurgical implications of our results will be discussed.
2. The bulk of the deleterious elements are hosted by sphalerite (Cd), galena (Bi) and pyrite/pyrrhotite (Co), although individual phases present as fahlore occur as accessory fine disseminations.
3. Trace element to major element ratios reveal distinctive whole-rock geochemical trends across the ore deposits in the A-GOD district. In the west, the Swartberg deposit is enriched in bismuth, cobalt and cadmium relative to major ore forming elements, whereas the respective elemental ratios consistently decrease with distance towards the east.
4. The E-W trends represent promising results that may be used in support of a previous hypothesis stating that the Swartberg deposit is formed proximal to an exhalative vent (Rudnick et al. 2013, 2015). However, this should be confirmed with further work investigating the deleterious element partitioning behaviour in the other A-GOD deposits (e.g., Broken Hill/Deeps, and Gamsberg).

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References


Modelling of the Kupferschiefer type deposit - the influence of cell size in model effectivity

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Abstract. The Cu-Ag deposit in the Lubin-Sieroszowice area is one of the world's largest Cu-Ag deposits. The highest content of metals are found in copper shale, which thickness is very thin in comparison to deposit size. To create block models for the deposit, a cell size for cell thickness needs to be assessed and optimized for accurate resource evaluation. A simulation of 20 block models with cell thickness ranging from 0.05 to 1 m have been calculated to analyse a relationship between Cu-Ag content and resources estimation. An optimum cell thickness for the selected part of the deposit has been shown to be 0.2 to 0.3 m, which is 1/3 of an average shale thickness for this area.

1 Introduction

The deposit located in Lubin-Sieroszowice district (SW Poland) is regarded as one of the world’s largest Cu-Ag districts. The deposit encompasses approximately 400 km² and it is situated at depth from a few hundred meters up to 1,500 m. Thickness of the deposit varies from 0.4 to 26 m, with an average of 4 m. The highest Cu and Ag content are found in copper shale and its average thickness varies from 0.3 to 0.6 m (Rydzewski 2007). In last few years a problem with 3D geological modelling of the deposit has arisen (Mucha and Wasilewska-Łaszczyk 2010). The models can be used for resources estimation, prediction of ore quality and ore mineral distribution, designing mining works or long term deposit management. In 2011, Pieczonka proposed a 2D model for ore mineral distribution and horizontal zonation within copper deposit (Pieczonka 2011).

Regarding modelling of the Kupferschiefer type deposit, problems come when a block model cell size needs to be determined. A major problem is that the deposit is thin compared to its lateral extent, thus it is crucial to find an optimum size for the block model. On the one hand, too small block size produces a huge and overloaded block model, whereas too large cell size decreases resolution of the block model and can lead to errors in resource estimation. In this work, an attempt to find an optimum block model cell size was made.

2 Geological characterization of study area

The Lubin – Sieroszowice Cu-Ag district is located in the south-west part of the Fore-Sudetic Monocline, close to the northern boundary of the Fore-Sudetic Block (Fig.1). The Monocline is composed of Upper Permian to Cretaceous sediments, and it is the part of the Permian sedimentary basin. It dips 3-6° to the north-east (Pieczonka et al. 2015). The Cu-Ag deposits of the Lubin-Sieroszowice district are examples of peneconcordant red bed-associated, stratabound deposits (Wodzicki and Piestrzyński 1994).

The ore horizon is connected with the lowermost part of the Zechstein Limestone, the Kupferschiefer and uppermost part of the Weisseliegende sandstone. The Cu-Ag deposit is mostly restricted to the Kupferschiefer bed (Piestrzyński 2007).

Figure 1. The localization of Cu-Ag deposit with simplified geological map of Poland (after www.geoportal.pl modified).

More than 140 different ore minerals have already been identified. Chalcocite, bornite, chalcopyrite, covellite, tennantite and silver minerals, accompanied by pyrite, galena and sphalerite, are the major ore minerals in the deposit. Chalcocite is the dominant ore mineral and locally can constitute up to 90 vol.% of the ore. In the deposit the following types of ore mineralization can be distinguished: dispersed, nests, lenses, ore bands, veinlets and veins, and massive (Pieczonka et al. 2015). Sulphides are characterized by their light Sulphur δ34S ranging from -10‰ to -45‰ (Wodzicki and Piestrzyński 1994).

3 Methodology

Geochemical results have been performed by KGHM Polish Copper S.A. Samples have been collected in profiles through whole ore interval. Each of the samples are represented by the channel sample with average length...
of 0.2 m. The geochemical results have been prepared in Microsoft Excel for further modelling. A software used for generating stratigraphic and block models was Minescape 5.11 by ABB company.

An area of approx. 0.38km² with 538 sampled intervals and containing 9,165 samples have been chosen for testing. The data have been imported into the program and stratigraphic model have been created. Only shale part of the deposit have been chosen for modelling on the grounds that it represents the highest content of ore minerals and it is most variable. Twenty block models have been created with cell size 1 m long, 1 m width and with thickness ranging from 0.05 to 1 m, with 0.05 m step each. With each of the block models a time, block model size and amount of assigned cells have been noted. Three attributes: Cu, Ag and lithology have been interpolated into each block model. An inverse distance to power was used as an interpolation method. Radius of interpolation was set to 100 m for X and Y and 10 m for Z direction. Flattening of ‘search bubble’ was caused by higher differentiation of Cu and Ag content in Z direction than in X and Y direction. Radius of 100 m was proved to achieve the best results from this specific data set.

Times of interpolation, reserves and basic statistics have been noted from each of the interpolations. All the block models have been calculated on separate PC computers with the same specification. Results have been normalized to block model with cell thickness 0.2 m (bm04).

4 Modelling

A stratigraphy model, which consisted of 3 layers: oldest, Weisselfeld sandstone; copper shale and carbonates, was the basis for the block model (Fig. 2).

For model verification, a numerous cross sections (Fig.3) have been performed and compared with data from the mine database. Validated stratigraphy model was a base for all of the twenty block models. In modelled part of the deposit, shale is characterized by relatively high average thickness (0.79 m) (Fig.4).

![Figure 3. The cross-section through stratigraphy model with channel samples from ore horizon, Weisselfeld sandstone – orange, copper shale – green, Zechstein carbonates – blue.](image)

Creating a block model for whole deposit is always related with choosing the cell size regarding shale thickness, that is usually thinnest compared with other stratigraphy model layers. Therefore all of the block models were prepared only for shale layer to analyse a behaviour of the model depending on the cell size. In each of the twenty block models a content of Cu and Ag (Fig.5) and reserves have been calculated.

![Figure 4. The thickness map of copper rich shale.](image)

![Figure 5. The fragment of cross section through the block model, with example of interpolated data in cell.](image)
5 Results

Twenty block models have been created with cell size (c.s.) 1 m length, 1 m width and thickness ranging from 0.05 (block model named bm01) to 1 m (block model bm20), with 0.05 m step. The results have been normalized to block model with 0.2 m cell thickness. Amount of cells ranged from 874,810 (bm20 with 1x1x1 m c.s.) to 10,938,410 (bm01 with 1x1x0.05 m c.s.) and the time of block model creation ranged from 1 min 47 s to 21 min 08 s for marginal block models have been noted.

The Cu and Ag reserves for block model with the biggest cell size (1x1x1 m) were calculated at 100.99% and 100.81% of bm04 reserves (1x1x0.2 m) respectively.

Decrementation of reserves as well as cell thickness reduction can be observed clearly in Fig. 6. Values of Cu and Ag mass stabilizes from bm07 (1x1x0.35 m) to bm04 and then begins to elevate to 100.05% in block model with cell thickness 0.05 m.

![Figure 6. The Cu and Ag reserves graph with time needed for interpolation of each of the block models, normalized to bm04 (cell thickness 0.2 m).](image)

Obvious is a fact that time of interpolation of Cu and Ag values for model will grow with cell size decrementation (rise of amount of cells in block model) with 100.00% time interpolation for bm04. Time needed for interpolation for block model with cell size 1x1x1 m is equal to 30.25% and for block model with smallest cell size is equal to 378.16% (Fig. 6). It gives the difference between outlying block models about 800%.

Basic statistics graph is presented in Fig. 7. Differences between minimum and maximum values interpolated in each block models are clearly visible. Authors were interested in interpolation that would give the most accurate values in comparison to raw data imported into software.

![Figure 7. The graph with basic statistics for Cu interpolation.](image)

Minimum value for Cu content in raw data is 0.05% and maximum is 14.7%, therefore block model with interpolated values close to those would be the most interesting one. Kurtosis for interpolated Cu values is >0 (3.47 to 5.26). It is known that the higher kurtosis, the closer values are scattered around mean value (Randolp and Myers 2013). In this case it is not desirable, because the values need to be closest to raw data. Fig. 7 shows that kurtosis rises from block model with cell thickness 0.3 m (bm06) and reaches its maximum in block model with cell size 0.45 m. With further expanding cell thickness, the kurtosis drops down reaching same level as in bm04 in block model with cell thickness 0.8 m. That would suggests that most accurate block model is a block model with cell size <0.35 m or >0.80 m. Looking at minimum and maximum values of Cu content, interpolated in created block models, the closest values to the raw data can be indicated - cell thickness <0.35 m, bm04, bm02 and bm01. From Fig. 6 it is obvious that difference in reserves calculations is very low for block models with cell thickness below 0.35 m (bm07) and the time of block model creating grows exponentially.

6 Conclusion

Taking into consideration the accuracy of the reserves calculation and the time of the block models creation, the most optimum cell thickness for analysed data can be concluded - it ranges from 0.15 to 0.35 m. Performed simulation indicates that for the selected part of the Cu-Ag deposit, an optimal cell thickness for the block model is from 0.2 to 0.3 m. Moreover, the length of 85% of all samples used in modelling is ranged from 0.2 to 0.3 m. It can be assumed that for areas of the deposit, where shale bed is continuous, an optimal cell size for the block model should be around 1/3 of an average shale thickness. In this case the optimal cell size equals to the sample length.

Acknowledgements

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S04, Uranium deposits: from source to ore

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Some recent advances in deciphering the genesis of unconformity-related uranium deposits in the Athabasca Basin, northern Saskatchewan, Canada

Keynote presentation

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Abstract. The “diagenetic-hydrothermal” model has been generally accepted for the formation of the unconformity-related uranium deposits in the Athabasca Basin. However, there are still many uncertainties, including the sources of uranium, depth of mineralization, timing of mineralization, fluid flow mechanisms, and ore precipitation mechanisms. This paper summarizes some of the recent advances in addressing these problems. Studies of sedimentary rocks far away from mineralized areas suggest that the basin has undergone extensive fluid convection and fluid-rock reactions, resulting in depletion of uranium in the sedimentary rocks, but basinal fluids with high uranium concentrations are limited in space and time. Pressure estimation from fluid inclusions in the deposits, together with ages of uranium mineralization and regional stratigraphy, suggests that the mineralization took place in much shallower environments than previously thought. Numerical modeling results suggest that reactivated basement faults played a critical role in controlling fluid flow related to mineralization, involving alternating deformational and thermal driving forces. Ore precipitation may have resulted from a combination of fluid mixing, fluid phase separation, and fluid-rock reactions.

1 Introduction

The unconformity-related uranium deposits in the Proterozoic Athabasca Basin (Canada) are located at or near the intersections of reactivated basement faults with the unconformity surface (Jefferson et al. 2007). They are generally believed to have formed from basinal brines (diagenetic) circulating in the basin and the basement, becoming hot (hydrothermal) and U-rich, and precipitating uraninite when they encountered reducing agents, as depicted in the “diagenetic-hydrothermal” model (Pagel 1975; Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kyser et al. 2000; Cuney et al. 2003; Richard et al. 2011, 2014; Mercadier et al. 2012). However, the uranium has been inferred to be sourced from either the basin (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kotzer and Kyser 1995; Fayek and Kyser 1997; Kyser et al. 2000) or the basement (Dahlkamp 1978; Annesley and Madore 1999; Hecht and Cuney 2000; Cuney et al. 2003; Richard et al. 2010; Mercadier et al. 2013). One of the arguments for the latter was the presence of a Ca-rich brine (in addition to a Na-rich brine) in many of the deposits (Derome et al. 2005; Richard et al. 2010, 2016). The Ca-rich brine was interpreted to be derived from the basement because the preserved sedimentary rocks in the basin are poor in Ca. A few recent studies, however, indicate that Ca-rich brines are developed not only in the deposits, but also within the Athabasca Basin, in areas far away from mineralization (Scott and Chi 2014; Chu and Chi 2016). These observations suggest that the precursor lithologies in the basin may have been significantly different from the currently preserved ones, implying that the potential of the basinal sediments as a source of uranium cannot be discounted by their low uranium concentrations in the current lithologies, although this cannot rule out the potential contribution of the basement either.

On the other hand, geochemical studies of paired red bed and bleached sandstone and mass balance calculations suggest that the basinal fluids had low uranium concentrations at the time when bleaching took place (Chu et al. 2015). Similarly, the fluids associated with xenotime mineralization in the Maw Zone REE deposit in the Athabasca Basin, which share similar alteration features (particularly development of magnesiofoitite) with the recent advances in the studies of the unconformity-related uranium deposits in the Athabasca Basin, and addresses some of the unsolved problems in the diagenetic-hydrothermal model.

2 Development of Ca-rich brines in the basin: implications for U sources

It is generally agreed that the mineralizing fluids of the unconformity-related uranium deposits were brines derived from the basin (e.g., Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kyser et al. 2000; Cuney et al. 2003; Richard et al. 2011, 2014; Mercadier et al. 2012). However, the uranium has been inferred to be sourced from either the basin (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kotzer and Kyser 1995; Fayek and Kyser 1997; Kyser et al. 2000) or the basement (Dahlkamp 1978; Annesley and Madore 1999; Hecht and Cuney 2000; Cuney et al. 2003; Richard et al. 2010; Mercadier et al. 2013). One of the arguments for the latter was the presence of a Ca-rich brine (in addition to a Na-rich brine) in many of the deposits (Derome et al. 2005; Richard et al. 2010, 2016). The Ca-rich brine was interpreted to be derived from the basement because the preserved sedimentary rocks in the basin are poor in Ca. A few recent studies, however, indicate that Ca-rich brines are developed not only in the deposits, but also within the Athabasca Basin, in areas far away from mineralization (Scott and Chi 2014; Chu and Chi 2016). These observations suggest that the precursor lithologies in the basin may have been significantly different from the currently preserved ones, implying that the potential of the basinal sediments as a source of uranium cannot be discounted by their low uranium concentrations in the current lithologies, although this cannot rule out the potential contribution of the basement either.

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unconformity-related uranium deposits (Adlakha et al. 2015; Rabiei 2016; Wang 2016), are inferred to have low concentrations of uranium based on lack of radiation-induced damage in quartz (Pan et al. 2013). These studies suggest that although uranium most likely was leached from detrital materials in the diagenetic history, uranium-rich fluids were not pervasively developed in the basin; instead, they were likely limited in time and space, thus restricting uranium mineralization to certain favorable locations.

3 Epithermal versus deep-burial mineralization environments

The conventional diagenetic-hydrothermal model inferred that the mineralization took place at deep burial of 5 km or more (Pagel 1975; Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kotzer and Kyser 1995). This inference was mainly based on a study of fluid inclusions in diagenetic quartz overgrowths in the central part of the Athabasca Basin, which yielded an estimation of high fluid pressures (up to 1.5 kbar) and temperatures (up to 220°C), a lithostatic fluid pressure regime, and a thermal gradient of 35°C/km (Pagel 1975). However, the high fluid pressures and the lithostatic fluid pressure regime appear to contradict with the sand-dominated nature of the Athabasca Basin, which is characterized by a hydrostatic fluid pressure regime (Chi et al. 2013, 2014a). It is suggested that the high fluid pressures reported in the previous studies were overestimated, possibly because the halite in the fluid inclusions is not a daughter mineral (Chi et al. 2015).

It was proposed that the unconformity-related uranium deposits may have been formed in an epithermal environment rather than a deep-burial environment (Chi and Chu 2016), as also proposed for those in the Beaverlodge (Liang et al. 2017) and Kiggavik (Chi et al. 2017) uranium districts in northern Canada. This hypothesis is consistent with a maximum thickness of ~1.5 km of the preserved strata between the unconformity and the stratigraphic interval where basinal brines may have been developed for the first time (i.e., the Carswell Formation; Ramaekers et al. 2007). It is also consistent with the estimation of the timing of mineralization to be pre-maximum burial (Alexandre et al. 2009a). Furthermore, the low fluid pressures estimated from fluid immiscibility or boiling (Chi et al. 2014b; Rabiei 2016; Wang 2016) as well as pervasive alteration features and vuggy structures can be better explained by a shallow rather than deep burial environment (Chi and Chu 2016).

4 Fluid flow mechanisms: alternating deformation-driven fluid flow and thermally driven fluid convection

Regardless the sources of metals and ore precipitation mechanisms, the formation of the unconformity-related uranium deposits requires the circulation of large amounts of fluids, which must be driven by some geologic forces; although the volume of fluid required would be greatly reduced if the uranium concentration in the fluid is elevated (Richard et al. 2012). Potential fluid flow driving forces in the Athabasca Basin include deviation of fluid pressure from hydrostatic pressure due to sediment compaction (Chi et al. 2013) and hydrocarbon generation (Chi et al. 2014a), topographic relief (Alexandre and Kyser 2012; Chi et al. 2013), geothermal gradient (Raffensperger and Garven 1995a; Schaubs et al. 2002; Cui et al. 2012a and b; Li et al. 2016; Pek and Malkovsky 2016), fluid density gradient due to salinity variation (Koziy et al. 2009), extensional deformation (Cui et al. 2012a), and compressional deformation (Schaubs et al. 2005; Cui et al. 2012a; Li et al. 2017), but the actual driving force(s) responsible for mineralization remains uncertain. A few studies bearing on fluid dynamics independent of numerical modeling include development of both sandstone-hosted and basement-hosted orebodies within a deposit (Sheahan et al. 2016), the steep thermal gradients revealed by fluid inclusions in quartz overgrowths suggesting extensive fluid convection in the Athabasca Basin (Chu and Chi 2016), and low fluid pressures revealed by fluid immiscibility or boiling (Chi et al. 2014b, 2017; Rabiei 2016; Wang 2016) suggesting suction pump style fluid flow mechanisms.

Given the close spatial relationship between the unconformity-related uranium deposits and reactivated basement faults, the roles of the faults in controlling fluid flow attracted a number of studies (Schaubs et al. 2005; Cui et al. 2012a; Li et al. 2016, 2017; Pek and Malkovsky 2016). Two empirical observations that have important impact on fluid flow modeling are: 1) the localization of orebodies and pattern of alteration appear to indicate egress fluid flow along some faults and ingress flow in other faults; and 2) most of the faults associated with mineralization show a reverse offset of the unconformity surface suggesting a compressional stress regime. It has been demonstrated that basement faults may have exerted some control on the localization of convection cells, and both ingress flow and egress flow can be developed depending on the hydraulic and thermal conductivities and the spacing of the faults (Li et al. 2016; Pek and Malkovsky 2016). Furthermore, it has been shown that both ingress flow and egress flow can be developed under a unified compressional stress field, depending on the degree of deformation (Li et al. 2017), rather than under alternating compressional and extensional stress conditions (Cui et al. 2012a). These results shed light on the hydrodynamic mechanisms responsible for the fluid flow related to uranium mineralization: both fluid convection, which is relatively sustainable, and deformation-driven fluid flow, which is relatively short-lived, are related to the basement faults, and the two fluid flow mechanisms may have occurred alternatingly to form the uranium deposits.

5 Ore precipitation mechanisms: fluid mixing, phase separation and fluid-rock reaction

Hydrothermal ore precipitation generally takes place due to a temperature drop, fluid-rock interaction, fluid mixing, and
fluid phase separation. Both fluid mixing and fluid-rock interaction have been proposed as the main mechanism for unconformity-related uranium mineralization, with graphite and ferrous iron-rich minerals being invoked as the main sources of reducing agents in fluids or directly acting as the reducing agents (Hoeve and Sibbald 1978; Raffensperger and Garven 1995b; Kominou and Sverjensky 1996; Alexandre et al. 2005; Yeo and Potter 2010). More recently, fluid phase separation has been suggested to have also played a role (Chi et al. 2014b). Graphite and hydrocarbons derived from it have been considered as the most important potential reducing agents (Hoeve and Sibbald 1978), but geochemical path modeling (Kominou and Sverjensky 1996) and reactive mass transport modeling (Raffensperger and Garven 1995b; Aghbelagh and Yang 2014) suggest that uranium precipitation may be caused by fluid-rock interaction with or without the involvement of graphite and methane. The importance of Fe$^{2+}$-rich fluids and lithologies as reducing agents were emphasized in several recent studies, and the use of Fe and Mg isotopes as well as Fe$^{3+}$/2Fe ratios as mineralization indicators were examined (Ng et al. 2013; Acevedo and Kyrz 2015; Potter et al. 2015). On the other hand, it has been increasingly realized that in many cases, it is the lack of uranium-rich fluids, rather than lack of reducing agents, that lead to a barren hydrothermal system (Alexandre et al. 2009b; Cloutier et al. 2010; Chu et al. 2015; Rabiei 2016). More comprehensive thermal-hydraulic-mechanical-chemical (THMC) modeling is required in order to determine the most effective ore precipitation mechanisms.

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References


U-Pb isotopic ages and associated REE geochemistry from the Phoenix and Gryphon uranium deposits (Wheeler River), Athabasca Basin, Saskatchewan, Canada

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Abstract. The Wheeler River Project hosts the high-grade Phoenix (sandstone-hosted) and Gryphon (basement-hosted) uranium deposits. The property is located within the eastern part of the prolific Athabasca Basin, overlying a crystalline basement complex of Archean/Paleoproterozoic age. The chemistry, isotopic ages, and rare earth element patterns of uranium oxides were determined for four representative samples; two from each deposit, so to establish the conditions and timing of primary and secondary mineralization events at each deposit. The oldest zones in uraninite (i.e. 1433 ±15 Ma, 1340 ±17 Ma, 1275 ±17 Ma) for the three oldest samples (WR403, WR525, WR569A) are considered tentatively to be primary mineralization ages. These ages and their associated REE contents are quite different for each sample, which means that the conditions and the timing for each generation of uraninite/uranium oxides were different. This difference is visible between deposits (Gryphon vs. Phoenix), but also at the scale of one deposit (Phoenix). The ~1430 Ma age coincides with the primary mineralization event recorded by many of the uranium deposits (1550 - 1400 Ma) within the Athabasca Basin. The ~1340 Ma age coincides with that from the basement-hosted Millennium uranium deposit. The ~1275 Ma event is identical within analytical error to the emplacement age of the Mackenzie dykes cutting the Athabasca Basin. Younger age determinations within the three oldest samples most likely reflect secondary fluid events. In summary, these new results provide good evidence for multiple primary and secondary events, both between and within deposits, on the Wheeler River property.

1 Introduction

The Athabasca Basin of northern Saskatchewan contains the world’s highest grade uranium deposits, the unconformity-type (U/C-type) deposits, which occur mainly at the interface between the Mesoproterozoic basin and its underlying Archean/Paleoproterozoic crystalline basement complex (Annesley et al. 2005; Jefferson et al. 2007; Kyser and Cuney 2009; and references therein). Overall, the genetic model(s) for this deposit type is (are) well established (cf., Jefferson et al. 2007; Cuney 2009; Kyser and Cuney 2009; Boiron et al. 2010; and references therein). However, several outstanding questions remain, including the uranium source(s) and most importantly the conditions and timing for the formation of the primary and secondary uranium mineralization.

This paper presents new U-Pb geochronological and REE geochemical results from the high-grade Phoenix and Gryphon uranium deposits of the Wheeler River Project (Fig. 1). These results provide evidence for multiple primary and secondary events, both between and within deposits; thus providing an opportunity to compare the geochronology of a sandstone-hosted deposit in close proximity to a basement-hosted deposit. Additional research may help identify the source of uranium.

Figure 1. Location of Wheeler River Project, uranium mines, other select uranium deposits, and uranium mills in the eastern Athabasca Basin, from Denison Mines Corp. (2016)

2 Regional geological setting

The Phoenix and Gryphon U/C-type uranium deposits are located within the eastern Athabasca Basin (Figs. 1 and 2), where essentially undeformed, late Paleoproterozoic to Mesoproterozoic sandstones, conglomerates, and mudstones of the Athabasca Group unconformably overlie Archean and early Paleoproterozoic crystalline basement rocks of the western Wollaston Domain. The basement rocks are intruded by Hudsonian-age granitoid and gabbroid rocks (Annesley et al. 2005).

The Wheeler River property is host to the high-grade Phoenix and Gryphon uranium deposits (Fig. 2). The Phoenix deposit is located at the U/C. The Gryphon deposit is hosted within Archean/Paleoproterozoic basement rocks below the U/C.
3 Wheeler River geology

The local geology of the Phoenix and Gryphon uranium deposits is quite consistent with the above-described regional geology (Figs. 2, 3, and 4).

The Phoenix deposit is located at the sub-Athabasca unconformity, at a depth of ca. 400 meters below the topographic surface, at the intersection of a graphitic/carbonaceous matter-bearing fault zone breaching the unconformity (Fig. 3).

Mineralization is primarily monomineralic uranium as uraninite/pitchblende. Geochemical values for other accompanying metals are low, particularly in comparison with the many other Athabasca uranium deposits, which can have very high values of nickel, cobalt, arsenic, copper, zinc, and/or vanadium. An updated mineral resource estimate for the Phoenix deposit was generated independently by RPA Inc. (Roscoe and Mathisen 2015).

The Gryphon zone consists of high-grade basement-hosted uranium mineralization within the K North area, approximately three kilometers northwest of the Phoenix deposit. Drill hole WR-556 was the discovery hole (Figs. 2 and 4). Here, drilling intersected 15.3% U3O8 over 4.0 meters; at approximately 650 meters below the surface and 180 meters beneath the sub-Athabasca unconformity. Follow-up drilling (50m x 50m grid) defined a major zone of high-grade uranium mineralization, that consists of several parallel, stacked lenses of variable thickness (up to 10s meters scale) that are concordant with the gneissic foliation of tightly folded, moderately east-dipping lithostratigraphic units, with an overall moderate plunge to the northeast. It is estimated currently to contain inferred resources of 43M lbs U3O8 at a grade of 2.3% U3O8.

Uranium mineralization within the two deposits occurs in a variety of styles, including: 1) massive, 2) massive replacement, 3) worm texture, semi-massive, and 4) foliation-parallel, semi-massive. Other styles are observed in drill core, including fine-grain aggregates associated with “mini” roll fronts. Four samples were prepared and analyzed by various geo-analytical techniques at GeoRessources (Universite de Lorraine): 1) WR-403-404.5m, 2) WR-525-409.5m, 3) WR-560-760.5m, and 4) WR-569A-682.5m (Figs. 5, 6, and 7). U-Pb isotopic ages

Several homogeneous and weakly altered zones were selected and analysed by ionic microprobe Ims-3f (CRPG laboratory, France) to obtain the U-Pb isotopic ages for the mineralized samples of the Phoenix and Gryphon uranium deposits.
deposits (Fig. 8). 207Pb/206Pb ages were determined for all four samples of uranium ore; however, one Gryphon sample (WR-560) yielded only very young ages.

The 207Pb/206Pb isotopic compositions of the Phoenix replacement style uraninite are highly radiogenic and give ages from 1450-1400 Ma. This age cluster is compatible with the ages reported for the main uranium depositional event at ca. 1550-1400 Ma for the formation of U/C-type uranium deposits within the Athabasca Basin (Alexander et al. 2005).

The Phoenix massive style uraninite and the Gryphon foliation-parallel, semi-massive style uraninite give 207Pb/206Pb ages that cluster between 1400-1200 Ma. These ages may be late-stage primary or early-stage secondary; the latter due to either lead loss or recrystallization by post-depositional fluids.

The uranium oxides, dated by U-Pb isotopic method, were also analyzed by a CAMECA IMS-3f ion microprobe (CRPG laboratory, France) and a laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) at GeoRessources to determine the REE concentrations/patterns of each uranium oxide generation (Bonhoure et al. 2007; Mercadier et al. 2013). A comparison of samples WR-403, WR-525, and WR-569A with other U/C-type uranium oxides from the Athabasca Basin.
Basin shows the characteristic bell-shaped REE pattern typical of U/C-type mineralization (c.f., Mercadier et al. 2013; Frimmel et al. 2014).

However, closer examination shows that there are distinct differences in the REE patterns of the two Phoenix samples (Fig. 9). This suggests that the conditions of crystallization are therefore distinct and this is augmented by the different U-Pb isotopic ages. Also interestingly, the REE patterns are identical for two of the analyzed uranium oxides from a different location (Gryphon vs. Phoenix) and different age (1430 Ma versus 1275 Ma). Why?

Figure 9. Chondrite-normalized REE spectra for the Phoenix and Gryphon uranium mineralization

6 Summary and conclusions

If we consider the oldest zones of the U1 (i.e., 1433 ±15 Ma, 1340 ±17 Ma, 1275 ±17 Ma) for the three oldest samples (WR403, WR525, WR569A) to be the primary mineralization, then both the ages and their associated REE contents are different for each sample. This means that the conditions and the timing for the formation of each uranium oxide or uraninite generation were different. This difference is visible between deposits (Gryphon vs. Phoenix), but also at the scale of one deposit (Phoenix).

If we look carefully to the U-Pb data from the Pheonix deposit, the difference in ages for the pristine part is significant. Considering also the difference in REE, we could assume that there were at least two events of mineralization at Phoenix (ca. 1430 and ca. 1340 Ma). For the Phoenix deposit, local variation in the basement geochemistry rocks could explain the variation in REE patterns between the different uranium oxides; meaning that the mineralizing fluids are buffered by the basement rocks.

Preliminary research using other trace elements (not presented here) suggests that these uranium oxides were formed probably at a different time and under different conditions (at least the composition of the fluids was locally different, if temperature was similar; however, more research is needed for proper documentation of the physiochemical conditions).

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References


Age and origin of the Camie River uranium deposit, Otish Basin, Québec (Canada)

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**Abstract.** The Camie River uranium deposit consists of disseminated and vein uraninite close to the unconformity between Aphebian fluviatile, pervasively altered sandstones and conglomerates of the Matoush Formation (Otish Supergroup) and the underlying sulfide-bearing, faulted, graphitic schists of the Archean Hippocampe greenstone belt (Tichegami Group). Re-Os geochronology of molybdenite intergrown with uraninite yields an age of 1724±5 Ma, whereas uraninite yields a slightly discordant 1724±29 Ma SIMS U-Pb age. Uraninite has high REE concentrations and flat REE spectra resembling those of uraninite formed in metamorphic conditions. The uranium mineralization formed approximately 450 million years after the Otish Gabbro dykes and sills intrusions (~2176 Ma) that provide a minimum age for the sedimentary host rocks. The age difference between basin fill and mineralization, the high REE content and the flat REE spectra of uraninite typical of metamorphic hydrothermal fluids, and the paragenetic sequence, do not support the previous interpretation that Camie River is an unconformity-related uranium deposit. Rather, the sitting along faults in basement and cover metasedimentary rocks, REE patterns in uraninite and age of uranium mineralization are more consistent with a Mesoproterozoic high-temperature hydrothermal event at 1724 Ma.

1 Introduction

The Camie River deposit is located in the Paleoproterozoic Otish Basin (Fig. 1), approximately 250 km northeast of Chibougamau, Québec (Canada). It was interpreted to represent an unconformity-related uranium deposit (Gatzweiler 1987; Höhndorf et al. 1987; Beyer et al. 2012), comparable to those described in the Athabasca (Canada) and McArthur (Australia) Paleo- to Mesoproterozoic basins. The uranium mineralization occurs near the unconformity between Aphebian fluviatile basin sedimentary rocks of the Otish Supergroup and Archean basement rocks of the Tichegami Group. Beyer et al. (2012) reported a discordant uraninite LA-ICP-MS age of 1721 Ma, above the Concordia thus suggesting anomalous Pb, and arguing that intrusion of Otish Gabbro
dykes, previously considered intruded at ca. 1720 Ma, caused basinal brine flow and uranium deposition in conditions similar those for unconformity-related U deposits. The age of the Otish Gabbro dykes and of their sedimentary host rocks, however, has been shown to be much older, with U-Pb ages from 2172-2162 Ma (Hamilton and Buchan 2016; Milidragovic et al. 2016). This indicates that uranium formed nearly 450 Ma after intrusion of the Otish Gabbro dykes, such that the unconformity-related interpretation must be re-evaluated.

We report here on the paragenetic position of uraninite in relation to the alteration of the basement and sedimentary cover rocks hosting the Camie River deposit. Re-Os and U-Pb geochronology of molybdenite and uraninite is used to re-assess the age of the uranium mineralization at the Camie River deposit and the REE pattern of uraninite is compared to that from other U-deposit types. These data are used to discuss the origin of the Camie River deposit.

2 Geology of the Camie River deposit

The Camie River deposit is hosted by the Paleoproterozoic Otish Supergroup, which records depositional facies ranging from high-energy fluviatile, syn-rift facies, to lower-energy, marginal, marine depositional environments, as a result of a marine transgression. The maximum age for the Otish Basin is provided by the Mistassini gabbro dyke swarm (2515 Ma: Hamilton, 2009), whereas the 2172-2162 Ma Otish Gabbro suite dykes and sills constrain a minimum age for the Otish Supergroup (Hamilton and Buchan 2016; Milidragovic et al. 2016).

The Camie River deposit is located along the southern rim of the Otish Basin (Fig. 1). Basement rocks comprise EW-trending and subvertical chlorite-altered metavolcanic and metavolcanoclastic rocks of the Hippocampe Belt (Genest 1987). The uranium mineralization is located near the fault-offset unconformity between the Matoush Formation conglomerates and massive sandstones, and the Hippocampe Belt (Gatzweiler 1987; Höhndorf et al. 1987; Beyer et al. 2012). Uranium mineralization is mainly hosted by subvertical reverse faults intersecting graphitic metapelites ± sulfides (Gatzweiler 1987; Beyer et al. 2012), and sandstones and conglomerates, near basement wedges (Genest 1987). According to Gatzweiler (1987) and Höhndorf et al. (1987), the main mineralized zone is a 550 m long, EW-trending, body plunging to the east and extending locally from the unconformity down to 20-30 m into the basement rocks and up to 30-50 m along fractures into the basin sedimentary rocks. Uranium grades are up to 1.71 wt.% U₂O₅ over 10.75 m, including a maximum grade of 25.9 wt.% U₂O₅ (Aubin et al. 2012). The uranium mineralization consists of Pb-rich uraninite (Urn1), in places intergrown with molybdenite, and replaced by Nb-rich brannerite (Ruzicka and Le Cheminant 1983; Gatzweiler 1987; Höhndorf et al. 1987; Lesbros-Piat-Dvesial 2014). The uranium mineralization is polymetallic with Mo, Cu, Co, Ni, As, Se, Nb, V, Ag and Au (± Th) Gatzweiler 1987; Höhndorf et al. 1987).

Feldspathic and muscovite hydrothermal alteration in sedimentary rocks are characterized by a common enrichment in U ± W ± Th, and by enrichment in Na₂O ± SiO₂ and K₂O ± Al₂O₃, respectively. Na₂O contents in feldspathic sandstones increases towards the unconformity. The Camie River feldspathic alteration consists of authigenic albite partly replaced by later authigenic orthoclase cement (Lesbros-Piat-Dvesial 2014). The basin wide muscovite alteration affected both the Matoush Formation and the top of the Tichegami Group, and shows a small Na₂O enrichment close to the unconformity (Lesbros-Piat-Dvesial 2014).

The muscovite alteration is cut by narrow (< 5 mm) early chlorite veins associated with moderate brick-red hematite alteration, commonly located near fracture zones. The early vein chlorite plots at the boundary between the clinochlore and penninite fields and yield an average chlorite temperature of 210 ± 20°C (Lesbros-Piat-Dvesial 2014). Disseminated and vein uraninite in sedimentary rocks is associated with a later generation of chlorite that plots at the boundary between the sheridanite and clinochlore fields, with an average formation temperature of 329 ± 18 °C (Lesbros-Piat-Dvesial 2014). In basement rocks the uraninite is associated with hydrothermal chlorite that plots at the intersection of the sheridanite, ripidolite, clinochlore and pyenochlorite fields, and with an average temperature of 317 ± 37 °C (Lesbros-Piat-Desvial 2014). Uranium mineralization and chlorite are cut by calcite and red-brick hematite veins in sedimentary rocks and by calcite, dolomite and sulfide veins in the basement rocks.

3 Methods

The rare earth element concentrations in uranium oxides were measured using a laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) system composed of an ArF excimer laser coupled to an Agilent 7500c, (Lach et al. 2013). U–Pb isotopic composition of uranium oxides were determined using a CAMECA 1280-HR2 ion microprobe. Molybdenite geochronology used the NTIMS Re-Os method described in Selby and Creaser (2004) and Markey et al. (2007).

4 Results

4.1 Mineral chemistry of uraninite

We report four LA-ICP-MS analyses for REE on two uranium (Urn1) crystals less than 1 cm apart in a polished thin section from a graphitic metapelite from a zone grading 3.49 wt.% U and 1.44 wt.% Pb. Urn1 is disseminated and shows a molten texture, and it is partly replaced by brannerite and U-phosphate, itself replaced byapatite. Urn1 is cut by veins of pyrite or pyrrhotite. Urn1 is characterized by high REE concentrations and a flat chondrite-normalized REE patterns, with REE/chondrite values near 1000 (Fig. 2).
4.2 Uraninite U-Pb geochronology

U-Pb isotope analyses by SIMS on the two Camie River uraninite (Urn1) crystals analyzed for the REE composition return 207\(^{\text{Pb}}/206\(^{\text{Pb}}\) ages ranging from 1540 to 1704 Ma, and yield a discordant U-Pb upper intercept age of 1724 ± 29 Ma with a lower intercept at 66±24 Ma (Fig. 3).

4.3 Molybdenite Re-Os geochronology

Molybdenite, from a graphitic metapelite grading 9.55 wt.% U and 1.37 wt.% Mo, is disseminated with a typical prismatic habit, and intergrown with Urn1 uraninite. Analyses of two fractions from the sample yield similar compositions in Re (58 and 48 ppm) and Os (1055 and 886 ppb). The Re-Os model ages are 1725±7 Ma and 1723±7 Ma, indistinguishable within analytical error. A weighted mean age of 1724.0 ± 4.9 Ma is computed for molybdenite, at the 95% level of confidence.

5 Discussion

Early albite replacement by orthoclase alteration and Na\(_2\)O enrichment indicate a decreasing Na/K as a consequence of albite precipitation, followed by basin-wide muscovite that indicates more acidic basinal fluids during progressive diagenesis of the sedimentary rocks. The early diagenetic alteration is cut by paragenetically later hydrothermal chlorite associated with the uranium mineralization in basement and basin sedimentary rocks, that shows an increase of fluid temperature from ca. 210 to ca. 320\(^{\circ}\)C, similar to values computed by Beyer et al. (2012). The chlorite composition forms an array between the clinochlore and chamosite end-members in the Al-Fe-Mg diagram (Lesbros-Piat-Desvial 2014). Beyer et al. (2012) reported late ("post-diagenetic") sudoitic chlorite in basement rocks that was not found in our study. This rare, paragenetically late relative to uraninite, sudoite is unlike that typically found in unconformity-related uranium deposits (Jefferson et al. 2007).

The high concentration and flat REE pattern of Camie River uraninite is similar to those typical of syn-metamorphic, higher temperature (~350\(^{\circ}\)C) uranium deposits (Mercadier et al. 2011), in agreement with the chlorite temperatures. The REE+Y pattern and REE abundance are different from those characteristic of worldwide unconformity-related uranium deposits Mercadier et al. 2011).

The late paragenetic stage of uranium relative to diagenetic assemblages in the Otish Basin is consistent with the age of uraninite. Uraninite has been dated by TIMS U-Pb (1723±16 Ma; Höhndorf et al. 1987) and by LA-ICP-MS Pb-Pb (1692±32 Ma; Beyer et al. 2012). Our SIMS U-Pb age of 1724±29 Ma and NTIMS Re-Os age of 1724±4.9 Ma are remarkably consistent with previous studies, and show a time gap of nearly 450 Ma with the minimum deposition age for the Otish Basin (> 2162 Ma). Höhndorf et al. (1987) reported TIMS U-Pb ages of 1717±20 Ma and 1711±2 Ma for the Lorenz Gully and “L” occurrences, respectively (Fig. 1). At the Matoush deposit (Fig. 1), Alexandre et al. (2015) reported a poorly constrained uraninite LA-ICP-MS U-Pb age of 1695±110 Ma, reset at 1010±25 Ma, they suggested likely as a result of the Grenville Orogeny. At Matoush (Fig. 1), Höhndorf et al. (1987) reported a TIMS U-Pb discordant 1359±28 Ma age, whereas they obtained a “Grenvillian” age (1072±5 Ma) at the Indicator Lake occurrence (Fig. 1). The hydrothermal fluid flow event, that formed the uranium mineralization at ca. 1724 Ma, also likely caused alteration of the Otish Gabbro dykes to yield the 1730±10 Ma Sm-Nd isochron age reported by Höhndorf et al. (1987).

The ca. 450 Ma minimum age difference between basin fill and uranium mineralization, anecdotal sudoitic chlorite, high temperature of chlorite (ca. 320 °C), specific whole-
rock geochemical signatures of the alteration (Na-rich) and mineralization and the REE-rich and flat REE pattern of uraninite, all point to formation of the Camie River deposit by high temperature syn-metamorphic fluids long after diagenesis of the sedimentary rocks, in contrast to previous interpretations that favored diagenetic-basin derived fluids and an unconformity-related deposit typology (Beyer et al. 2012).

The cause for the metamorphic hydrothermal system remains highly speculative. A likely event would be emplacement of the Kivalliq Igneous Suite and Timpton Large Igneous Province (LIP) across Siberia and Laurentia emplacement of the Kivalliq Igneous Suite and Timpton remains highly speculative. A likely event would be 2012). and an unconformity-related deposit typology (Beyer et al. 2015) that has an alkaline geochemical affinity, akin to lamprophyres and kimberlites, and which is unrelated to the Otish Gabbro dykes (Milidragovic et al. 2016). The age of the Matoush dyke is unknown, but it could be a manifestation of a large-scale mantle-derived magmatic event that heated the crust and set into motion metamorphic fluids that formed the Otish Basin uranium mineralization. Another causative event could be related to granitic magmatism related to the 1744-1704 Ma Yavapai Orogeny at the southern boundary of the Superior Province (Raharimahafena et al. 2014).

6 Conclusions

The age of uraninite (1724 Ma), almost 450 Ma after the minimum age for the host sedimentary rocks, the temperature of fluids depositing chloride, to ca. 320 °C, typical of low grade metamorphism, combined with the REE+Y trace element pattern of uraninite, similar to those of metamorphogenic uranium deposits are consistent with a metamorphic origin for the uranium mineralization at Camie River and elsewhere in the Otish Basin. We infer that the hydrothermal fluid flow that formed the uranium mineralization at 1724 Ma may have been triggered by the Timpton-Kivalliq LIP at 1750 Ma, or by the magmatism related to the 1744-1704 Ma Yavapai Orogeny.

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References


Uranium mineralization and structural controls in the Spitfire prospect, Hook Lake project, Patterson Lake trend, Canada

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Abstract. Several drillholes with acoustic televiewer (ATV) data were studied to determine the structural controls of the Spitfire Zone. Three types of mineralization associated with three different types of structures were identified: (A) relative low grade mineralization associated with hydraulic/hydrothermal breccia; (B) relative medium grade mineralization associated with ductile shear zones; (C) relative high grade mineralization associated with veins or breccia faults. The ATV data indicates that the mineralized hydraulic/hydrothermal breccia and ductile shears are oriented N015-N025. Mineralized veins and faults form systems oriented N015 dipping NW. Four major tectonic events are interpreted. D1 and D2 are responsible for ductile folds and shear zones. The D2 event rotates D1 structures from N040 to N015. A N015 shortening event (D3) is responsible for the opening of the reoriented N015 ductile shear zones, allowing for mineralizing fluids migrating through to mineralize shear zones. A later state (D4) is assumed to have a compressional σ1 oriented N015 and to be responsible for the formation of NNE-trending fracture corridors cross-cutting previous structures, locally branching into shear zones, and bringing another mineralizing event.

1 Introduction

The Hook Lake Project (Purepoint Uranium Group Inc.-21%, Areva-39.5%, Cameco-39.5%) is located in the south-west Athabasca Basin (Fig. 1). The Spitfire prospect is located in its southern boundary along the Patterson Lake conductive trend (Fig. 1). This paper presents the 2016 structural studies completed about the Spitfire Zone, where mineralization was first intersected in 2015. It is based on structural analysis of acoustic televiewer (ATV) data and observations on mineralized unsplit core. ATV was run and processed by DGI Geoscience Inc., and interpreted by the authors. Complementary structural studies are ongoing on the 2017 drill-holes and ATV data.

2 Geological background

The Spitfire prospect is located northeast of the Triple R (Fission Uranium Corp.) and Arrow (NexGen Energy Ltd.) deposits along strike of the Patterson Lake structural corridor (Fig. 1). The Patterson Lake trend is located at the western edge of the East Lloyd domain. The Lloyd domain is underlain by magnetic dioritic-granodioritic orthogneisses and subordinate supracrustal rocks (Card et al. 2007; Card et al. 2014). Recent chronology data indicates that the Lloyd domain (2.46Ga) is older than the Taltson orogeny (2-1.9Ga) and constitutes a unique tectonic entity distinct from the Thelon orogeny and tectonic zone (Card et al. 2014). In the Patterson Lake area, two major basement rocks are identified (Colin and Noll, 2016): orthogneiss derived from quartz monzodioritic and dioritic protholits, and a suite of mafic to ultramafic rocks that intruded the orthogneiss. To our knowledge, other than the study by Hillacre et al. (2016), there is not yet a characterization of the tectonic style and its control on mineralization in this zone.

3 Mineralization settings

This structural study identified three types of mineralization that are associated with three different types of structures. The mineralized settings are, from
A) Relative low to medium grade mineralization (e.g., 0.88% $\text{U}_3\text{O}_8$ over 20.1m) associated with hydraulic/hydrothermal breccia. Mineralization is disseminated within grey clay-rich breccia cement and locally leaks from the cross-cutting breccia into the foliation (Fig. 3a). This type of mineralization forms the lower ore body (Fig. 2), with the mineralization occurring parallel to the foliation. It is spatially associated with strong clay (illitic) alteration beneath the breccia.

B) Relative medium grade mineralization (e.g., 1.3% $\text{U}_3\text{O}_8$ over 10m, 1.2% $\text{U}_3\text{O}_8$ over 5.4m) associated with ductile shear zones involving granitic and/or graphitic gneisses, with or without visible sulfides (Fig. 3a). Mineralization within these shear zones postdates foliation and ductile shearing. Mineralization is massive or botryoidal along foliation and shear planes. It is locally of higher grade where it is associated with redox fronts containing botryoidal/spherulitic pitchblende with electrolysis rims (Fig. 3b). This mineralized shear zone constitutes what is called the upper ore body (Fig. 2). It is spatially associated with moderate clay (illitic) alteration.

C) Relative high grade mineralization (e.g., 10.3% $\text{U}_3\text{O}_8$ over 10.0m, 4.1% $\text{U}_3\text{O}_8$ over 3.1m) associated with veins or breccia fault zones, locally leaking into the foliation (Fig. 3b). These late brittle structures cross-cut both the upper and lower mineralized setting or branch into the pre-existing graphitic shear zones (Fig. 2). These types of mineralized structures have a better expression at the intersection with pyrite-rich graphitic layers. Detailed observations suggest the following chronology: 1) N45°-trending ductile graphite±pyrite shears; 2) N015°/50-60° trending quartz-veining and breccia that branch into and re-utilizes the pre-existing graphitic shear zones; 3) quartz dissolution in quartz veins and breccia networks; and 4) uraniferous fluid circulation and pitchblende precipitation within the dissolution voids in fractures and between the breccia clasts at the intersection with the graphitic shears.

4 Acoustic televiewer structural analysis

High quality ATV data provides accurate structural data. The mineralized hydraulic/hydrothermal breccia and ductile shear zone in the Spitfire Zone are dominantly oriented N015°-N025° (Fig. 4). Mineralized veins and faults form systems oriented similarly between N170° to N020° (mean N015°), with dips dominantly to the NW (Fig. 4); which explains common branching of these fractures into pre-existing foliation and shear zones. Mineralized intervals also coincide with relatively shallower dips (50°-60°) than the non-mineralized intervals (70°-80°).

WNW-ESE non-mineralized faults offset the composite ore body. They often correlate with low gamma breaks suggesting uranium remobilization/leaching. ATV structural data and slickensides on core indicate reverse left-lateral strike-slip for most of these faults.

5 Regional structural interpretation and implications

Figure 5 is a structural interpretation on the tilt derivative of the total gradient VTEM-map at the scale of the Hook Lake Project. The VTEM-total gradient (Aeroquest, 2014) was chosen for this upscaling and display because it best highlights the structural details of the region and how they are related to core observations.

In their interpreted (simplest) relative timing, figure 5 displays the following structures. Two generations of folds: the first generation, axis in blue on the map, strikes NE-SW, dominantly N040° and locally N015°. The two major “shear zones” (NW and SE shear zones) are interpreted being related to this folding phase and constitute major reverse shear zones. This tectonic phase is here considered the metamorphic deformation D1, accommodating NW-SE shortening. The second fold generation, axis in red on the map, strikes NW-SE. This second generation of folds indicates NE-SW shortening and is attributed to a D2 event. It creates superposed folding with local complex geometries. E-W shear zones may be attributed to this event but there is no constraint on them to date. They are interpreted left-lateral reverse shear zones. This tectonic phase is responsible for local rotation and reorientation of the pre-existing N040° folds to N015°.
Structures resulting from the superposition of D1 and D2 display a rhombohedral shape, with left-lateral dominant rotation.

Figure 3. a Mineralized hydraulic/hydrothermal breccia (setting A). b Massive or botryoidal pitchblende foliation parallel (setting B). c High grade massive mineralization and mineralized cataclasite in a NNE fault (setting C).

A N015 shortening event (D3) is interpreted to be responsible for the Mode I (dilation) opening of the reoriented to N015 folds and ductile shear zones. This could allow for hydrothermal fluids migrating through to mineralize shear zones in the form of hydraulic/hydrothermal (stockwork) breccias or as foliation/shear parallel mineralization. It may be possible that during this stage, the D1 shear zones were reactivated as left-lateral strike-slip faults accounting for the apparent left-lateral offset of the D2 shear zones. The WNW-ESE fault zone that offsets the mineralization in the Spitfire Zone is attributed to such a type of reactivation during this tectonic event. Note, that if this happened, this reactivation could produce: i) compressional strain along N040-striking shear zones segments reducing their capability to move fluids, ii) extensional strain along structures or segments that are (re)oriented to N015 enhancing their capability to move fluids.

A final stage of brittle deformation and vein-related high grade mineralization is needed (D4). This stage is assumed to have a compressional $\sigma_1$ oriented N015. This tectonic event is interpreted to be responsible for the formation of NNE-trending conjugate-fracture corridors cross-cutting all previous structures and mineralized settings, locally branching into shear zones (graphitic or non-graphitic), and resulting in another mineralizing event. Additionally, it is possible that conjugate faults result from an extensional strain $\sigma_3$, as Mode II fractures, rather than to a compressional $\sigma_1$ as Mode I fractures, which suggests a dominant extensional WNW-ESE regime rather than a NNE-SSW compressional one. Further investigation is ongoing to evaluate this hypothesis.

6 The protoliths in the Spitfire zone

Recent observations of very fresh rocks from holes allows
identifying some of the protoliths of the altered rocks that host the mineralization in the Spitfire zone and along the Patterson Lake trend. These are in agreement with those identified by Colin and Noll (2106). In a transect from east to west, these are:

(i) Granitic gneiss with preserved feldspars, often hydrothermal quartz silicification;

(ii) Mylonite zone (>50m-thick) which contains: a) syntectonic-garnet rich granitic gneiss. Garnets appear approaching the mylonite zone and are fresh out of the mylonite, chlorite- rimed at the edges and completely chloritized within the mylonite core. The garnets are progressively stretched and rotated indicating high temperature deformation (>600-800°C); b) Very fine grained mafic rocks with local small but very abundant garnets. These mafic rocks vary in location from above to below the graphitic pelite. Fresh examples of these mafic rocks contain disseminated sulfides. c) Graphitic pyrite-rich pelitic gneiss within the mylonite core (ultramylonite).

(iii) Pyroxene-garnet rich mafic rocks with pyrite as disseminated grains or in veinlets, and magnetite in veinlets. This mineralogy and the rock textures are so far interpreted as reminiscent of eclogites. Petrographic studies are in process to confirm or deny this hypothesis. Hydrothermal quartz is abundant locally modifying the protolith rock fabric and overprinting a pseudo-granitic gneissic fabric.

(iv) Granodioritic rocks.

Further petrographic analysis is in progress.

7 Conclusions

The following points summarize the main observations of the Spitfire zone.

- Three mineralized settings have been observed: 1) The upper zone of low grade mineralization is associated with late cross-cutting fractures (mineralized setting C). These fractures are dominantly oriented NNE (N015). 2) An intermediate zone of relative low to medium grade mineralization is associated with a ductile shear zone (mineralization setting B) that involves granodioritic, mafics rocks and graphitic gneiss. This shear zone is oriented NNE (N015-N025). Mineralization is massive or botryoidal along foliation. 3) The lower mineralized body is associated to a shear zone involving granitic and granodioritic gneiss (no graphite). The upper part is mineralized by the high grade massive or botryoidal parallel to S1 mineralization, in a dominantly oxidized interval (mineralization setting B). The lower part hosts low grade mineralized hydraulic/hydrothermal breccia (mineralization setting type A). Massive and disseminated mineralization is observed. The intermediate and lower mineralized zones are interpreted as belonging to the same shear zone offset by a later WNW-ESE fault. WNW-ESE non-mineralized faults offset the composite mineralized body.

- High quality ATV data indicates that the mineralized breccia and ductile shear zones are dominantly oriented N015-N025 which falls out of the classical NE orientation (N040-050) of the Patterson Lake trend. Mineralized intervals also coincide with relatively shallower dips (50º-60º) than the non-mineralized intervals (70º-80º). The observed change in both azimuth and dip within the mineralized horizon suggests the presence of structural bends which serve as structure-related geometrical traps.

- Four major tectonic events are interpreted. D2 is responsible for local rotation of the pre-existing N040 (D1) structures to N015. A N015 shortening event (D3) is responsible for the opening of the reoriented N015 ductile shear zones, allowing for migration of mineralizing fluids through, and pitchblende precipitation within these shear zones. A later state (D4) is assumed to have a compressional σ1 oriented N015 and responsible for the formation of NNE-trending fracture corridors cross-cutting previous structures, locally branching into shear zones, and bringing another mineralizing event.

- Among the observed protoliths it is interesting to note the presence of possible eclogites below the mafic-graphitic shear zone at the Spitfire zone, thus below the Patterson Lake trend. This hypothesis needs confirmation by further petrographic studies.

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References


New insights for the genesis of granite-related vein-type uranium deposits in Xiazhuang and Zhuguang ore fields, SE China

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Abstract. Granite-related vein-type uranium deposits from the world-class Xiazhuang and Zhuguang ore fields are located within the Nanling Metallogenic Belt in SE China. These deposits are mainly hosted in peraluminous Indosinian and Yanshanian granites, which also represent the main uranium source rocks for the mineralization. Amongst the five deposits that were studied, the Baishuichai deposit dated at 177±9 Ma and the Shituling deposit dated at 134±2 and 127±2 Ma correspond to early mineralization episodes compared to the main stage (85-60 Ma) that occurred during the Cretaceous-Cenozoic crustal extension. These deposits most likely formed under high temperature conditions as indicated by Th-bearing uranium oxides and their association with alteration minerals such as epidote and chlorite. In contrast, Xiwang (72±2, 66±1, 62±1 Ma), Manhuakeng (81±2, 80±9, 74±1, 65±5, 62±1 Ma) and Xianshi (52±2, 41±1 Ma) deposits formed during the main mineralization stage related to low temperature ore-forming processes and are characterized by W-Y-Nb-Ti-rich pitchblende mainly associated with quartz, fluorite, carbonate and pyrite. Therefore, the genesis of granite-related vein-type uranium deposits in Xiazhuang and Zhuguang ore fields occurred over a long time span (>100 Ma) during the Yanshanian post-orogenic extension in SE China, in several stages that involved different ore-forming processes.

1 Introduction and geological setting

The South China Uranium Province (SCUP) is part of the South China Metallogenic Belt (SCMB) and accounts for the largest amount of explored uranium deposits and resources in China (≈ 50% of identified uranium resources; Dahlkamp 2009; Mao et al. 2011; OECD-NEA/IAEA 2016). This province covers some 600000 km² of southeast China extending from Zhejiang Province in the northeast to southwestern Guanxi (Fig. 1). The SCUP comprises several types of uranium deposits (Dahlkamp 2009), from the most to the least economic: (i) granite-related vein-type deposits, (ii) volcanic-related vein-type deposits and (iii) black shale-related deposits also referred to as carbonate-siliceous-pelite-type (C-Si-pelite; Dahlkamp 2009; Pirajno 2013). Some small sandstone-type deposits are also hosted in several Mesozoic-Cenozoic basins of the province (Dahlkamp 2009).

Besides uranium, the SCMB-comprising the southern margin of the Yangtze Craton and Cathaysia Block-is also renowned for W, Sn, Bi, Sb, Mo, Au, Ag, Cu, Pb and Zn deposits (Mao et al. 2011, 2013; Pirajno 2013), with some falling in the world-class category. Although some Triassic granite-related Sn and Nb-Ta-W-Sn deposits have been reported, the multitude of ore systems that developed within the SCMB have ages ranging from 180 to 80 Ma (Mao et al. 2011, 2013). These deposits were formed in several large-scale metallogenic stages controlled by the regional geodynamic evolution and related to successive major magmatic-thermal events that occurred during the Indosinian orogeny (240 Ma) and the Yanshanian post-orogenic event (early Yanshanian: 160 Ma, late Yanshanian: 125 Ma; Chen et al. 2005; Mao et al. 2011, 2013; Pirajno 2013).

However, granite-related vein-type uranium deposits from the world-class Xiazhuang (eastern part of the Guidong batholith) and Zhuguang ore fields (OF) within the Nanling Metallogenic Belt (NMB; Fig. 1) mainly formed during the late Yanshanian and tend to show younger ages of mineralization, dominantly ranging from 138 to 47 Ma with a peak at 85-60 Ma (Hu et al. 2008; Dahlkamp 2009; Luo et al. 2015). Hence the mineralization mainly occurred during the Cretaceous-Cenozoic post-orogenic extension (Deng et al. 2002; Chen et al. 2005; Hu et al. 2008). Nevertheless, some deposits also formed during the early Yanshanian (the Zhushanxia deposit dated at 165-146 Ma; Hu et al. 2003) indicating that early stages of mineralization also occurred and may potentially be related to different genetic conditions.
During the Mesozoic, mainly I- and A-type biotite granite and S-type biotite and two-mica granite were emplaced in the SCMB (Ling et al. 2004, 2005; Li XH et al. 2007; Wang et al. 2007; Mao et al. 2011, 2013; Chen et al. 2012; Deng et al. 2012; Pirajno 2013; Zhao et al. 2013; Gao et al. 2014; Li et al. 2015). Jurassic and Cretaceous granites (Yanshanian) were first believed to be the main host-rock and source of uranium for the granite-related vein-type deposits (Dahlkamp 2009) but recent studies also characterized Triassic (Indosinian) peraluminous two-mica granite as another major host-rock and even more favorable uranium source for the deposits that formed in the Xiazhuang and Zhuguang OF (in the Xiazhuang OF, the Triassic Xiazhuang two-mica granite has an average U content of 22 ppm; Chen et al. 2012).

A large amount of granite-related vein-type uranium deposits occur in the Xiazhuang and Zhuguang OF, representing about 40000t of identified uranium resources in China (OECD-NEA/IAEA 2016). The endogenic ore bodies are mainly distributed along NNE-SSW and ENE-WSW oriented silicified fractures or at the intersection with WNW-ESE oriented mafic dykes. The uranium mineralization mostly occurs as pitchblende that can be disseminated, as warty aggregates or massive in veins or breccia. Uraninite and coffinite occur in minor quantities. These uranium minerals are commonly associated with several generations of quartz, carbonate, fluorite, pyrite, and other gangue and alteration minerals. Until now, the most consistent model for the genesis of the uranium mineralization proposes that: (i) a large scale hydrothermal system developed during the Cretaceous-Cenozoic crustal extension in which groundwater percolated downwards and then ascended after heating and most likely mixing with deeper connate granite water and mantle-derived fluids (Hu et al. 2008; Dahlkamp 2009), (ii) thermal solutions leached uranium from uranium-rich granites during their migration along faults, (iii) uranium was transported mainly as uranyl-carbonate and uranyl-fluorine-carbonate complexes, (iv) the ore-forming fluid was relatively low temperature (120-250 °C; Hu et al. 2008), (v) in response to intense brittle deformation at the ore stage, the abrupt decrease of the hydrostatic pressure of the hydrothermal system (from 400 bar in average for the pre-ore fluid down to 10-60 bar for the ore-forming fluid; Dahlkamp 2009) was responsible for the precipitation of uranium that was reduced by various reductants and crystallized as pitchblende together with SiO₂. However, the example of the early high-temperature (> 250°C) uranium mineralization in the Zhushanxia deposit suggests that early mineralization stage(s) involving different ore-
forming processes also occurred in the NMB.

Therefore, this study aims to characterize the mineralogical, chemical and isotopic signatures of the uranium mineralization from several deposits in Xiazhuang and Zhuguang OF through detailed petrographic and mineralogical studies and the measurements of the trace element concentrations and U-Pb isotopes in uranium oxides. The main purpose of this study is then to discuss the genetic conditions of granite-related vein-type uranium deposits in the NMB following the insights of these new data.

2 Material and methods

Nine mineralized samples were collected from five representative granite-related vein-type uranium deposits (Fig. 1) including Baishuichai, Shituling, Xianshi and Xiwang in the Xiazhuang ore field and Mianhuakeng in the Zhuguang ore field. The mineralogical characteristics of the uranium mineralization were determined through detailed petrographic studies by optical reflected light microscope and scanning electron microscope (SEM). The chemical composition of the uranium minerals was analyzed by electron microprobe (EMP). The trace element concentrations of the uranium oxides were measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and U-Pb isotopic dating was performed by secondary ion mass spectrometry (SIMS) in order to constrain the age(s) of the uranium mineralization.

3 Results

3.1 Petrography and mineral assemblage of the uranium mineralization

The uranium mineralization from the five deposits that were studied presents different mineral assemblages: (i) the Baishuichai deposit is characterized by disseminated aggregates of subhedral uraninite (average of 94.5 wt% UO₂ at the EMP) within pervasively altered zones of the host granite. Uraninite is mainly associated with secondary quartz and pyrite; (ii) the Shituling deposit is dominantly characterized by pitchblende, massive or as spherulite aggregates with minor overgrowth of uraninite crystals, distributed along silicified fractures. These uranium minerals are mainly associated with subhedral and microcrystalline quartz populations, hematite, chlorite and epidote; (iii) the uranium mineralization in Xianshi, Xiwang and Mianhuakeng deposits occurs as spherulite aggregates, massive veins and breccia cements associated with fluorite, quartz, calcite and pyrite. The pitchblende composition (77.1 ≤ UO₂ ≤ 90.9 wt%) of these deposits generally shows low SiO₂ (0.1-7.8 wt%) and significant CaO (3.0-11.5 wt%) contents. Coffinite may also occur in minor quantity in these deposits (Dahlkamp 2009) but has not been observed in the studied samples.

3.2 Trace element concentrations in uranium oxides

The concentration of rare earth elements (REE) and other trace elements including W, Y, Nb, Ti, Zr and Th in uranium oxides was measured by LA-ICP-MS. Chondrite-normalized REE contents in uranium oxides from the five studied deposits display typical “gull-winged” patterns of vein-type uranium deposits (Mercadier et al. 2011) that also may reflect the main source of the REE, monazite or xenotime. Uraninite from the Baishuichai deposit has a very specific signature mainly represented by high to very high W (up to 0.8 wt%) and Y (up to 0.6 wt%) concentrations and moderate to high Nb (up to 0.3 wt%) and Ti (up to 0.2 wt%) contents. Low Zr (128 ppm) and Th (17 ppm) contents are also noticeable in pitchblende from Shituling.

3.3 U-Pb isotopes dating on uranium oxides

U-Pb isotopic dating was performed by SIMS on uranium oxides from the five studied deposits. The results are presented in weighted average ages using the 206Pb/238U system for concordant dates and the 207Pb/235U system for discordant dates as the 206Pb/238U system has likely been affected by 226Ra and/or 222Rn losses during the active period of the hydrothermal systems. Seven concordant dates on uraninite from the Baishuichai deposit indicate that crystallization occurred from 185 to 150 Ma and give a weighted average 206Pb/238U age of 177±9 Ma. Pitchblende in two samples from the Shituling deposit mainly shows discordant dates giving weighted average 207Pb/235U ages of 134±2 and 127±2 Ma, respectively. Nine discordant dates on pitchblende from the Xianshi deposit indicate two mineralization stages with weighted average 207Pb/235U ages at 52±2 and 41±1 Ma. Pitchblende in two samples from the Xiwang deposit mainly shows discordant dates giving a weighted average 206Pb/238U age of 72±2 Ma for the first sample and indicating two mineralization stages at 66±1 and 62±1 Ma for the second one. Pitchblende from the Mianhuakeng deposit was also dated on two samples. In the first sample, seven concordant dates indicate two mineralization stages with weighted average 206Pb/238U ages at 80±9 and 65±5 Ma. Six discordant dates on pitchblende from the second sample shows three mineralization stages with weighted average 207Pb/235U ages at 81±2, 74±1 and 62±1 Ma.

4 Discussion and conclusions

Granite-related vein-type uranium deposits from the world-class Xiazhuang and Zhuguang ore fields in SE China represent a significant part of uranium resources in China. Recent works already demonstrated that Indosinian (Triassic) peraluminous two-mica granites represent
another major host rock and even better uranium source than Yanshanian granites (Jurassic-Cretaceous) for these deposits. New U-Pb SIMS dating presented in this study indicate that uranium mineralization has occurred over a long time span (> 100 Ma) in several major episodes from 185 to 40 Ma. The disseminated Th-bearing uraninite from the Baishuichai deposit that crystallized at 177±9 Ma represents one of the oldest uranium mineralization stages in the Nanling Metallogenic Belt, most likely related to high temperature ore-forming processes. The Shituling deposit dated at 134±2 and 127±2 Ma corresponds to another early mineralization stage, also related to high temperature ore-forming conditions as indicated by the occurrence of epidote and chlorite associated with the mineralization. Moreover, these early stages of granite-hosted uranium mineralization related to high temperature hydrothermal systems are the only occurrences of this type in the world. In contrast, the Xianshi, Xiwang and Mianhuakeng deposits formed during the main mineralization stage (late Cretaceous-early Cenozoic) mainly characterized by W-Y-Nb-Ti-rich pitchblende associated with quartz, fluoride, carbonate and pyrite that precipitated under low temperature conditions.

Therefore, granite-related vein-type uranium deposits in Xiazhuang and Zhuaguang ore fields formed over a long time span during the Yanshanian post-orogenic extension in SE China. Successive magmatic events that occurred over this period are most likely responsible for the high temperature early mineralization stages that preceded the main stage of uranium mineralization that occurred under low temperature conditions during the Cretaceous-Cenozoic crustal extension.

Acknowledgements

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Identification of sandstones above deeply buried uranium deposits using multivariate statistical methods

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Abstract. The Athabasca Basin in northern Saskatchewan, Canada, hosts the world’s largest high-grade U resources. Principal component analysis (PCA) of sandstone chemistry from the Wheeler River property shows that U is positively associated with Y, Cu, Zn, Na, W, Co, Ni, B, Mg, HREEs, Cr, Sc, Mo, V and LREEs due to cryptic alteration associated with the U mineralization. In contrast, PCA of the regional sandstones shows that U is positively associated with Th, Ti, Zr and Hf, suggesting that U is hosted by detrital heavy minerals. Linear discriminant analysis (LDA) based on PCs of elements associated with U shows three groups of sandstones with high accuracy (95.5%) of discrimination; those above the Phoenix ore (Group PHX), in the Wheeler River property (Group WR) and regional sandstones (Group Regional). Several samples in Group WR are classified into Group PHX by LDA, suggesting that these samples are considered possibly cryptically altered, even far (>200 m) from the ore. Therefore, there may be potential of U mineralization underlying these sandstones. This study shows that PCA and LDA are able to identify elemental assemblages associated with U and sandstones that are cryptically altered.

1 Introduction

Many unconformity-type U deposits occur in the Athabasca Basin in northern Canada along the unconformity between sandstones and the crystalline basement. Major U deposits, including the world’s largest McArthur River deposit, are located in the eastern margin of the Basin (Fig. 1) where the sandstones are relatively thin (less than 400 m) compared to those in the interior of the basin where they are up to 1400 m in thickness. The thick sandstones pose difficulty in exploration in the central area of the Basin and thus the recognition of the composition of the sandstones that have underwent uraniumiferous hydrothermal activity may help in exploration for deeply buried U deposits.

This study uses R-Q mode PCA to determine element assemblages associated with U in sandstones and linear discriminant analysis (LDA) to investigate whether sandstone compositions in the area overlying by U deposits are different from regional background sandstones in the Athabasca Basin. The Wheeler River property is ideally suited to examine the elemental assemblages of sandstones. The property hosts the Phoenix and Gryphon U deposits (Figs. 1 and 2) and is not disturbed by mining activities. Furthermore, high-quality geochemical data are available since the analysis was done at the Saskatchewan Research Council with the same analytical method since 2010.

2 Study area

Unconformity-related U deposits in the Basin are accompanied by extensive alteration halos extending over several hundred meters from deposits, which overprint diagenetic minerals in the sandstones and the metamorphic minerals of the basement rocks (e.g., Hoeve and Quirt 1984). Common alteration minerals include kaolinite, illite, chlorite, and dravitic tourmaline, aluminum phosphate-sulphate (APS) minerals and chlorite (e.g., Hoeve and Quirt 1984; Jefferson et al. 2007; Adlakha and Hattori 2015).

The Phoenix deposit is located along the unconformity, at a depth of approximately 400 m below the surface. The Gryphon deposit is a newly discovered U deposit which is approximately three kilometers northwest to the Phoenix deposit. The Phoenix deposit is estimated to contain indicated resources of 70.2M lbs U3O8 at a grade of 19.1% U3O8 (Roscoe 2015). The Gryphon deposit is hosted in basement rock and currently estimated to contain inferred resources of 43M lbs U3O8 at a grade of 2.3% U3O8 (Denison Mines 2016).

Alteration in the study area is typical unconformity-associated style. The Athabasca Supergroup sandstones are mostly ~ 400 m in thickness in the research area and consists of four formations of the Manitou Falls Group: the Read (MFr), the Bird (MFb), the Collins (MFc) and the Dunlop (MFd) (Fig. 2).
3 Data sources and methods

All data are obtained after near-total digestion (Analytical code 3AMS at Saskatchewan Research Council). This study uses three sets of data; sandstones above the Phoenix deposit (n=4625, 47 elements), in the Wheeler River property, far (>200 m) from the deposit (n=6305, 47 elements) (Fig. 2), and regional data from unmineralized areas (> 5km from any known deposits,) in the Athabasca Basin sandstone data set (n=2175, 43 elements, Wright et al. 2015) (Fig. 1). This study uses R-Q mode PCA with scripts developed by Grunsky (2001). When elements associated with U are identified, another PCA was conducted to the subset of the elements to produce linear combinations of these elements. Analysis of variance was applied to determine the 8 PCs with best discriminating ability. Linear discrimination analysis (LDA) based on the 8 PCs was conducted using “lda” procedure in R statistical software environment.

4 Results

4.1 Principal component analysis

Figure 3. Biplot of PC1 vs.PC2 of Wheeler River data set, after log centred transformation of the composition data.

The PC1 and PC2 account for a large part of total variability (26.8% for PC1 and 17.6% for PC2) of the
Wheeler River data set. Therefore, these PCs reflect the major geological process producing the elemental assemblages of the sandstones. PC1 also accounts for the majority of the U variability, 65.2%. The U variability in other PCs is much smaller (<3.6%). Figure 3 shows that U is positively associated with REEs+Y, Cu, Na, Zn, W, Co, Ni, B, Mg, Pb, Sc, Mo and inversely with Th, Zr, Hf, Fe, Ti etc in PC1. Positive, but very weak association of U and Zr+Hf+Ca+Ga is observed in PC2.

4.2 Linear discriminant analysis

The LDA based on the elements positively and inversely associated with U yields three groups; PHX, WR and Regional groups. They represent the sandstones above the Phoenix ore (PHX), sandstones far from the ore but within the Wheeler River (WR) and regional background sandstones of the Athabasca Basin (Regional) (Fig. 5) These three groups have very minor overlaps with total accuracy rate of 95.5%.

![Figure 4](image)

**Figure 4.** a Biplot of PC2 vs.PC5 of regional data set, after log centred transformation. b Biplot of PC1 vs.PC3 of regional data set.

The regional sandstone data shows that PC2 and PC5 account for the majority of U variability, 32.8%. The biplot shows that U is strongly associated with HREEs, Y, Th, Ti, Zr and Hf (Fig. 4a). PC1 and PC3 account for the majority of variability of REEs+Y (62.7%~84.6%) and they are not associated with U (Fig. 4b). The elemental assemblages suggest that U are not in REE-hosting minerals but mainly in detrital heavy minerals.

5 Discussion

Uranium is positively associated with REEs+Y, Cu, Na, Zn, W, Co, Ni, B, Mg, Pb, Sc, Mo. The abundances of Cu, Pb, Mo, Co, Zn and Na are usually low in sandstones because they are not present in detrital minerals. The data suggest that these elements were likely introduced to sandstones through hydrothermal activity. Sudoite is Mg-rich chlorite and common as an alteration mineral associated with unconformity-type U deposits (Hoeve and Quirt 1984). Magnesiofritite, alkali-deficient Mg tourmaline, is the only mineral containing a significant amount of B in the study area and also a common alteration mineral (Rosenberg and Foit 2006; Adlakha and Hattori 2016). Close association of LREEs, P and Sr with U in PC2 suggests these elements are also associated with the alteration minerals, such as such as monazite and aluminum phosphate sulfate (APS) minerals. Xenotime is the major host of HREEs in the hydrothermal REE deposit, the Maw Zone (Chen et al. 2016), located ~4 km southwest of the Phoenix deposit.

The high discrimination of LDA indicates that the
elemental assemblages can characterize the lithogeochemistry of sandstones of three groups. The composition of sandstones in the Wheeler River Property are similar to those directly above the Phoenix deposit reported earlier by Chen et al. (2015), suggesting that these sandstones were likely affected by uraniferous hydrothermal activities. There are 156 samples of Wheeler River sandstones classified into the Group PHX, indicating that these samples are cryptically altered as samples overlying Phoenix ore. Figure 6 shows that these sandstones mostly located close to the Phoenix deposit. The drill holes above the Gryphon deposit also show similar lithogeochemistry as those above the Phoenix ore. The sandstones with similar geochemical features also occur in the northeast part of the area where weak mineralization has been identified at the unconformity.

Figure 6. Locations of the WR drill holes containing cryptically altered sandstones. The size of symbol reflects the number of cryptically altered sandstones in a WR drill hole

6 Summary

Elements associated with U in sandstones in the Wheeler River Property are different from those in the regional sandstones in the Athabasca Basin. The difference reflects cryptic alteration in the sandstones of the Wheeler River Property. LDA based on the elements positively and inversely with U, identifies sandstones associated with U mineralization. The use of PCA and LDA in shallow sandstone compositions is useful in exploration for buried U deposits.

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References

Characterization of natural brannerite: implication for U deposit fingerprints and dating mineralizing events

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Abstract. Uraninite and coffinite are the most frequent U(IV) ore minerals. Brannerite represents a significant potential of minable uranium, but recovery of uranium is more difficult because brannerite is poorly soluble. These U-Ti oxides are currently found in several deposit types such as intrusive-related, hydrothermal or metamorphic. The results of this work demonstrates that a combination of textural observations, major and trace elements distribution and U-Pb dating allows to decipher the conditions of their genesis. REE patterns can be used as a specific signature for each deposit type. A better understanding of the formation of natural brannerite could provide precious data for the mining industry and the potential future use of this mineral as an U source (i.e. uranium leaching from brannerite).

1 Introduction

The rising demand for energy requires innovations by the mining industry, which now explores other potential ores. U-Ti oxides, such as brannerite (ideally UTi2, but commonly reported as (U, Ca, Th, Y, REE)(Ti, Si, Fe, Al)2O6-8(OH)x), are frequently found in different types of U ore deposits (Lumpkin et al. 2012), sometimes in economic amounts (e.g. Mount Isa, Australia; Wilde et al. 2013). They may represent a potential future source for use in nuclear fuel. However, efficient recovery from brannerite is not straightforward, as brannerite is considered to be refractory compared to uraninite. Application to natural ores of leaching tests made on synthetic brannerite is currently difficult, as these oxides are nearly always found in impure and highly altered forms with a complex composition (Charalambous et al. 2012). In addition, the radioactivity of U leads to a progressive loss of the crystalline structure, known as metamictisation, altering durably the physico-chemical properties of natural brannerite and perturbing at crystal scale the isotopic systems potentially usable to date them. To face this crucial issue, it is necessary to provide careful analysis of the brannerite-bearing ores, as well as good chemical, isotopic and crystallographic constraints of the brannerite in different geological settings. This will lead us to propose a typological classification of brannerite, together with updating our knowledge about the conditions of formation of U-Ti oxides. Finally, these results will be crucial for selecting natural ores and further optimize leaching processes developed on synthetic minerals. This study is part of the NEEDS-transdisciplinary project, named UTiLe (Uranium Titanate Leaching), which aims at understanding the conditions of formation of natural brannerite and optimize U leaching-based ore processing.

2 Materials and methods

Samples from six different occurrences were selected. According to their conditions of genesis, they belong to three deposit types, following the IAEA classification:
- Hydrothermal: Bou Azzer, Morocco and La Gardette, France
- Intrusive-related: Lodrino, Switzerland and a new occurrence from Namibia
- Metamorphic: Domes region, Zambia

Polished thin-sections and plugs were prepared from rock samples and mineral chips. Identification of the paragenesis and textures were carried out by using FEI Quanta 450 SEM hosted by the French RENATECH network at the Femto-ST lab, Besançon. Major element composition of brannerite was obtained by using a Cameca SX100 microprobe (EPMA), at GeoRessources, Nancy. Trace element contents were analyzed using Laser Ablation (Geolas Q Plus system) Inductively Coupled Plasma Mass Spectrometry (Agilent 7500c Quadrupole) at the GeoRessources laboratory. The calibration material is a SRM NIST 610 glass standard. U-Pb isotopic composition was determined using a Cameca IMS1270 ion microprobe at CRPG, Nancy.
3 Results

3.1 Morphology and texture of brannerite

Hydrothermal brannerite from Bou Azzer is associated with galena and barite. In the altered crystals, primary brannerite is replaced by a mixture of low U and high U titanate (Fig. 1a). At La Gardette, REE phosphates were found in the U-depleted rim around the fresh tabular brannerite crystals.

For the intrusive-related type, the brannerite crystals are bigger in size (more than 1 mm) and generally (sub-) euhedral (Fig. 1b). Brannerite from Lodrino displays a very narrow alteration rim, characterized by a thinly laminated texture. In samples from Namibia, no evidence for alteration was found; brannerite locally displays a collomorphic texture as well as inclusions of co-genetic uraninite, coffinite and hematite.

Brannerite from metamorphic rocks collected in the Domes Region are generally of large size and wrapped into the schistosity. They are hosted in metasomatic Mg-rich pelitic schists. Pristine brannerite crystals including anatase are associated with cogenetic uraninite (Fig. 1c). Oscillatory-zoned brannerite shows radial cracking (Fig. 1d). Brannerite also contains inclusions of Mg-rich chlorite and phlogopite suggesting a syn-metamorphic formation. In quartz-bearing domains, Si-rich U minerals, such as coffinite fills the fractures within the host rocks around brannerite.

3.2 Major and trace element composition

All analysed brannerite grains present different chemical compositions as a result of primary chemical substitutions and further alteration or metamictisation. Substitution occurs at the A-site, with the incorporation of Ca, Th and REE instead of U (Fig. 2a), while Ti of the B-site is replaced by Al, Si and Fe. Altered samples are characterized by low U, Th and Ca contents. The substitution effect is well observed in oscillatory-zoned brannerite from samples ZA25 (metamorphic type). This probably reflects a variation of the composition of the mineralizing fluids, as shown by the low U/Ti ratio (Fig. 2b). This ratio also significantly varies between samples.
While brannerite from metamorphic and intrusion-related occurrences show ratios close to the theoretical value \((U/Ti = 0.5)\), hydrothermal brannerite from Bou Azzer and La Gardette have lower \(U/Ti\) (0.3 to 0.4). Alteration of brannerite is characterized by a variable \(Si/Ti\) ratio (Fig. 2b). These deposits also show significant variations of the recalculated \(U\) valency with \(U^{IV}/(U^{IV}+U^{VI})\) ratio ranging between 0.34 (Domes) and 0.96 (Lodrino).

**Figure 2.** a) \(Th + Ca\) vs. \(U\) plot showing the substitution in the A-site of brannerite. b) \(Si/Ti\) vs. \(U/Ti\) plot of brannerite, showing the alteration effects. Large (small) symbols are for non-altered (altered) spots.

Trace element contents of non-altered natural brannerite are also very different between the deposit types. The sum of REE varies between 1350 ppm (mean value) for Namibia and 33000 ppm (mean value) for Bou Azzer (Fig. 3). Except for sample ZA25, which show both positive and negative Ce anomalies, each deposit contains brannerite with homogenous anomalies (e.g. Eu for Bou Azzer and Lodrino). It is worth noting that the REE patterns for the metamorphic brannerite display exactly the same shape as cogenetic uraninite (Eglinger et al. 2013). For each type of deposit, regardless the REE enrichment, the general shape of the REE patterns is similar between deposit types (intrusive, hydrothermal and metamorphic). Hydrothermal deposits are characterized by MREE enrichment relative to LREE and HREE, giving a bell shape to the curves. Intrusive-related deposits are characterized by low LREE/HREE. Metamorphic deposits are characterized by a slightly positive slope from La to Gd and a plateau from Tb to Lu.

**Figure 3.** Chondrite-normalized (Sun and McDonough 1989) REE patterns of non-altered brannerite from different deposits.

### 4 Discussion

#### 4.1 Fingerprints of brannerite

Major and trace elements contents of natural brannerite vary between deposits, but are relatively similar for a given deposit, except in the domains affected by alteration-metamictisation. In addition, the typology of ore deposit can be discriminated by combining different parameters such as the REE signatures and the \(U/Ti\) ratio. It means that brannerite bears the signature of a deposit and this can be used for provenance studies. Such “fingerprints” were also reported for U-oxide minerals; they reflect the conditions of their genesis (Mercadier et al. 2011). As for uraninite, which shares similar features with brannerite, we may infer that crystallography, fluid/magma composition and temperature controlled the incorporation of REE within brannerite.
4.2 Effects of alteration

Regardless the initial U/Ti ratio, there is a significant difference of this ratio between non-altered and altered brannerite, which displays low U/Ti. (Fig. 2b). As Ti is considered to be immobile (Lumpkin et al. 2012), alteration is characterized by U loss. Uranium further precipitated in the fracture, in the rim or around brannerite as coffinite or U-oxides. Alteration is also characterized by Si enrichment (with or without U loss). If such a trend is obvious for brannerite from hydrothermal deposits, those crystallised in metamorphic conditions are more difficult to interpret. Non-altered brannerite (samples ZA19 and ZA29) shows high Si/Ti ratio (up to 0.2), which may reflect a substitution between Si and Ti. Lumpkin et al. (2012) also noted this substitution, without reporting such high ratios in their intrusive-related and hydrothermal brannerite grains. High Si/Ti in non-altered brannerite is probably a signature of metamorphic deposits. This substitution is also obvious for sample ZA25, which displays a very good positive correlation between Si/Ti and U/Ti in the oscillatory-zoned brannerite.

4.3 Application for dating U mineralisation

The presence of U and to a lesser extent of Th, makes brannerite a good candidate for dating mineralizing events. Such geochronological analyses were previously obtained with dissolution TIMS (Darnley et al. 1961) and LA-ICPMS (Oberthür et al. 2009) techniques. The calculated ages are similar to those obtained with other geochronometers, but as brannerite often displays a complex texture, these techniques appear to be limited to unaltered crystals. Based on our detailed study of the texture and chemical composition of brannerite, we carried out analyses of U-Pb isotope ratios, using SIMS facilities.

For Lodrino brannerite, individual analyses plot along a discordia line with an upper intercept at 19.06±0.5 Ma (Fig. 4a); this age is consistent with the Alpine setting of these pegmatitic intrusions (20 to 25 Ma; Graeser and Guggenheim 1990). For sample ZA29 from the Domes, the upper intercept of the discordia line is at 537±36 Ma, in good agreement with the SIMS U-Pb ages obtained on uraninite at 532±18 Ma (Fig. 4b; Eglinger et al. 2014).

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References


2D numerical modelling of geological factors affecting fluid flow related to the formation of the Cigar Lake uranium deposit, northern Saskatchewan, Canada

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Abstract. The unconformity-related uranium deposits in the Athabasca Basin are hosted within basement faults, at their intersection with the unconformity surface, and/or along fault extensions into the sandstone. In the two latter cases, most deposits straddle the basin and basement lithologies, but some are entirely hosted within the sandstone (e.g., Cigar Lake). In this work, we study the effects of unconformity surface topography, basement lithologies, basement faults, and extended faults (basement faults extended into the sandstone due to fault reactivation) on fluid flow and localization of the Cigar Lake deposit. The results show that changes in unconformity topography or basement lithologies alone may affect the number of convection cells in the basin, but they are not sufficient to change the fluid flow pattern in the basin unless high permeable zones such as faults are inserted. Densely developed basement faults present below a minor unconformity topographic high appear to coincide with upward (egress) fluid flow. Such a fluid flow pattern appears to be significantly strengthened if faults are also developed in the sandstone above the basement high, suggesting that extended faults may be an important factor for fluid focusing and thus the development sandstone-hosted uranium mineralization in the Athabasca Basin.

1 Introduction

The high-grade uranium deposits in the Athabasca Basin, northern Saskatchewan, are classified as unconformity-related uranium deposits as they are located near the unconformity surface between the Paleoproterozoic Athabasca Group and the basement (Hoeve and Sibbald 1978). The deposits are divided into three major types: 1) basement-hosted, 2) along the unconformity surface, and 3) within the sandstone (Quirt 2003; Jefferson et al. 2007). Although it is widely accepted that the mineralization resulted from fluid-rock interaction in the basement (ingress flow) or mixing of oxidized basinal fluids with reduced basement fluids in the sandstone (egress flow) (e.g., Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Jefferson et al. 2007), the mechanisms controlling the fluid flow patterns and localization of mineralization are still not well understood. A few recent numerical studies have demonstrated that basement faults may have played an important role in controlling fluid flow directions (ingress versus egress) (Schaubs et al. 2005; Cui et al. 2012a; Li et al. 2016, 2017; Eldursi et al. 2016; Pek and Malkovsky 2016). However, these studies are based on arbitrary simplified basement fault geometries (e.g., the inclination angle, width, depth and number of basement faults). In addition, they did not take into account the heterogeneity of basement lithology and/or the variation of unconformity profile, and they have not extended their models to simulate specific deposits with realistic local geological constraints.

In this paper, we carried out 2D numerical modelling of geological factors affecting fluid flow related to the formation of the Cigar Lake uranium deposit, with constraints from local geology (although still simplified). This deposit, with 234.9 million pounds of \(U_3O_8\) at an average grade of 17.84% \(U_3O_8\) (Bishop et al. 2016), is one of the largest and richest uranium deposits in the world. The orebodies are entirely hosted in the sandstone above the unconformity surface and, as such, belong to the third type above. We aim to understand what geological factors controlled the fluid flow responsible for the formation of this deposit by considering the morphology of the unconformity surface, lithologies in the basement, basement faults, and extended faults (basement faults extended into the sandstone due to fault reactivation).

2 Physical model and numerical modelling parameters

A 2D model of the Cigar Lake uranium deposit was built based on a structural and lithological cross-section (Bishop et al. 2016) and data provided by AREVA. The model is 10 km wide and consists of three layers, including a top layer of relatively low permeability (referred to herein as “cover”, 4 km) representing the upper part of the basin fill that has been mostly eroded (with the Douglas and Carswell formations remaining), a middle layer of relatively high permeability (sandstone, referred to herein as “basin”, 2 km), and a lower layer of low permeability (“basement”, 0.5 km thick) (Figure 1a). The “cover” and “basin” are approximated by mudrock and sandstone respectively, whereas the basement includes granitoid rock, meta-arkose, pelitic gneiss, graphitic pelitic gneiss, and pegmatite. The basement faults range from 10 m to 25 m wide and are inclined from 50° to 80°.
Five sub-models or scenarios were considered in this study. The first sub-model (scenario 1, Figure 1a) consists of the three layers as described above without any faults or morphological variation, and is referred to as the base model. In the second sub-model (scenario 2), a topographic high of the unconformity surface is added in the middle of the model (Figures 1b & c). The third sub-model (scenario 3) was built from the previous one by adding different basement lithologies around the basement high (Figure 1d), as found in the Cigar Lake deposit. The fourth sub-model (scenario 4) was constructed by adding basement faults (Figure 1e). In the fifth sub-model (scenario 5), extended permeable zones (faults) are added to three basement faults above the basement high (Figure 1f), as depicted in a local cross section of the Cigar Lake deposit (Bishop et al. 2016). Table 1 shows the physical properties used of each unit.

### Table 1. Physical parameters used in the numerical modelling. Ф is porosity, K is permeability, k is thermal conductivity, α is thermal expansivity, and C is heat capacity (the data are provided by AREVA and generally are similar with previous studies, e.g., Li et al. 2016).

<table>
<thead>
<tr>
<th>Rock unit</th>
<th>Ф (%)</th>
<th>K 10^-12</th>
<th>C 10^3</th>
<th>k 10^-3</th>
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This study simulates thermally-driven fluid flow (fluid convection) using the FLAC3D (Fast Lagrangian Analysis of Continua 3D version) program (Itasca 2012). FLAC3D is an explicit finite difference code designed to simulate the interaction of fluid flow, heat transfer, and deformation (the latter is not considered in this part of our study) in porous media. It has been successfully used to simulate fluid flow and heat transfer in porous media with or without deforming rock masses (e.g., Schaub et al. 2005; Oliver et al. 2006; Cui et al. 2012a; Li et al. 2016, 2017).

The impermeable or ‘no flow’ condition was applied on all the external boundaries of the model except the top boundary, which was open to fluid flow. The fluid pressure within the model was set as hydrostatic, following Chi et al. (2013, 2014). The thermal isolation condition was applied to two sides of the model whereas the top of the model was maintained at 20 °C. The geothermal gradient was fixed at 35 °C/km (Pagel 1975). The present models follow the hypothesis of deep burial (5 km depth, Pagel 1975); supplementary modelling dealing with the hypothesis of shallow burial (2 km depth, Chi et al. 2015) is being conducted.

### 3 Modelling results and discussion

In scenario 1, characterized by a flat unconformity surface and homogeneous lithology, eight convection cells were developed in the sandstone. In scenario 2 (uniform
basement lithology with a topographic high), the modelling results show eight convection cells at the steady-state, similar to the previous model; the downwelling flow was shifted to be above the basement high.

The basinal fluid flow appears to concentrate at the gentle slope of the basement high, as represented by the accumulation of flow arrows on one side (the arrows and their size represent the fluid flow and fluid velocity respectively) (Figures 1b and c).

In scenario 3 (with varied basement lithology), the number of convection cells decreased to four instead of eight in the previous scenarios. Fluid flow is still downward above the basement high and concentrates on one side (Figure 1d).

In scenario 4 (insertion of basement faults into the previous scenario), the number of convection cells increased to six within the sandstone. In addition, the basinal fluid flow switched to an upwelling flow rather than downwelling flow above the basement high, where the basement faults are inserted, as basement fluids are discharged to the basin through the basement faults. Six of the seven basement faults show egress flow, whereas one fault shows ingress flow (Figure 1e). A supplementary model with basement faults but without unconformity topography results in egress flow in all the faults, suggesting that the unconformity topography may have influenced the fluid flow in the basement faults.

In scenario 5 (with basement faults extended into the sandstone above the basement high), the number of convection cells increased to eight again, with fluid flow characterized by upwelling flow above the basement high. The increase in the number of convection cells might be related to the increase in the volume of discharged basement fluids into the basin through the basement faults. Fluid flow appears to concentrate along the extended faults as well as at their intersections with the unconformity (Figure 1f). The fluid flow pattern within the basement faults is similar to that in the previous scenario, i.e., egress flow in six faults and ingress flow in one fault (Figure 1f).

4 Significance for localization of uranium mineralization

At the initiation of this study, four geological factors were suspected to have possibly affected the fluid flow related to mineralization at Cigar Lake: i) a topographic high of the unconformity surface, ii) variation in lithology of basement rock, iii) basement faults, and iv) extended faults. The numerical modelling results (scenarios 1, 2, and 3) suggest that the unconformity profile and/or variation in basement lithology have no significant effect on the fluid flow patterns. In particular, positive topography of the unconformity surface or relatively heat-conductive lithologies (such as graphitic pelitic gneiss and granitoid) in the basement alone seem to be unable to provide a locus for upward fluid flow, as has been interpreted for the formation of the Cigar Lake deposit.

On the other hand, development of high-permeability zones (faults) in the basement (scenario 4) appears to significantly affect the fluid flow patterns. The basement faults may have played a role as fluid conduits and this may have enhanced the heat anomaly, causing an overall strong egress fluid flow responsible for the formation of the Cigar Lake deposit. Scenario 5 demonstrates that the presence of extended faults above the basement high strengthens the upwelling flow. The basement faults may have also been involved in forming a structural trap by accumulating both basinal and basement fluids in two sites: i) within the extended faults, and ii) in the area where the extended faults cut one another as well as the unconformity surface. This may have contributed to relatively higher fluid flux, and hence mineralization potential, in these areas. Overall, the results of this study emphasize the importance of the presence of both basement and extended faults in localizing egress fluid flow, and thus are important in the metallogenesis of the Cigar Lake uranium deposit.

Acknowledgements

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The Kiggavik-Andrew Lake structural trend uranium deposits: An overview

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Abstract. The Thelon Basin, Nunavut, Canada, shares many similarities with the U-producing Athabasca Basin in Saskatchewan. The NE-SW Kiggavik-Andrew Lake structural trend (KALST) is ~30 km long, located near the north-eastern edge of the Thelon Basin and contains several U deposits and showings. It has been suggested that these U deposits are unconformity-related, similar to the deposits from the Athabasca Basin. Here we provide an overview of the KALST deposits and compare some of their characteristics to the more extensively studied unconformity-related U deposits from the Athabasca Basin.

The KALST deposits have U mineralization and alteration styles similar to the Athabasca Basin deposits, especially the basement hosted deposits. The KALST deposits formed from 200°C fluids, and the U-bearing minerals have U-Pb ages from ~1500 Ma to ~500 Ma and bell-shaped REE patterns. Alteration minerals have Ar-Ar ages from ~1600 Ma to ~1100 Ma. These features are similar to the Athabasca Basin deposits. The isotopic composition of the fluids associated with the KALST deposits have low $\delta^{18}O$ and $\delta^D$ values (-1‰ to +8‰, and -130‰ to -40‰, respectively) and the deposits have been significantly impacted by numerous post depositional fluid events that have altered the U minerals to coffinite, boltwoodite, and uranophane.

1 Introduction

Sedimentary basins are host to some of the largest (e.g., Olympic Dam, Australia) and richest (e.g., Athabasca Basin, Canada) U resources in the world. Uranium mineralizing processes are generally associated with complex hydrothermal systems that involved repeated fault slip and fluid flow along major lithospheric structural features. Determining the sources of fluid and U in these deposits remains uncertain. Consequently, understanding fluid movement through structures within these terrains and the source of U is of great importance for mineral exploration.

Proterozoic sedimentary basins contain approximately 30% of the world’s U resource, and host unconformity-related U deposits (Nash et al. 1981; Dahlkamp 1993; Fayek 2013). These Proterozoic unconformity-related deposits are associated with major structures and unconformities between Archean-Paleoproterozoic metamorphosed basement rocks and overlying Paleo-Mesoproterozoic sandstone units in marginal or intracratonic basins. They provide a natural laboratory to study the effects of tectonics and sources of fluids on mineral deposit formation.

There are two principal sub-types of deposits in the Athabasca, McArthur and Thelon basins; (1) unconformity-contact deposits where large clay mineral alteration halos are associated with the main ore-body, which is mostly hosted by the Paleo-Mesoproterozoic sandstone units; commonly called egress-style unconformity-related deposits (e.g., Cigar Lake, Collins Bay) (Quirt 2003; Jefferson et al. 2007; Fayek 2013). Most of the ore bodies have root-like extensions into the basement, and mineralization can extend into the sandstone cover along breccias and fault zones forming “perched mineralization”, and (2) breccia or fractured-controlled deposits where the main ore-body is hosted in the metamorphic basement rocks; commonly called ingress-style unconformity-related deposits (e.g., Rabbit Lake, Eagle Point, Sue C, and Millennium, Athabasca Basin, Canada; Kintyre, Jabiluka, and Ranger, Australia; Kiggavik, Bong, End, and Andrew Lake, Thelon Basin, Canada). Disseminated and vein uraninite/pitchblende occupies fractures and breccia matrix, but may also replace the host rock. The diagenetic-hydrothermal metallogenetic model attributes the precipitation of U minerals to redox reactions, and the formation of associated clay alteration minerals to hydrolytic acid-base reactions (Hoeve and Sibbald 1978; Hoeve and Quirt 1984, 1987).

The Thelon Basin is similar in size, geology, and geometry to the Athabasca Basin. It has been suggested that U deposits located adjacent to the Thelon Basin, in the Kiggavik region, are also unconformity-related deposits (Miller and LeCheminant 1985; Fuchs et al. 1986; Weyer et al. 1987; Fredrich et al. 1989; Fuchs and Hilger 1989). However, while the Athabasca Basin has been thoroughly
studied in terms of its stratigraphic, sedimentological, diagenetic, fluid, and metamorphic histories (e.g., Hoeve and Sibbald 1978; Hoeve and Quirt 1987; Kotzer and Kyser 1995; Fayek and Kyser 1997; Alexandre et al. 2005; Ramaekers et al. 2007; Cloutier et al. 2009; Mercadier et al. 2012; Richard et al. 2013; Sheahan et al. 2016), the Thelon Basin has a much smaller body of literature documenting such characteristics.

Most previous publications on the Thelon Basin have focused on understanding the sedimentology and lithostratigraphy (e.g., Donaldson 1965; Jackson et al. 1984; Gall et al. 1992; Rainbird et al. 2003), sequence stratigraphy and hydrostratigraphy (Hiatt et al. 2003; Rainbird et al. 2003; Palmer et al. 2004; Beyer et al. 2011), and the diagenetic fluid history (Renac et al. 2002; Hiatt et al. 2010; Davis et al. 2011). Fewer studies have focused on the U metallogeny and genesis of the Kiggavik-Andrew Lake trend deposits (e.g., Miller and LeCheminant 1985; Weyer et al. 1987; Fuchs and Hilger 1989; Miller et al. 1989; Riegler et al. 2014; Sharpe et al. 2015; Chi et al. 2016).

Historically, U mineralization at Kiggavik has been described as primarily pitchblende, with some alteration to coffinite, and reported U-Pb isotope ages are between 1400 and 1000 Ma. Associated chlorite, hematite, and illite alteration minerals have also been described (e.g., Miller and LeCheminant 1985; Weyer et al. 1987; Friedrich et al. 1989) and K-Ar ages of 1358 and 1073 Ma (Weyer, 1992) have been reported for intensely clay-altered samples associated with uraninite. More recent studies have shown that the mineral paragenesis is much more complex, with several stages of U mineralization and remobilization (e.g., Sharpe et al. 2015), and multiple generations of clay mineral alteration (Riegler et al. 2014). As for the Athabasca deposits, these studies have largely attributed the precipitation of U minerals to redox reactions, and the formation of associated clay alteration minerals to hydrolytic acid-base reactions.

Here we present an overview of the U deposits associated with the Kiggavik-Andrew Lake structural trend (KALST). We will compare these deposits to the unconformity-related U deposits from the Athabasca Basin.

2 KALST geology

The dominant lithology that hosts the KALST U deposits is Neoarchean polydeformed and metamorphosed supracrustal rocks: epiclastic rocks of the Snow Island Suite (Johnstone et al. 2016) and Piperedream assemblage metagreywacke of the Woodburn Lake group (Pehrsson et al. 2012). Lesser host rocks include the complex 1.83 and 1.75 Ga Lone Gull granite (Scott et al. 2013), paragneiss of the Marjorie Hills assemblage and intermixed 1.83 Ga Hudson granite and Martell Syenite of the Schultz Lake Intrusive Complex (SLIC) (Miller and Peterson 2015) that structurally overlies the epiclastic rocks and metagreywacke (Tschrhart et al. 2016). All of the deposits in the Kiggavik region are located at the intersections of multiple fault systems trending ENE-WSW (Thelon, Judge Sissons), NE-SW (Andrew Lake), and S-SE (Fuchs et al. 1986; Fuchs and Hilger 1989). These faults are sites of intense brittle deformation and alteration associated with hydrothermal activity. Alteration generally consists of strong bleaching of the host rock, chloritization, illitization and hematitization (Fuchs and Hilger 1989; Riegler et al. 2014; Sharpe et al. 2015).

3 Our approach

Our study includes the three Kiggavik deposit zones (Main, Centre, and East), and the Bong, End, and Andrew Lake deposits. The geological context and samples from the KALST were provided by AREVA Resources Canada (ARC) and the Geological Survey of Canada (GSC). We developed a mineral paragenesis for each deposit, used in used in situ analytical techniques to obtain O and H isotopes and calculate the fluid compositions and temperature of U ore formation, and U-Pb isotopic data to obtain the ages of U mineralization. We also analysed rare earth element (REE) concentrations in U minerals. These data allow us to compare the KALST U deposits to the Athabasca Basin U deposits.

4 Results and discussion

Overall, the quartzofeldspathic metasediments that host the U deposits along the KALST have undergone retrograde metamorphism and contain chlorite after biotite, coarse-grained muscovite, and pyrite. Uranium mineralization generally occurs in three textural forms: (1) disseminated grains, (2) along fractures (vein-style), and (3) along mini roll-fronts. Uranium minerals include uraninite, coffinite, boltwoodite, and uranophane. Uraninite appears to be the only primary U mineral. Illite is the dominant clay mineral associated with U mineralization, with lesser sudoite. Organic matter is only occasionally associated with U mineralization.

Using the O and H isotopic composition of clay minerals associated with U mineralization and the O isotopic composition of uraninite, the temperature of formation for the KALST deposits was calculated to be ~200°C. This is similar to the temperatures of formation calculated for the Athabasca U deposits (e.g., Kotzer and Kyser 1995).

The calculated isotopic composition of the fluids associated with the KALST deposits have δ18O and δD values between -1% and +8‰, and -130‰ and -40‰, respectively. These values are slightly lower compared to the fluids associated with the Athabasca Basin U deposits, which have values δ18O and δD values between +2‰ and +10‰, and -10‰ and -100‰, respectively (e.g., Sheahan et al. 2016).

U-Pb isotopic ages of U minerals from the KALST deposits broadly group at ~1500 Ma, ~1300 Ma, ~1100 Ma, ~1000 Ma, ~750 Ma, ~500 Ma and <1 Ma. Ar-Ar ages
from muscovite are 1800 Ma and 1600 Ma, whereas illite gives ages of ~1500 Ma, 1300 Ma, 1100 Ma, and 1000 Ma. The strong correlation between the U-Pb and Ar-Ar isotopic ages of U and associated clay minerals suggest that there were major tectonic or thermal events that reactivated the faults along the KALST at various times, which triggered fluid events that affected the U deposits.

These ages correlate with several far- and near-field tectonic events and are similar to the ages obtained for U and alteration minerals from the Athabasca Basin (e.g., Sharp et al. 2015; Sheahan et al. 2016).

Rare earth element patterns in U minerals from the KALST are bell-shaped, which is typical of unconformity-related deposits (Mercadier et al. 2011).

5 Conclusions

The U deposits of the KALST have characteristics similar to the unconformity-related U deposits of the Athabasca Basin. Some of these characteristics include mineral textures and alteration styles, temperature of formation, ages, and REE patterns. However, the fluid composition is slightly different and the deposits have been significantly impacted by post-depositional fluid events.

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Structural controls on uranium mineralization at the Kiggavik Project (NE Thelon area, Canada)

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Abstract. This paper deciphers the complex multiphase fracture network associated with uranium mineralization of the unconformity-related uranium deposits in the Kiggavik area. It combines field work, drill-core logging and sampling, and macro- to micro- petro-structural analyses. Key results from this study show that uranium bearing ENE-WSW and NE-SW fracture systems formed early during the Thelon and Trans-Hudsonian orogenies and were mineralized in three stages with distinctive fracture patterns, alteration and mineralization types. The first stage mineralization, inferred from a magmatic source, is related to micro-brecciation and is crosscut by intense quartz brecciation and veining (silica breccia) that predated formation of the Thelon basin. The second stage of mineralization (fluids of unconstrained origin) is coeval with the formation and reactivation of the E-W trending faults in the area, locally reusing the previously formed quartz veins of the silica breccia event. The third stage of uranium enrichment and reconcentration occurred with post-Thelon NE-SW compression and reactivation of the NE-SW and E-W trending faults, and is inferred to form from oxidizing basal brines circulating on trans-tensional fault zones. Later sinistral offset by NNW-SSE faults and uranium remobilization by meteoric fluids gave uranium ore bodies their final architecture.

1 Introduction and geologic framework

Uranium deposits in the Kiggavik area, located 80km west of Baker Lake in Nunavut Territories (Canada) (Fig. 1), are commonly described as unconformity-related (Friedrich et al. 1989). A noteworthy role of faults as fluid conduits through impermeable basement metamorphic rocks or as traps is observed in the formation and location of ore bodies that are otherwise hosted by a variety of lithologies (Fig. 1). However, the tectonic framework remains poorly understood due to the lack of outcrops, the complex fracture pattern that results from a long lasting polyphase tectonic history (~2.00-1.27 Ga), and strong fluid-related alteration that often obliterates fracture and fault attributes in exploration drill-hole cores.

This work establishes the structural controls of the uranium mineralization at Kiggavik, with focus on the recently discovered Contact and 85W prospects (Fig. 1). Uranium deposits in Kiggavik are hosted in metamorphosed sedimentary, volcanic/plutonic rocks (ca. 2.7 to 2.5 Ga) of the Amer and Ketyet River groups and in granitic gneiss of Archean age (Fig. 1). These rocks are intruded by the Hudson (ca. 1.84 Ga) and Nueltin (ca. 1.72 Ga) intrusions, and the Mackenzie diabase dyke system considered to be the last tectonic event in the region (ca. 1.27 Ga). In Kiggavik, dextral-oblique collisional tectonics occurred as the Slave foreland province was subducted beneath the Rae hinterland to the east (Thelon-Taltson orogeny, ca. 2.0-1.9 Ga; Hoffman, 1988). The Trans-Hudsonian orogeny (ca. 2.0-1.8 Ga) overprinted and reworked the inherited tectono-metamorphic signature. The region was then marked by extensional to transtensional tectonics leading to the development of the Baker Lake and Wharton basins (Baker Lake and Wharton groups at ca. 1.85-167 Ga). These tectonic events were followed by thermal relaxation and normal faulting that gave birth to the intracratonic Thelon basin (ca. 1.67-1.54 Ga) which detrital rocks that unconformably overlie the metamorphic basement.

The Thelon, Judge Sissons and Andrew Lake regional faults of the Kiggavik area (Fig. 1) are still poorly known. They are inferred to be formed through this complex tectonic history before the formation of the Thelon basin. These faults were likely active from ca. 1.80-1.27 Ga and later reactivated under successive far-field tectonic stresses (Hadlari and Rainbird 2011).

2 Methods

Re-filtering and re-interpretation of ground magnetic and VLF (Very-Low-Frequency) maps with field observations and structural analysis of oriented data from drill-cores allow for accurately depicting the fracture network. Acoustic televiewer probing provided better definition of selected fracture and fault zones. Macro- and micro-
petrostructural analyses using optical, Scanning Electron and cathodo-luminescence microscopy helped to define the textural, geometrical and chronological relationships between fluid-related alteration, mineralization and fractures. Oriented data were processed with Dips (Roc Science) software.

The most significant and key structural controls (I to V, Fig. 2) for all the fracture phases identified (12) are presented in the following sections from the oldest to the youngest events (Fig. 2).

3 Structural controls on U-bearing fluids

3.1 Pre-Thelon micro-fracturing and first stage of uranium mineralization (I)

A first stage of uranium mineralization is observed at Kiggavik Main, Bong, End and Andrew Lake deposits (Fig. 1). Mineralization is characterized by fine micro-fracturing to micro-brecciation of the host rock that can locally be foliation-parallel (Fig. 2). Monomictic mm to cm-scale clasts display dissolved boundaries. Alteration of the host rock is weak to non-observable and is characterized by bleaching (destabilization of iron oxides) along with incipient illitization around fractures.

At the micro-scale, fractures display small steps and perpendicular micro-stylolites. Fractures are filled with Fe-rich chlorite, anatase, sulphurs, uraniferous-titanate and pitchblende. This micro-fracturing is usually observed in the vicinity of granitic intrusions at Kiggavik, and has been locally observed associated to granitic veins. This mineralization is cross-cut or overprinted by quartz-rich hydrothermal breccia (II) and so far is interpreted as being the oldest recognized mineralization stage predating the formation of the Thelon basin, inferred from a magmatic origin. This early brecciation and mineralization stage likely prepared the host-rock for later fluid circulation and new uranium mineralization.

3.2 Hydrothermal quartz breccia (II)

A major hydrothermal quartz-rich brecciation and veining event is recognized at Kiggavik along the Judge Sissons and Andrew Lake faults (Figs. 2 and 3). A pervasive deep red hematization is linked to this fracturing event. The breccia displays abundant pervasively hematized heterolithic clasts from various hosting rocks, sealed by massive quartz. Breccia and veins crosscut and/or silicify previous features. At the Contact prospect, the main m-thick breccia core trends NE consistent with the main strike of the Andrew Lake fault (Fig. 3).

The so-called quartz or silica breccia played a major role in the Contact prospect in terms of fracture accommodation and fluid compartmentalization, since most fractures, alteration and mineralization occurred within its hanging wall. Accordingly, at Andrew Lake,
End, Bong and Kiggavik deposits where silica brecciation is less intense, ore bodies are found both above and below the silica breccia fault zone.

The silica breccia formation has been correlated with the deposition of the Baker and Pre-Thelon Wharton groups (Hadlari and Rainbird 2011). The related dextral movement along the Judge Sissons and Andrew Lake faults, deduced from the offset of the Hudsonian intrusions (Fig. 1), therefore predates the hydrothermal silica event. It is inferred that the quartz-rich breccia formed synchronously with the emplacement of rhyolitic flows of the Pitz formation and the associated Nueltin granite intrusions of the Wharton group, in response to a likely NNW extensional stress. The silica breccia is capped by the Thelon formation, hence predates its deposition.

3.3 Formation and reactivation of E-W fractures/faults and second stage of uranium mineralization (III)

The second stage of mineralization occurred in cataclastic faults and in associated fractures coated with uranium and sulphurs, and locally in re-utilized quartz veins inherited from the quartz-rich brecciation event (Figs. 2 and 3). Mineralized micro-fractures cut orthogonally across former quartz veins and are usually restricted to the quartz veins with rare propagation into the host rock. Macro- and micro-structural cross-cutting relationships support that this fracturing event postdates the hydrothermal quartz breccia event.

Ore minerals related to this second mineralization stage are mostly represented by colloform and xenomorphic pitchblende and coffinite, uraniferous titanate, titanium-oxides with pitchblende micro-inclusions and iron sulphide, mainly pyrite but also chalcopyrite, bravoite and illite. Mineralization is observed along the boundaries of the quartz veins, associated with quartz dissolution. Rare occurrences of native bismuth and unidentified Ni-As xenomorphic minerals have been also observed.

Oriented data indicate that the second stage of uranium mineralization occurred along east-west oriented faults and along re-opened quartz veins from the previous hydrothermal stage (Fig. 3).

3.4 Oxidizing fracturing event and third stage of uranium mineralization (IV)

The third stage of uranium mineralization is associated with brown to brick red oxidation and clay alteration of the host rock (Figs. 2 and 3). It often appears as pervasive and involving greater volumes of rocks compared to the second mineralization stage. Nevertheless, in some holes and samples, it appears clearly driven by faults and fractures, and often re-uses previous quartz vein generations. Remnant minerals like iron sulphide, micro-
grains of pitchblende of primary mineralization are common, together with spherulitic pitchblende with iron-removal halos, and disseminated pitchblende grains. Pitchblende is observed associated with/or in impregnation of clay minerals such as illite and sudoite. Sudoite especially fingerprints the circulation of Mg-rich brines in the Athabasca Basin uranium deposits (Renac et al. 2002). This supports downward flow of oxidizing basal diagenetic-hydrothermal fluids at this stage, leading to new uranium mineralization and re-concentration (Figs. 2 and 3).

This stage is linked to the post-Thelon reactivation of the pre-existing fracture networks along the Andrew Lake and Judge Sissons faults (Fig. 3). Regional kinematic data indicate sinistral-reverse reactivation of the Judge Sissons fault under a roughly NE-SW compression, and dextral strike-slip reactivation of the Andrew Lake fault. The Contact, Andrew, End, and Kiggavik deposits appear to be located in transtensional jogs along the reactivated pre-existing faults.

3.5 Post mineralization faulting stages (V)

At Contact or 85W, several distinctive structures are observed in barren zones or cutting across the uranium mineralization stage 3. These faults are characterized by strong to complete clay alteration (illitization) of the host rock. Clasts of pitchblende with various clay generations (illite and sudoite) are observed within fault zones, and are interpreted to be relics from the third mineralization stage.

Oriented data indicate that this stage is linked to a NNW-SSE compression reactivating NNW-SSE and NW-SE faults as sinistral and dextral strike-slip faults, with extensional fault jogs providing favourable conditions for fluid circulation and alteration. The sinistral offset of the ore bodies observed in various deposits (i.e. End or Main Zone) by NNW faults can be linked to this tectonic stage, along with strong clay alteration of the host rock.

NNW-trending faults and ore deposits were ultimately cut by the Mackenzie dykes (1.27Ga). After 1.27 Ga, the fracture/fault network was only weakly reactivated under changing far-field stress. Meteoric water circulated through the fracture system and led to local remobilization and re-concentration of uranium oxides along redox fronts (Fig. 2). Still later, spotty to widespread bleaching of the host rock destabilized and removed iron bearing oxides.

4 Discussion and conclusions

Petrological, textual and structural studies allowed for the characterization of the nature and sequence of the successive tectonic, alteration and mineralizing episodes that occurred and controlled the mineralization in the Kiggavik Uranium Project. This work shows that in the Kiggavik area the uranium mineralization deposition was controlled by faults and related fractures that formed and were reactivated several times in the brittle tectonic domain, but also with different types of fluids and P-T conditions.

The first stage of uranium mineralization predates the development of the Thelon basin, and appears to be the oldest uranium enrichment of the host rock, probably intrusion-related by analogy to the Nueltin intrusions timing. Oxygen isotopes studies on illite synchronous to pitchblende at Main Zone and Bong deposits indicate that fluids were of meteoric-hydrothermal (Sharpe et al. 2015) to magmatic hydrothermal (Friedrich et al. 1989) origin. The Nueltin granite (observed at Kiggavik) which is associated with a more fractionated melt and which displays enrichment in U, Th and REE compared to the Hudson intrusions (Scott et al. 2015) is inferred to be the source of the first mineralization at Kiggavik. Complementary geochemical studies are in progress. Later, syn-to post Thelon reactivation of fault zones generated further uranium enrichment and re-concentration (mineralization stages 2 and 3). Finally, lately reactivated NW and NNW faults offset orebodies and drove fluids that strongly altered the host-rock. Late meteoric water circulation locally remobilized and re-concentrated uranium oxides along redox fronts.

This study emphasizes (1) the key role played by fractures and faults on fluid circulation within the basement at various times, (2) how macro- to micro-structural studies are essential to precisely decipher the fracture pattern, its relative chronology and its relationships with alteration and mineralization. (3) It also demonstrates that uranium deposits are more complicated that initially proposed as unconformity-related, the similarities with Athabasca uranium deposits are not as numerous as supposed.

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References

Structural analysis, paragenesis, and preliminary geochronology of the Arrow uranium deposit, Athabasca Basin, northern Saskatchewan, Canada: Implications for controls on mineralization

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Abstract. The Athabasca Basin in northern Saskatchewan hosts the world’s highest-grade uranium deposits. These deposits are commonly spatially associated with structural zones that have undergone multiple episodes of brittle reactivation. This study examines the relationship between the ductile framework and brittle reactivation of structures, mineral paragenesis, and uranium mineralization at the Arrow deposit. Through this study, the structural system at Arrow has been interpreted as a strike-slip dominated fault system of complex Riedel-style geometry. The Arrow system originally developed along sub-vertical, northeast-southwest-trending chloritic-graphitic shear zones. Detailed analysis of the major structural trends suggests a predominantly sinistral Riedel-type system, where multiple brittle reactivations of primary shear fractures have occurred, allowing for migration of hydrothermal fluids, alteration of host rocks, and precipitation of uranium mineralization. Semi-massive to massive uraninite is spatially associated with hematite-limonite alteration, chlorite alteration, and late carbonate veins, whereas disseminated uraninite is present in clay/chlorite/muscovite-rich zones. Sulphides and graphite are pre-, syn-, and post-mineralization, whereas dravitic structures are dominantly post-mineralization. The relative timing and spatial association of structural events/re-activations, alteration, and mineralization has been constrained, which is critical to understanding the mineralized system, and provides the framework for the ongoing determinations of the ages of mineralizing events.

1 Introduction

The Arrow uranium deposit is a significant recent discovery in the southwestern Athabasca Basin, and is the flagship discovery on NexGen Energy’s Rook I property. It is considered to be a structurally-controlled, unconformity-associated deposit, entirely hosted by basement rocks below the Athabasca Basin. The southwestern Athabasca Basin has been the focus of intense exploration activity in the last few years; however, the characteristics and setting of uranium mineralization in the area are poorly understood. This study is the first comprehensive analysis of the structural and paragenetic relationships of a uranium deposit in this region, and aims to define constraints on the origin and evolution of basement-hosted unconformity-associated uranium deposits across the Athabasca Basin.

1.1 Regional and local geology

The Rook I property is situated in the Churchill Province of the Precambrian Shield (Fig. 1), which is divided into the Rae Province to the west and the Hearne Province to the east, separated by the Snowbird Tectonic Zone (STZ). Historically, the basement rocks south of the Athabasca Basin and west of the Virgin River shear zone (VRSZ), a segment of the STZ, have been termed the Lloyd Domain and considered to be Archean in age (Lewry and Sibbald, 1977). However, recent mapping and geochronology in the Lloyd Domain suggest that the rocks, and their metamorphic and structural history, may be correlative with those present within the Paleoproterozoic Taltson magmatic zone (e.g., Card et al. 2014).

The Lloyd domain underwent multiple high-grade metamorphic and deformational episodes between approximately 1.95 to 1.85 Ga (Card et al. 2008). The composite S1/S2 foliation was deformed by upright NNE- to NE-trending folds (F3) with sub-vertical axial planes. Younger F4 cross folds are subtle, striking NW with axial surfaces near orthogonal to those of F3. The VRSZ contains outcrop evidence for multiple displacement episodes under ductile, brittle-ductile, and brittle conditions. Brittle reactivation of the VRSZ along the Dufferin Lake Fault played a role in the formation of uranium deposits at the base of the Athabasca Basin along this trend (Card et al. 2007; Reid et al. 2014).

In the Rook I project area, the Lloyd Domain is dominated by NNE- to ENE-trending, sub-vertical oriented, granodiorite orthogneiss intercalated with Paleoproterozoic-aged metasedimentary psammitic to pelitic gneiss, often garnetiferous and graphitic, with lesser quartzite, amphibolite and ultramafic gneiss. Distinct blue quartz is common throughout all metamorphic rock types on the property. Overall, the dominant basement lithologies encountered within the Arrow zone (Fig. 1) are variably silicified quartz-garnet-biotite (+/- graphite) semi-pelite gneiss and orthogneisses consisting of quartz monzodioritic to quartz dioritic gneiss with subordinate granodioritic and tonalitic gneiss. Minor rock types include mafic-rich amphibolite and pyroxenite (“garnetite”), and local porphyroblastic feldspar and quartz-rich in situ anatectic pegmatites (Card et al. 2016).
Graphite-bearing, quartz, chlorite, and biotite-bearing mylonites (named A1 to A5 Shears within the Arrow zone) correlate with interpreted geophysical electromagnetic conductors across the property. Flat-lying mid-Proterozoic Athabasca sandstones unconformably overlie the basement rocks in the northern portion of the property (Gittings 1980). The Athabasca sandstones are poorly sorted, medium- to coarse-grained, quartz arenite to conglomeratic sedimentary layers of the Read and Bird Formations of the Manitou Falls Group (Bosman and Ramaekers 2015). In the southwestern part of the property, the basement rocks are unconformably overlain by sandstones of the Devonian La Loche Formation which themselves are overlain by black siltstones, mudstones and shales, with local coal seams, of the Cretaceous Mannville Group.

2 Structural analysis

The methodology for structural analysis includes interpretations of individual structural measurements from oriented drill holes obtained during drill programs up to the end of 2016. Structural measurements include alpha and beta angles of planar structures including foliations, fractures, veins, shears, mylonites, breccias, cataclasites, and fault gouges, as well as gamma angles of linear structures including slickenslides and ductile lineations. The working data set is comprised of more than 18,000 measurements taken from a minimum of two consecutive three meter lengths of oriented drill core that have undergone beta rotation correction and confidence level assignment for quality assurance and quality control (QAQC). True orientations are then determined and stereographically assessed. Drill hole orientation sampling

Figure 1. Arrow plan map showing simplified basement geology and resource projected to surface, interpreted graphitic structures, and location of the Arrow deposit with respect to the Athabasca Basin.
bias is accounted for through the application of the Terzaghi weighting method, involving the application of a correction factor to each feature with subsequent stereographical analysis on the weighted dataset (Terzaghi 1965). All measurements of planar features have undergone Terzaghi weighting to account for sampling bias, adding another layer of QAQC.

In the formation of a structural system such as that hosting the Arrow deposit, the regional ductile structural framework can act as a limiting or accommodating factor for subsequent brittle reactivation, fluid movement, and metal deposition. Regional F3 and F4 folds are interpreted to be pervasive through the study area providing the foundation for formation of the Arrow deposit. Because re-folding and fold interference patterns create variability in fold geometry, this can play a role in the spatial formation of zones of dilation (fluid accommodating) and zones of compression (fluid limiting). Despite local variability, stretching and intersection lineations are a useful tool in fold analysis as they preferentially form co-linear to fold axes. Plotting lineation measurements from the Arrow deposit reveals a pattern which resembles the resulting Type 1, dome and basin, fold geometry produced by the F3 and F4 folds. Early ductile to brittle-ductile shear structures (A1-A5) along the limb of a regional F3 fold. More conclusive interpretation of the major structural trends suggests a predominantly sinistral strike-slip fault system of complex Riedel-style geometry, where the primary R-, R'-, P- and P'-shear fractures experienced multiple episodes of brittle structural reactivation and fluid migration. Integration of subsequent structural interpretations in three dimensions, as well as determination of relative alteration mineral paragenesis, provides corroborating evidence for the deposit model in terms of timing, and spatial association between fault linkages/concentrations and structural controls on mineralization.

3 Mineral paragenesis

The structural evolution of Arrow can be related to episodes of uranium mineralization and extensive and varied hydrothermal alteration products. Paragenetic relationships have been determined through examination of drill core and 41 polished thin sections. At least four phases of uranium mineralization have been identified, including early euhedral and brecciated uraninite (Fig. 3), remobilized uraninite, and late uranophane and coffinite. The most prominent alteration type observed is partial to complete sericitization of all pre-existing minerals, suggesting the importance of K-bearing fluids. Sericite (muscovite) dominantly forms as alteration of feldspars and pyroxene, but in extreme cases may alter all minerals present, including quartz. Sericite grains tend to be coarse and often obliterate any original mineralogy and texture. Chlorite is not as common or intense as sericite; however, there is evidence for multiple episodes of chloritization. Retrograde metamorphic chlorite commonly alters pre-
existing biotite and garnet, whereas later episodes of chlorite form as cross-cutting fracture linings or as small veins. Although commonly observed proximal to and within mineralized zones, dravite forms either as late veins or larger hydraulic breccias that crosscut all pre-existing minerals (including uraninite). Crosscutting calcite veins are frequently observed throughout the Arrow deposit, and are associated with uraniferous minerals as crosscutting stockworks or mineralized veins. Sulphide mineralization within the Arrow system consists largely of pyrite, with subordinate pyrrhotite, pentlandite, galena, and chalcopyrite. Sulphides are hosted largely in veins, commonly with quartz and/or carbonate, crosscutting the dominant foliation and late alteration phases such as dravite. Hematite and limonite alteration is variable, occurring as discrete stains intimately associated with high-grade uranium mineralization overprinting earlier sericite alteration, or contemporaneous with sericitization, and as groundmass alteration of brittle re-activated quartz-clastic breccias. Paragenesis has been integrated with detailed structural analysis and will be used as the framework for the ongoing determinations of the ages of mineralizing events.

Figure 3. Electron backscatter image of early euhedral and brecciated uraninite from the A2 Shear. #B00066, AR-16-63c2, 531.0 m.

4 Preliminary geochronology

The basement rocks under the southwestern Athabasca Basin were subjected to multiple deformational and metamorphic events. The age of the earliest metamorphic event is unclear because the oldest rocks, the Careen Lake Group, have no reliable age constraints (Card et al. 2007). The brittle-reactivated shears within the Arrow deposit, akin to other fault zones west of the VRSZ, are likely related to reactivation of major shear zones in the region during the Taltson (1.9 Ga) and Hudsonian (1.8 Ga) orogenies (Card et al. 2014). These deformational events are likely contributors to the early structural and fluid interaction within the Arrow deposit, and ongoing determination of chemical and isotopic ages of uranium mineralization at Arrow will further constrain the evolutionary timeline of the deposit.

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Lithostratigraphic and structural controls of uranium mineralization in the Kiggavik East Zone, Centre Zone, and Main Zone deposits, north-central Rae Subprovince, Nunanuit, Canada

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Abstract. The Kiggavik uranium deposits are hosted in highly deformed Archean and Paleoproterozoic basement rocks marginal to and underlying the Thelon Basin of the north-central Rae Subprovince of the Canadian Shield. These basement rocks comprise three major unconformity-bounded sequences, ~2.71 Ga metagreywacke of the Woodburn Lake group (WLg), ~2.6 Ga felsic volcanogenic rocks of the Snow Island suite (SIS), and <2.3 Ga orthoquartzites of the Ketyet River group (KRg). All units are strongly foliated and form a shallowly north-dipping sequence that is truncated by the Thelon fault. Early ductile deformation involved tight to isoclinal recumbent/sheath-style folding, with inferred thrusting and translation of SIS-suite rocks and the KRg quartzites over older, more rigid Pipedream metagreywacke. Subsequent brittle deformation is manifested by a Riedel shear system developed via dextral strike-slip displacement along the Thelon Fault. Uranium mineralization in the Main-Centre zones was associated with infiltration of fluids along steeply dipping D- and P-shears. While some fluids permeated the Pipedream greywacke below, most were focused into the weaker and more porous-permeable SIS volcanogenic rocks above. Uranium was likely sourced from intrusive Hudson (~1.83 Ga) and Kivalliq (1.76 Ga) granites, along with highly differentiated SIS felsic volcanic rocks. Fold-thrust repeated quartzites of the KRg were significant barriers to fluid flow.

1 Introduction, location and purpose

The Kiggavik uranium deposits are located 80 km west of Baker Lake, Nunavut, in the north-central Rae Subprovince of the western Churchill Province, Canadian Shield (Fig. 1). The property is primarily owned by and operated by Areva Resources Canada and consists of numerous promising deposits and prospects hosted in Archean and Paleoproterozoic rocks marginal to and underlying the Thelon Basin.

Despite recent work by the Geological Survey of Canada (GSC), the lithostratigraphic relations of the metasedimentary and volcanogenic rocks hosting the Kiggavik deposits remain poorly understood. In addition, while the structural geology is known to have influenced the localization of uranium in most showings, the exact nature of the structures involved, including the relative role of early ductile versus later brittle deformation, is poorly constrained. Accordingly, this field-based study was undertaken to: 1) better determine the lithostratigraphic and overall structural relationships of rocks hosting Kiggavik East, Main and Centre Zone deposits; and 2) better establish the nature, sequence and kinematics of all structures and their relationship to uranium mineralization.

2 Regional geology

Rocks of the north-central Rae Subprovince in the vicinity of the Kiggavik property record a protracted tectonic history spanning over one billion years. As displayed in Fig. 2, the oldest rocks in the area are Meso- to Neoarchean (ca. 2.87 Ga) granitoid orthogneisses. These rocks are unconformably overlain by 2.73-2.68 Ga supracrustal rocks of the Woodburn Lake group (WLg) that
comprise as many as six aerially discrete assemblages (Jefferson et al. 2014). In the Kiggavik area, the WLg is represented by the ~2.71 Ga Pipedream assemblage of metagreywacke turbidites. Regionally, rocks of the WLg, including the Pipedream greywacke, are unconformably overlain by a suite of 2.63-2.58 Ga felsic volcanogenic rocks termed the Snow Island Suite (SIS) (Peterson et al. 2015). At Kiggavik, the SIS is represented by metarhyolite and epiclastic rocks. The SIS is in turn unconformably overlain by another major supracrustal package, the Paleoproterozoic Ketyet River group (KRg), regionally correclusive with the Amer group to the north (Rainbird et al. 2010; Jefferson et al. in press). At Kiggavik the most prominent unit is an orthoquartzite of basal sequence (PS1) of the Amer-Ketyet, with an inferred age of 2.3 to 2.15 Ga. All of these rocks are overlain by the Dubawnt Supergroup comprising the Baker Lake, Wharton and Barrensland groups, the latter two being prominent in the Thelon Basin.

**Figure 2.** Lithostratigraphic column for the Kiggavik area modified from Jefferson et al. (2011, in press).

The sub-Dubawnt basement rocks at Kiggavik have undergone at least four phases of ductile deformation and are metamorphosed to lower-middle amphibolite facies (McEwan 2012; Pehrsson et al. 2013). Archean effects have largely been obliterated by intense Paleoproterozoic deformation attributed to the Snowbird and Trans-Hudsonian orogenesis. Peak metamorphism at ~1.83 Ga (Pehrsson et al. 2013) was followed by uplift and exhumation. Major strike-slip and extensional brittle faulting ensued, accompanied by subsidence, felsic magmatism (~1.83 Ga Hudson and ~1.76 Ga Kivalliq igneous suites (Scott et al. 2015)) and intracratonic (Baker Lake, Thelon) basin formation (Jefferson et al. 2014).

**3 Local geology and lithostratigraphy**

As shown in Fig. 3, the basement rocks marginal to the Thelon Basin at Kiggavik include three main tectonostratigraphic packages. The oldest and structurally lowermost package comprises ~2.71 metagreywacke (Pipedream assemblage) of the WLg. This is succeeded upward by ~2.6 Ga volcanogenic rocks of the SIS which are intercalated with <2.3 Ga orthoquartzites of the KRg. In the Kiggavik East area these units form a gently north-dipping (10-20°) sequence that is truncated by the Thelon fault to the north.

An important finding of this study is that the SIS is more extensive than previously thought. In particular, a distinctive package of ‘epiclastic’ volcanogenic rocks, part of the Pukiq Lake formation (Jefferson et al. in press), was recognized at structurally higher levels (Fig. 3) where it is interlayered with more readily identifiable units of SIS quartz porphyritic metarhyolite and KRg quartzite. The epiclastic unit comprises a heterogeneous assemblage of interbedded metavolcanoclastic and metagreywacke-metapelitite with local tuffaceous horizons.

**Figure 3.** Geological map of the study area (top) and related strike-perpendicular cross-section in the Kiggavik East area (bottom), based on surface and drill hole data (line of section shown in red).

**4 Structural geology**

**4.1 Ductile structures**

All of rocks in the uniformly north-dipping sequence (Fig. 3) carry a strong penetrative foliation and stretching lineation. In addition, primary bedding is ubiquitously transposed parallel to foliation. Based on the regional stratigraphic relations (Fig. 2), one can infer that, down-section, there are multiple younging direction reversals (Fig. 3). This, coupled with strongly transposed bedding
and highly strained contacts, indicates that the repetitions are tectonic. Overall, and as depicted in Fig. 4, the structural style is consistent with nappe-style folding and thrust repetition, possibly with a décollement along the contact between the more competent Pipedream greywacke and overlying weaker volcanic rocks of the SIS.

The relationship between the stretching lineation and the strike of rocks units (and sub-parallel foliation) across the map area (Fig. 5) provides additional constraints on the style of folding. For example, in the Granite Grid and Bong North areas (Fig. 3) rock units/panels dip to the ENE, and the stretching lineation plunges to the ENE (Fig. 5) whereas in the Kiggavik East and North areas (Fig. 3) rocks units/panels dip to the NW and the stretching lineation plunges to the WSW (Fig. 5). The stretching lineation therefore has a relatively uniform NNE–WSW-trending azimuth but exhibits variable plunges (to the ENE- or WSW). Such a pattern is best explained by the development of non-cylindrical fold hingelines associated with subhorizontal axial surfaces, with the attitude of the latter corresponding to the average attitude of the regional foliation (Fig. 5). It is thus inferred that sheath folds with WSW-verging, ENE-dipping axial surfaces developed with an ENE to WSW mass-transport direction.

Figure 4. Structural hypotheses proposed to explain the configuration of basement rock units at Kiggavik. Analysis of mesoscopic structural data (Fig. 5) strongly support the presence of sheath folds. The black arrow indicates the mass transport direction (WSW) during sheath fold development.

4.2 Brittle structures

The analysis of structural measurements in outcrop and oriented drill core, together with linear features compiled from satellite and geophysical imagery, has identified six major brittle structural trends in the Kiggavik area. The orientations and kinematics of these brittle fault sets are consistent with a Riedel shear system that developed in response to NW–SE-directed compression and related dextral strike-slip motion along the Thelon fault (Fig. 6, top). In this system, the main Thelon-Judge Sissons fault trend of 255° represent D-shears, while subsidiary fault sets with trends of 065°, 110–290° and 145–325° constitute P, R and R’ shears, respectively. Two other major fault sets are the 030–210°-trending Andrew Lake fault and the 350–170° Bathurst faults hosting Mackenzie dykes.

5 Uranium mineralization

Figure 6 shows a plan view map of the geology around the Centre Zone deposit, where a controlled research drill-hole CZ-15-01 was logged. As shown in the related cross-section (Fig. 6, bottom), two major normal brittle faults were intersected, one trending 255° and dipping 70° N and the other trending 065° and dipping 50° SE. In addition, two intervals of mineralized SIS epiclastic rocks were encountered above and below a 60 m interval of quartzite. A deeper ~10 m thick mineralization zone was also intersected in the metagreywacke. Structural study by Fuchs and Hilgar (1989) suggested that faults with very similar orientations exerted a strong control on mineralization the Main Zone deposit. The plan-view map (Fig. 6), constructed in part from their mapping, shows that both D-shears (255° Thelon-trend) and P-shears (065°-trend) form a linkage between the Main Zone and Centre Zone deposits. Note that there is a tendency, expressed here and elsewhere in the camp, for mineralization to be preferentially localized within the epiclastic unit, as well as along and proximal to the basal contact with Pipedream metagreywacke.
Based on the relationships above, it is hypothesized that D- and P-shears, in particular, played large roles in controlling primary (stage 1) mineralization at the Centre Zone deposit. When looking at mesoscopic-scale mineralized structures in CZ-15-01, all three uranium paragenetic stages described by Sharpe et al. (2015) for Kiggavik’s Bong deposit (Fig. 3) are present. In general, uraninite is primarily located in veinlets, fracture planes and massive blebs representing later stage 2 and 3 remobilization (Fig. 5). Uraninite located along foliation planes, representing early stage 1, is rare. Overprinting of primary uraninite is inferred to have taken place through later fault reactivation, fluid infiltration and remobilization.

6 Summary and conclusions

The main findings of this study are: 1) The pre-Thelon basement rocks hosting the Kiggavik deposits contain three main rock packages, the ~2.71 Ga Pipedream metagreywacke, ~2.6 Ga felsic volcanogenic rocks of the SIS, and <2.3 Ga orthoquartzites of the KRg; 2) Together, these units form a homoclinal sequence that dips shallowly to the NNW in the Kiggavik East area and shallowly to moderately WNW in the Bong and Granite Grid areas to the west; 3) The epiclastic rocks of the Snow Island suite (SIS) are far more extensive than previously thought; 4) Numerous stratigraphic repetitions, coupled with younging directions reversals are inferred to result from isoclinal, recumbent and sheath-style folding and thrusting, with probable translation of the upper package of SIS volcanic-epiclastic rocks and intercalated KRg quartzites over the Pipedream metagreywacke below. The degree to which the Pipedream greywacke is repeated at higher structural levels remains uncertain; 4) All rocks are cut by a network of younger brittle structures representing a Riedel sheal system produced during dextral strike-slip displacement along the Thelon Fault; 5) U mineralization in the Main-Centre zones was associated with infiltration of fluids along steeply dipping D- and P- shears, which may have been reactivated as normal faults, with further fluid infiltration and remobilization. Here and elsewhere, fluids were focused into the weaker and more porous-permeable SIS volcanicogenic rocks. Uranium was likely sourced from the Hudson and Kivalliq suite granites, along with SIS felsic volcanic rocks. Quartzites of the KRg were significant barriers to fluid flow.

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References

Formation of the unconformity-related uranium deposits in the Athabasca Basin, Canada: insights from hydrodynamic modelling

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Abstract. The unconformity-related uranium deposits in the Athabasca Basin, Canada, are generally associated with reactivated basement faults crosscutting the basin-basement unconformity with variable reverse displacements. The fluid flow related to uranium mineralization may be driven by thermal convection and/or tectonic deformation; however, little is known regarding exactly how basement faults influence convection, how basement faults may affect fluid flow during compressional deformation, and the interrelationship between thermal convection and compression. These questions are addressed through numerical simulations with various configurations of basement faults using FLAC3D software. Modelling undertaken with thermal convection only indicates that during periods of tectonic quiescence, basement faults with elevated permeabilities and thermal conductivities affect fluid convection cells in the basin. Fluid may flow into one fault, out of another fault, or into and out the same fault, potentially forming ingress, egress, and hybrid styles of mineralization. The modelling related to compressional deformation only suggests that sandstone- and basement-hosted deposits may be generated at different stages of deformation within the same fault system, depending on the degree of the compression. In addition, the strain rate controls the interaction between thermal convection and deformation-driven fluid flow.

1 Introduction

The Athabasca Basin in northern Saskatchewan and Alberta, Canada, is well-known for hosting the richest unconformity-related uranium deposits in the world (Fig. 1). Uranium deposits in the basin may be hosted in the sandstones, in the underlying basement, or along the unconformity (Thomas et al. 2000; Quirt 2003), and are associated with reactivated basement faults that cut and variably displace the unconformity surface and are commonly (but not exclusively) graphite-bearing (Thomas et al. 2000; Jefferson et al. 2007). A generally accepted model for the formation of unconformity-related uranium deposits involves circulation of basin-derived, oxidizing, uranium-bearing fluids in fault zones crosscutting the unconformity, where uraninite was precipitated through fluid-rock interaction and/or fluid-fluid mixing with basement-derived reducing fluids (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Jefferson et al. 2007; Kyser and Cuney 2009).

Figure 1. Location and regional geologic framework of the Athabasca Basin (after Jefferson et al. 2007). Black squares represent major uranium deposits.

Two models have been proposed for the migration of fluids related to uranium mineralization in the Athabasca Basin (Chi et al. 2013). These include fluid flow induced by tectonic deformation (Schaubs et al. 2005; Cui et al.
and fluid flow driven by thermal convection (Hoeve and Quirt 1984; Raffensperger and Garven 1995; Boiron et al. 2010; Cui et al. 2012a, b; Pek and Malkovsky 2016). However, the exact mechanism(s) controlling fluid flow related to mineralization in the Athabasca Basin remains poorly understood. While it is generally thought that fluid flow was either downward from the basin into basement fault zones (ingress flow), or upward into the Athabasca Group and outward from such zones (egress flow) (Hoeve and Quirt 1984; Fayek and Kyser 1997; Thomas et al. 2000), it is not clear how this fluid flow is related to the fault zones (Jefferson et al. 2007). In particular, although recent studies advocate thermal convection as a possible driving force for fluid flow related to uranium mineralization, little is known regarding how basement faults, which are spatially associated with most unconformity-related uranium deposits, influence fluid convection and how this may affect the localization of mineralization. On the other hand, the spatial association of the unconformity-related uranium deposits with reactivated basement faults suggests that the fluid flow responsible for mineralization may have been related to the deformational processes during fault reactivation (Alexandre et al. 2009; Cloutier et al. 2011). There is also the question of whether ingress flow and egress flow were associated with alternating compressional and extensional stress fields (Cui et al. 2012a), or whether both egress flow and ingress flow can occur under a unified compressional stress regime. Furthermore, the interaction between thermal convection and deformation is not well understood.

In recent years, we have carried out several studies aiming to address these questions and to better understand the mechanisms controlling fluid flow related to uranium mineralization in the Athabasca Basin (Li et al. 2016, 2017, in prep). This paper summarizes the results and discusses their significance for fluid flow and uranium mineralization models.

2 Effects of basement faults on thermal convection

Using FLAC3D software, a series of numerical modelling experiments with equal horizontal and vertical scales and various combinations of fault geometry and spacing, permeability, and thermal conductivity were carried out to investigate the roles that basement faults may have played in thermal convection during periods of tectonic quiescence (Li et al. 2016). The modelling results indicate that the location, spacing, orientation, and thermal conductivities of basement faults influence the size and location of thermally-driven fluid convection. In a model with a single, isolated fault, the fault coincides with an upwelling plume and the dip angle of the fault does not affect the fluid flow pattern; when the fault is moved laterally in the model, the upwelling plume shifts accordingly. In the case of two vertical faults, the faults may either coincide with upwelling flow between two convection cells or be located below individual convection cells, depending on fault spacing. In the latter case, the size of the convection cells varies slightly and fluid may flow into and out of individual fault zones. Similar results were also observed for the models with two oblique faults.

Convective flow can penetrate the uppermost basement when the permeability is less than two orders of magnitude lower than that of the overlying sandstone. In this case, the basement faults can not only control the location of ascending flow, but also can passively act as fluid conduits of either ingress or egress flow, depending on their thermal conductivities and relative locations within the models.

3 Effects of basement faults on fluid flow during compressional reactivation

Most of the unconformity-related ore-bounding structures demonstrate apparent reverse displacements, suggesting fluid flow related to mineralization may take place in a compressional regime, although intermittent extensional and thermal events during the mineralization periods may also play a role during the protracted and complex history of the basin (e.g., Sheahan et al. 2016). Another study was formulated to more fully explore the hydrodynamic relationships between the unconformity-related ore-bounding structures and uranium mineralization by undertaking numerical modelling of fluid flow in relation to reactivation of basement faults within a compressional stress regime (Li et al. 2017). Various two-dimensional models were tested to systematically investigate the effects of dip angle, pre-existing fault offset and volumetric strain, on fluid flow patterns.

The results indicate that the fluid flow pattern associated with structural reactivation is sensitive to the degree of bulk shortening. At a low bulk shortening stage (0.2 %), fluids are driven up along the fault zone into the sandstone in the basin, whereas at a relatively high bulk shortening stage (2 %), fluids tend to flow down into the fault zone and the basement. This is interpreted to indicate that the fluid pressure within the fault zone increases at the early stage of deformation due to pore volume decreases in relation to shortening, whereas the fluid pressure within the fault zone decreases at later stages of deformation due to dilation in relation to fracturing and reverse displacement. Variation of the dip angles and pre-existing offsets of the faults shows little effect on the strain distribution and fluid flow patterns.

4 Interaction between thermal convection and compressional deformation

Oliver et al. (2006) explored the relationship between thermal convection and extensional deformation and discussed the implications for unconformity-related uranium deposits in the McArthur Basin in Australia; however, they did not consider the possible effects of compressional deformation. As reverse faulting has been documented in many Athabasca Basin uranium deposits and compressional deformation may be of vital importance to their formation, it was deemed important to
systematically investigate the hydrodynamic effects of thermal convection coupled with compressional deformation.

Our modelling results suggest that after stable thermal convection is established in the basin, the introduction of compressional deformation with a strain rate on the order of $10^{12}$ s$^{-1}$ or smaller, does not affect the related thermal convection patterns. In other words, the deformation-driven upward flow in basement faults coexists with the thermally-driven convective flow in the basin. In contrast, when the compressional strain rate is on the order of $10^{12}$ s$^{-1}$ or greater, compressional deformation destroys the thermal convection patterns established in the basin. In such cases, the fluid flow in the whole model is dominated by deformation.

5 Implications for the formation of the unconformity-related uranium deposits

Our studies indicate that during periods of tectonic quiescence, thermal convection may be the dominant mechanism driving fluid flow, and the permeable and thermoconductive fault zones may play a critical role in the ore-forming fluid circulation system. The graphite-rich basement faults may have triggered the onset of thermal convection in the permeable sandstone unit, and interacted with the convection framework by controlling the location of ascending flow (Hoeve and Quirt 1984) or by acting as fluid conduits of either ingress or egress flow. The paleo-regolith and/or existence of microfractures probably promoted the pervasive basinal Na-rich fluids to infiltrate the basement (Boiron et al. 2010; Mercadier et al. 2010). At this stage, they then may either have interacted with reducing lithologies and/or fluids to form the basement-hosted deposits, or interacted with Ca- and U-rich basement rocks to extract uranium and evolve towards Ca-rich brines, and then migrated upwardly along the highway of the more permeable fault zones into the sandstone where they mixed with Na-rich fluids to form sandstone-hosted deposits (Boiron et al. 2010; Richard et al. 2010).

During compression, the fault zones most likely acted as fluid conduits, providing upward and outward (egress) flow, or downward and inward (ingress) flow, depending on the distribution of strain (contraction or dilation), which was in turn related to the degree of compression. At relatively low degrees of bulk shortening, the fault zones were dominantly under contraction and egress flow was favoured; at higher degrees of bulk shortening, dilation prevailed within the fault zone and the adjacent footwall sandstone wedge, as a result of reverse displacement along the fault, and ingress flow into the basement was favoured. The modelling results thus allow for the formation of both sandstone-hosted and basement-hosted mineralization in the same fault system at different stages of bulk shortening within a unified compressional stress regime. Episodic reactivation of a given fault in response to different far-field deformational events may result in a complex combination of sandstone-hosted and basement-hosted orebodies within a deposit, and/or the superposition of orebodies formed at different times, as exemplified in the Shea Creek project (Sheahan et al. 2016).

In summary, the large and high-grade uranium deposits in the Athabasca Basin may have been formed by alternating thermal convection and deformation-driven fluid flow, both influenced or controlled by basement-rooted faults.

6 Conclusions

Both thermal convection and deformation may have alternatively dominated fluid flow related to uranium mineralization in the Athabasca Basin. During periods of tectonic quiescence, thermal convection may have dominated and the interaction between thermal convection and basement faults provided conditions for fluid exchange between the basement and the overlying sandstone aquifer, facilitating uranium transportation and precipitation. Under the conditions of superimposed far-field compressional deformation, pre-existing shear zones/faults within the basement may have been reactivated to variable degrees, which may have given rise to both egress and ingress flow, and the potential for both sandstone-hosted and basement-hosted mineralization to form within single fault systems.

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References


Multiple mineralizing events at the Cigar Lake deposit: an integrated-study of uranium oxide dating and geochemistry

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Abstract. Multiple ages from uranium oxides spanning over more than 1 Ga have been proposed as markers of several U-mineralizing events in the Athabasca basin (Saskatchewan, Canada). Such a spread of ages together with a global lack of detailed characterization (paragenesis, chemistry) of the dated material make the understanding of the nature of the potential distinct U-mineralizing events difficult. To unravel this complex sequence of fluid-flow events, an integrated and systematic study coupling mineralogy, in situ U-Pb dating, and trace element geochemistry of UO$_2$ has been carried out at the Cigar Lake deposit, a sandstone-hosted endmember of unconformity-related U deposit. This study shows that five main fluid events contributed to the formation and evolution of the deposit, at ~1430, ~340, ~225, and ~205 Ma and one poorly constrained major brecciation event occurring between 1000 and 700 Ma. Each mineralization stage is characterized by a specific fingerprint including distinct mineralogical associations and geochemical signatures in trace elements. The spatial repartition of the distinct U oxide types reveals that the U stock of the deposit was deposited during the first mineralizing stage but has been latter greatly remobilized so that the present mineable stock is in fact young mineralization (<350 Ma).

1 Introduction

With 613,400 t of mineral reserves at an average grade of 15.9% U$_3$O$_8$, including proven reserves of 209,600 t at 19.86% U$_3$O$_8$ ( Cameco 2016) the Cigar Lake unconformity-related uranium deposit is the world’s second largest high-grade uranium deposit in the world after McArthur River, also located in the Athabasca Basin 45 km south-west of Cigar Lake. It occurs right at the unconformity between a Paleo- to Mesoproterozoic intracratonic sedimentary basin and an Archean to Paleoproterozoic crystalline metamorphic basement. The sedimentary strata consist of undeformed quartz sandstones and conglomerates belonging to the ca. 1700 Ma Athabasca Group. The crystalline basement mainly consists of Paleoproterozoic metasediments and Hudsonian plutonic rocks of the Wollaston Group. The orebody is sandstone-hosted and has an elongated lens shape 1900 m long, 100 m wide, and 10 m high. Uneconomic, structurally controlled, perched mineralization also occurs in faults rooted in the main orebody.

The deposit hosts a rather complex mineralogy, first addressed by Bruneton (1987) and Reyx and Ruhlmann (1993). Such complexity expresses multiple episodes of fluid-rock interactions from ca. 1.5 Ga to the present time, attributed to major fluid flow events in the Athabasca Basin and the basement as a result of far-field tectonic events (Kotzer and Kyser, 1995). They were recorded in many deposits of this world’s highest grade uranium district and a considerable amount of effort in the past decades has been directed at unravelling the nature, timing, and significance of each event.

After basin deposition at ca 1.70 Ga, the diagenetic processes and the earliest hydrothermal fluid event associated with the primary mineralization stage account undoubtedly for most of the current research effort as they define the currently accepted model of genesis for unconformity-related U deposits in the Athabasca basin. It involves fluid mixing between uranium-bearing Na-Ca oxidized basinal brines and basement-derived reduced fluids and/or fluid-rock interaction between the oxidized basinal brines and the reduced basement lithologies (Hoeve and Quirt 1984; Fayek and Kyser 1997; Hecht and Cuney 2000; among others). If there is today a fairly good understanding of this early event occurring at ca. 1.45-1.5 Ga (Fayek et al. 2002; Alexandre et al. 2007), the nature and significance of the later fluid circulation events and related ages remain in contrast poorly documented and understood. In that sense, numerous geochronological studies have been published (mainly U-Pb dating on uranium oxides and K-Ar or $^{40}$Ar/$^{39}$Ar dating of associated clays). However the analytical limitations of the early studies together with the fact that the dated material is rarely put into context (spatial location, detailed mineralogy of the associated phase, etc.) led to a multitude of ages ranges whose overall interpretation is challenging.

In the case of the Cigar Lake deposit, U-Pb dating was carried out i) on dissolved UO$_2$ by thermal ionization mass spectrometry (TIMS) giving maximum upper Concordia ages at 1341 ± 17 Ma, 1335 ± 55 Ma (Philippe et al. 1993) and 1362 ± 11 Ma (Cumming and Krstic, 1992) and ii) in situ by secondary ion mass spectrometry (SIMS), giving maximum upper Concordia ages at 1461 ± 47 Ma (Fayek et al. 2002). Younger ages were obtained for both perched mineralization and UO$_2$ in the deposit, with upper Concordia ages of 1287 ± 16 Ma, 1176 ± 9 Ma, 959 ± 31 Ma, 876 ± 14 Ma and 318 ± 23 Ma (Cumming and Krstic 1992; Philippe et al. 1993; Fayek et al. 2002). Although the geochronological study carried out by Philippe et al. (1993) is based on well characterized samples (Reyx and
Rulhmann 1993), the analytical limitation of the method (micro-drilling and conventional wet chemical technique) led to a certain deal of scatter in the concordia plot and therefore less robust interpretations. Inversely, while the in situ technique used by Fayek et al. (2002) enabled the avoidance of μm-size intergrowths of galena, coffinite, or inclusions of alteration products, a precise characterization (textures, associated minerals, and spatial location in the deposit) of the dated uranium oxides is lacking.

Therefore, to bring new insights on the nature and significance of each mineralizing and remobilizing event in the complex evolution of the Cigar Lake uranium deposit, a coupled and integrated study combining U-Pb isotope, trace element geochemistry, and mineralogical systematics on the uranium oxides has been carried out on two selected cross-sections.

2 Methodology

A systematic sampling of 185 pieces of drill core from 12 drill holes from two N-S transversal crosssections through the main orebody were carried out.

Mineralogical characterization was carried out on thin sections through optical and scanning electronic microscopy (SEM). In total, uranium oxides coming from 19 mineralized thin sections covering a great spatial distribution through the two cross-sections were analyzed. U-Pb isotopic compositions of the uranium oxides were determined using a CAMECA ims 1280 ion microprobe at CRPG-CNRS (Nancy, France), the major element contents were analyzed with an electron microprobe, and the trace elements through LA-ICP-MS at GeoRessources (Nancy, France).

3 Results

3.1 Petrological characterization

Four major ore types were defined based on the uranium oxide textures and their mineralogical associations. Primary mineralization occurs as either millimeter-scale nodules or botryoidal aggregates of uranium oxides UO$_2$(I), showing a slightly fibrous aspect embedded in a matrix of grey-greenish sudoite (Al-Mg di-trioctahedral chlorite) intimately mixed with illite. A suite of sulfides and sulfarsenides is commonly associated with this mineralization. They occur disseminated in the clay matrix either around the uraninite grains or in the fractures crosscutting them. These uranium oxides can also occur in a variety of shapes (toothedged, folded bands, or micrometer scale angular grains) resulting from a brecciation event after primary mineralization. Evidence of brecciation of the primary mineralization is a major process observed in almost all the samples from this ore type. Sulfarsenides are associated with this brecciation stage. Besides textural modification of the uranium oxides, this process also significantly altered the U oxides leading to strong Pb loss as observed through SEM and EMP analyses.

A second type of ore is characterized by uranium oxides UO$_2$(II), occurring as impregnation of clay minerals either as irregular masses bathing in the clay matrix or as massive areas between corroded and brecciated quartz. Those concretions are often associated with pyrite-marcasite and spatially associated with a second generation of dark green chlorite also intimately associated with illite.

A third type of UO$_2$(III), also shows an aspects of massive clay impregnation often in close association with siderite either in fracture or more massively around siderite spherules.

A fourth type of UO$_2$(IV), has only been encountered in one sample and occurs as homogeneous and very massive brecciated masses with angular and irregular shapes. Clasts of such oxides are cemented by colomorphic homogeneous dark green greenalite (ferrous serpentinite) and later hematite and calcite.

3.2 In situ U-Pb age dating on uranium oxides

Systematic in-situ U-Pb dating of the different uranium oxides from the distinct ore types revealed four major mineralizing events, respectively based on upper intercept in Concordia plots.

Discordias obtained from primary mineralizations show a certain spread from one sample to another with discordant age ranging from 1312 ± 15Ma to 1513 ± 64 Ma, however, since all the uranium oxides from this stage show similar characteristics, both geochemical and mineralogical, all the data have been regressed together and indicate a primary mineralization stage at 1430 ± 17 Ma (Fig. 1) in agreement with the first age of 1467± 63 Ma proposed by (Fayek et al. 2002). The isotopic ratios obtained from spots in altered areas are characterized by significant lead loss but even avoiding coffinite and
fractures do not provide a reliable discordia with scattered $^{207}\text{Pb}/^{206}\text{Pb}$ ages ranging from 700 to 1000 Ma, interpreted as a poorly constrained minimum and maximum age of the brecciation process and arsenic-sulfides deposition. Uranium oxides from the second ore type show a discordant age of 337.2 ± 7.2 Ma (Fig 1.). Uranium oxides from the third generation UO$_2$(III), show a discordant age of 226.1 ± 7.0 Ma whereas isotopic ratios from UO$_2$(IV) give a concordant age of 204.1 ± 4.7 Ma (Fig. 1). The spatial distribution of the distinct mineralization types through the two studied crossections indicates that primary mineralization (UO$_2$(I)) at the Cigar Lake deposit only occurs in the core of the lenticular orebody, in a restricted area of about five meters above the unconformity, whereas most of the orebody consists of younger mineralization, mainly UO$_2$(II) and UO$_2$(III). The younger mineralization occurs either at the edges of the deposit or are structurally controlled, in faults crosscutting the main orebody.

3.3 Trace element geochemistry of the uranium oxides

Of the 38 analyzed elements, only 5 elements were systematically below or near detection limits: Ga, Li, Rb, Se, and Ta. Besides major elements and the 15 lanthanides, uranium oxides from the Cigar Lake deposit commonly incorporate As, B, Mn, Mo, Sb, Sr, Th, Ti, V, W, Y, and to a lesser extent Bi, Ba, Co, Cr, Ni, Nb, and Zr. Variations in trace element contents occur between the uranium oxides from distinct ore types and also between unaltered UO$_2$(I) and altered UO$_2$(I)$_{alt}$, indicating different physico-chemical processes for these different mineralization stages.

Indeed, altered areas of uranium oxides from the first generation show clear changes in geochemical characteristics indicating clear fluid-mineral interaction between this brecciation episode. Besides substitution of radiogenic Pb by Ca, Si, and Fe as already described by Alexandre et al. (2005) in uranium oxides from the McArthur River deposit and the Virgin River prospect, alteration of primary uranium oxides is characterized by a significant increase in Ti, V, W, B, and LREE contents and to a lesser extent Bi, Ba, Co, Cr, Ni, Nb, and Zr. Variations in trace element contents occur between the uranium oxides from distinct ore types and also between unaltered UO$_2$(I) and altered UO$_2$(I)$_{alt}$, indicating different physico-chemical processes for these different mineralization stages.

Regarding to the other generations, unaltered primary oxides UO$_2$(I) are characterized by low As, B, Ba, Mn, Sr, and Th contents, Cr contents being below detection limits and high contents in Ti, V, and W and to a lesser extent Ni, Mo, Co. UO$_2$(II) has a specific geochemical signature with elevated contents in As, Mn, V, Y, and Cr (only generation containing significant amount of Cr) and relatively low Ti, W, Sb, and Th contents. Bi, Co, and Ni contents fall below detection limits. UO$_2$(III) is characterized by particularly high, V, Th, Sr, As, and Mn and low content in Y, whereas Bi, Cr, Co, and Ni contents are below detection limits. Finally, the fourth and last generation of uranium oxides UO$_2$(IV) show elevated contents in B, V and W, and low Mn and Ti contents whereas As, Bi, Cr, Co, Ni, Sb, and Th contents fall below detection limits (Fig. 2).

Figure 2: Box-and-whiskers plots of selected elements showing variations with alteration/brecciation and from one ore-type to another

Chondrite-normalized REE patterns also show typical patterns regarding to the mineralization type (Fig. 3). Thus, primary mineralization show the typical “bell-shape” of the unconformity-related deposits (Mercadier et al. 2011) Alteration tends to very slightly lower the HREE and increase the LREE contents of the uranium oxides. REE patterns of UO$_2$(II) also show a global “bell-shape” but with significant enrichment in Ce, Pr, Nd, and Sm. Those uranium oxides although show the highest $\Sigma$REE contents. UO$_2$(III) REE patterns have relatively flat to LREE enriched patterns and show the lowest $\Sigma$REE contents. Finally, UO$_2$(IV) show a more typical bell-shape pattern. However, overall the HREE content and patterns do not change significantly between the distinct mineralization types.
4 Conclusions

By coupling dating and geochemistry on UO₂, five main fluid flow events have been recognized in the Cigar Lake deposit. It consists of four main U mineralizing events at 1430 ± 17, 337.2 ± 7.2, 226.1 ± 7.0 and 204.1 ± 4.7 Ma, plus one poorly constrained major brecciation event between 1000 and 700 Ma. Each mineralization stage is characterized by a distinct paragenesis and a specific geochemical fingerprint in trace elements and REE patterns of the uranium oxides. Brecciation also induced specific geochemical changes in the UO₂(I). UO₂ is a non-stoichiometric mineral with highly variable chemical composition as a function of temperature of crystallization, element availability, and substitution during alteration processes (Mercadier et al. 2011; Frimmel et al. 2014; Alexandre et al. 2015).

Very few trace element datasets on UO₂ have been published to date, making interpretation on the nature of mineralizing fluids difficult. However, all mineralization types show some similar characteristics: HREE contents and patterns, and trace element contents near those published for unconformity-related deposits (Alexandre et al., 2015) indicate that all the uranium stock of the deposit was probably deposited during the first and primary mineralization stage. This stock was greatly redistributed and remobilized during later fluid events, under distinct physico-chemical conditions (pressure, temperature, fluid chemistry, etc.) leading to specific changes in the different UO₂ compositions. Thus, if primary mineralization shows very typical features of the unconformity-related uranium oxides (Alexandre et al., 2015), UO₂(II) in contrast shows peculiar features with an enrichment in REE, V, Mn, and As. Similarly, UO₂(III) shows some specific geochemical features which tend to approach those of lower temperature sandstone-hosted deposits (flat REE to LREE enriched pattern, high content in V, Mn) but with surprising Th enrichment, since Th is considered as immobile in low-temperature hydrothermal environments. Finally, the last stage UO₂(IV) show chemical features are near those of UO₂(I) but also with distinct features such as higher contents in V and Sr, among others, probably because of distinct element availabilities. The systematic study at the deposit scale of the distinct mineralization types also indicates that much of the actual uranium stock was deposited shortly after basin deposition, at 1430 ± 17 Ma, but that the present mineable stock has been greatly remobilized and consists of younger mineralization types, mainly UO₂(II) and UO₂(III) and thus emphasizes the significance of later processes in the evolution of the deposit.

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References

Mid-Proterozoic continental extension as a control on Athabasca region uranium emplacement, Saskatchewan and Alberta, Canada

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Abstract. Athabasca region ‘unconformity-type’ ore is emplaced near the base of three stacked, overlapping Proterozoic basins (Jackfish, Cree and Mirror): the Athabasca Basin in older literature. Most reported U-Pb ages of uraninite coincide with formation of the Mirror Basin (1550-1500 Ma), with the oldest ages (ca. 1600 Ma) corresponding to the upper evaporitic unit of the Cree Basin, the Wolverine Point Fm. More common U dates of around 1550-1500 Ma coincide with the formation of the Mirror Basin. Its fill consists of over 2300 m of clastics, minor evaporites and dolomites. The Jackfish and Cree basins form simple troughs, trending NNE and NW respectively, in response to late movement associated with the Trans-Hudson Orogen. The Mirror basin consists of deeper NE trending troughs, consistent with rifting as continental extension was leading to breakup of Laurentia. Mirror Basin subsidence dominates the shape of the underlying basement-sandstone unconformity. Uranium orebodies are located at the ends of the resultant troughs at the basal unconformity, and in faults related to their formation. This suggests that the formation of the Mirror basins was a controlling factor in guiding Wolverine Point U-emplacing brines to basement U traps, and that Mirror Basin related faulting marks the limit of Athabasca region unconformity ore.

1 The Athabasca basins

The Athabasca Basin of the older literature consists of three stacked and overlapping basins deposited under different tectonic conditions and separated by unconformities. They are the Paleoproterozoic Orosirian to Stratherian Jackfish Basin (ca. 1810 – 1760 Ma), the Stratherian Cree Basin (ca. 1760 – 1630 Ma), and the Mesoproterozoic Calymmian Mirror Basin (ca. 1590 – 1500 Ma). Although their structural history and depositional lithologies vary considerably, they share a prolonged diagenetic history that reduced their clastic lithologies to quartz arenite. The Jackfish and Cree basins are in contact with the crystalline basement, and both host unconformity-type uranium deposits. The stratigraphy and lithology of the Athabasca basins are described in Ramaekers et al. (2007). Revision of the Hudsonian sedimentary packages in the area is in progress, e.g. Bosman and Ramaekers (2015). Figure 1 shows an updated map of the surface geology.

1.1 Jackfish Basin

The Jackfish Basin underlies the western third of the Cree Basin but is exposed at its western and northern margins. The depositional fill of the Jackfish Basin is arkosic like that of the underlying Martin Group. Its location, and NNE axis orientation also is more akin to that of the Martin Group, and for these reasons it is here regarded as part of that late Hudsonian sequence. Diagenetically it is like the Cree and Mirror basins and alteration and mineralization patterns suggest that it was subject to the fluid circulation that emplaced uranium in these basins.

Figure 1. Athabasca basins stratigraphy. Stratigraphic abbreviations: FP Fair Point – not coloured; MF Manitou Falls; LZ Lazenby Lake; LL Locker Lake; O Otherside.

1.2 Cree Basin

The Cree Basin began as a NW trending trough filled
with the conglomeratic sandstones of the Read and Bird formations (Figs. 2 and 3). It may have formed as a rift due to continuing northward movement of the Superior Craton relative to the area west of the Thompson Belt as documented by Machado (1990). It formed parallel to the SW margin of the plateau like uplifts of the Trans-Hudson Orogen (THO) mapped by Pehrsson et al. (2016).

The initial 400 m of conglomerates in the trough were buried during the following sag phase of the rifting. This deposited 500 m of fluvial sandstones, up to 450 m of paralic sandstone, and the deltaic, sabkha and eolian sediments of the evaporitic Wolverine Point Fm in a wider basin (Fig. 4). Limited drill hole data indicate the Cree Basin was a simple trough and sag sequence with little in the way of embayments.

1.3 Mirror Basin

The time of Mirror Basin formation, ca. 1550 Ma suggests among other reasons that it formed as part of the Mid-Proterozoic extension of the Nuna supercontinent leading to its eventual breakup. This contrasts with the localized extension in an overall Hudsonian compressive setting of the Jackfish and Cree basins. Extension may have been along such faults as the Howard Lake Shear Zone linking the Athabasca and Thelon basins and the Virgin River shear zone and/or one further to the east. The extensional movement along such faults is not prominent, as it takes only a few km of extension of a crustal scale fault to cause basin-scale subsidence.

Mirror Basin isopachs (Fig. 5) of the basal 800 m of fluvial clastics (conglomeratic Locker Lake, and sandy Otherside fms) show a complex pattern not unlike those attained in analogue modelling of segmented oblique rifts (Amilibia et al. 2005). Oblique segmentation in the Mirror Basin might be due to basement shear zones such as the Grease River and Black Bay. The three preserved Mirror Basin troughs trend NE across the Cree Basin, and the easternmost is over 800 m deep. The thickness of the Mirror Basin clastics is known in detail due to geophysical surveys showing the depth to the conductive Wolverine Point Fm over much of the central part of the Mirror Basin (Dahrouge and McCallum, 2005).

The estimated more than 1500 m of lagoonal black muds (Douglas Fm), anhydritic evaporites and dolomites (Carswel Fm) overlying the fluvial
sandstones are preserved only in the Carswell impact structure. The Douglas mudstones are still black and organic rich, in contrast to the green and red mudstones of the Wolverine Point Fm, likely to have been as rich in organics originally.

Figure 5. Mirror Basin clastics isopach. Locker Lake Fm conglomeratic sandstones (outer 3 red and brown colours) and Otherside Fm sandstones (inner 2 paler colours). Total thickness ca. 850 m. Contour intervals: pale red 100m, dark red 200m.

2 Basin shapes and fluid pathways in the Cree Basin

The conglomeratic sandstones of the Bird and Read formations (Figs. 2 and 3) provided permeable pathways from the central Cree Basin overlain by the evaporitic Wolverine Point Fm (Fig. 4). Thus, reflux brines from the Wolverine Point Fm had a ready pathway to the eastern margin of the basin at the time of Wolverine Point deposition (ca 1640 Ma), also the time of the oldest uraninite in the ore zones.

3 Topography of the basal unconformity

The topography of the basal unconformity below the Cree Basin did not remain simple once subsidence within the transverse Mirror troughs began. The result was the surface shown in Figure 6. The central and western side of the Athabasca region basin floor consists of a series of NE trending troughs progressively deeper from west to east. The eastern Cree Basin floor is known only from limited drill hole data, and thus far does not show the NE troughs that characterize Mirror Basin subsidence to the west.

4 Uranium deposits

Figure 6 shows the basal unconformity topography as well as the location of known uranium deposits. Deposits are shown by red plus signs, with size proportional to the size of the deposits. Many of the deposits are located at the end of troughs or at faults along their margins.

Figure 6. Athabasca basins basal unconformity shape and uranium deposits. Sub-Athabasca elevation contours: +600 m at southern margin to -1600 m at basin center. Darkest blue contours have basement at surface with a 100m interval. Medium blue contours are subsurface with a 200m interval. Pale blue lines are 100m supplementary contours. Black dashed contour line is at -1000m m above sealevel. Uranium deposits shown by red + signs. They are located at the end and faulted margins of troughs: Cree Basin conglomeratic troughs in the east, and the Mirror basin troughs in the center and west.

Figure 7. Patterson Lake South area, generalized tectonic map, ca. 1500 Ma. Extension of southern basin margin to the southwest resulted in the formation of the Mirror basin troughs. Post-Cree Basin faulting resulted in a NS trending graben at the west side of the trough, and a complex left-stepping sinistral trans-tensional fault system that hosts the bulk of the known mineralization on the east side of the trough.
The setting of the large orebodies of the Patterson Lake area is shown in more detail in Fig. 7. The orebodies occur at the southern end of the deepest Mirror Basin trough where trough margins converge and focus fluid flow. Regional considerations suggest that the overall basin extension was to the southwest. This is supported by what is known to date of the local structures. The west margin of the trough is flanked by a north-trending graben indicated by drill data and southward deflection of stratigraphic marker beds in outcrop. They suggest no change of thickness in the basin margin strata, and thus, a post-depositional graben due to normal faulting. The eastern margin of the trough is a complex en echelon fault system forming a left stepping sinistral system in the western Patterson Lake area. Slickensided surfaces with near horizontal and steeply dipping slickensides are widely present, suggesting the system was transtensional or that episodes of normal faulting preceded, followed, or alternated with the wrench movement. Alteration geochemistry of the two fault systems are similar, suggesting a temporal link.

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References


Abstract. The Wollaston-Mudjatik Transition Zone (WMTZ), located in northern Saskatchewan, Canada, is an important litho-structural boundary between the Archean orthogneisic Mudjatik domain to the west and the Paleoproterozoic metasediments overlying Archean gneisses of the Wollaston domain to the east. In northern Saskatchewan, the transition zone is overlain by the Paleoproterozoic Athabasca basin and is associated with some of the largest and highest grade uranium deposits in the world.

A small project area (12x15 km) along the WMTZ has been chosen as a test case study of the 3D Geomodeller software on its capabilities in interpolating complicated basement geology from sparse drill-hole data to aid in three-dimensional visualization and target optimization. The ultimate objective of the project is to obtain well constrained three-dimensional geometry in order to better correlate the main metallogenic guide for uranium mineralization along the eastern Athabasca Basin; graphitic metasediments. Interpretation and modelling of the basement geology is complicated by an overlying thick sequence of Athabasca sedimentary rocks; therefore, the objective is accomplished through the use and integration of geophysical data reconciled with drill-hole intersections. The reconciliation between the 3D model and field data is completed through the comparison of drill-core physical property values with observed geophysical responses.

1 Geological framework and exploration strategy

The modelling area encompasses most of the Getty-Russell and Martin Lake uranium exploration projects operated by AREVA Resources Canada and is located near the south-eastern edge of the Athabasca Basin (Fig. 1); a late Paleoproterozoic sandstone basin underlain by Archean to Paleoproterozoic crystalline basement rocks of the Western Churchill Structural Province of the Canadian Shield. The project areas straddle a NNE trending litho-structural transition zone between the Wollaston and Mudjatik domains, henceforth referred to as the Wollaston-Mudjatik Transition Zone (WMTZ). Both domains are part of the south-eastern Cree Lake Zone which in itself is part of the larger Hearne sub-province (Hoffman 1990). The WMTZ has shown to be a favourable basement zone for producing high grade unconformity-type uranium deposits with many of the world’s largest and highest grade deposits found along the trend (Jefferson et al. 2007). The projects southern claims border the Key Lake uranium mine-site where 73 900t U at an average grade of 2% was produced over 14 years (Thomas et al. 2000).

The Cree Lake zone was formed as a result of the Trans-Hudson Orogeny, a continent-continent collision of the Superior and Hearne cratons circa 1.8 Ga. The WMTZ is one of the resulting suture zones separating the distinct litho-structural Wollaston and Mudjatik domains and has been characterized in detail by Annesley et al. (2005). The Wollaston domain, underlying most of the Martin Lake and Getty-Russell projects, is a distinct “fold-thrust” belt of Paleoproterozoic metasedimentary rocks overlying and intercalated with granitic domes. In the project area the Wollaston group is dominantly composed of garnet and/or cordierite bearing pelitic to psammino-pelitic gneiss, graphitic pelitic gneiss, silicified gneiss and calc-silicate gneiss. The western-most margins of the Wollaston domain have undergone upper amphibolite grade metamorphism (Card et al. 2007) and have an approximate thickness of 1000 metres. The Athabasca Basin unconformably overlies the metamorphic basement rocks in the project area and is a large, unmetamorphosed arenitic sandstone sequence formed during crustal subsidence following the Trans-Hudson orogeny (Ramaekers et al. 2007).

The genetic model for unconformity uranium mineralization along the WMTZ is well constrained by previous authors and consists of the precipitation of uranium via redox interactions at the unconformable contact between graphitic basement gneisses and the Athabasca group sandstone (Hoeve and Quirt 1984; Quirt 1989; Quirt 2003; Jefferson et al. 2007). Structural reactivation of the graphitic horizons plays a key role in the localization of uranium deposition as reactivated graphitic structures are a favourable fluid pathway for the transportation of reduced basement fluids to the unconformity (Hoeve and Quirt 1984). Mineralization localization can occur as polymetallic unconformity and/or sandstone hosted ‘egress-type’ deposits or effectively monometallic ‘ingress-type’ basement deposits (Hoeve and Quirt 1984; Quirt 1989; Quirt 2003; Jefferson et al. 2007). Across the project area there are several low grade uranium showings mostly constrained to basement style ‘egress-type’ mineralization along graphitic pelitic gneisses with minor localized showings at the unconformity.
Exploration via geophysics (grid-scale EM, gravity and resistivity coupled with regional scale magnetics) and diamond drilling is currently on-going with approximately 360 drill holes previously drilled across the two project areas. Targeting is concentrated along the graphitic pelitic horizons delineated by historical EM and resistivity surveys and confirmed through drill-hole intersections (Doney et al. 2015). Drilling is an expensive method of exploration and as such the goal is to maximize and concentrate drilling meterage in relevant areas. 3D geological modelling can aid in this goal by better constraining and visualizing the behaviour and trend of the main metallogenic guide, the graphitic metasediments.

2 Methodology

The Geomodeller software uses geological and structural contact and orientation data that is either measured or interpreted to create 3D surfaces and volumes in order to represent a reasonable approximation of how geological formations behave at depth (Calcagno et al. 2005). The contact and orientation data is computed using an implicit co-kriging method where various statistical parameters can be defined in order to change the shape of the interpolation; namely defining the range, nugget effect and anisotropy for each data series (Calcagno et al. 2008). Once these parameters have been input, Geomodeller interpolates the geometry based on the provided data. Interface data can be in the form of plan maps, cross section or drill-hole intersections and the interpolation will inherently be stronger the more constraints are given to the data. Yet, geometrical interpolation also strongly depends on the orientation data which are used as a pseudo-potential local measurement, parallel to the bedding or layering, for processing.

The geological interpolation is based on a defined ‘stratigraphic pile’ (overburden, sandstone and basement stratigraphy) that drives the sequence of interpolation between the different geological units under consideration. It also creates the rules for how each geological layer behaves relative to each other. There are two options for behaviour: ‘onlap’ which is treated as stacked or simple infilling of the remaining volume; and ‘erode’ which deals with cross-cutting type contacts (i.e. erosional surfaces and intrusive bodies). As with any type of modelling, in order for the resulting models and sections to be relevant, time must be taken to ensure the results are reasonable and logical within the geological context. Resulting from the extensive Athabasca sandstone cover, outcrop is absent in this area. Therefore the only definitive constraints on geology are drill-core data which is often sparse yet must be adhered to as closely as possible. Drill-holes normally penetrate 30 to 120 metres into the basement resulting in highly interpretable basement geology at depth. Historical interpretations by authors having completed detailed studies of the WMTZ have been used for constraining geological behaviour at depth (Annesley et al. 2005; Tran 2006; Jeanneret et al. 2016). Because of these concerns, a cohesive, continuous and relatively simple geological interpretation is necessary for modelling purposes.

The following method has been applied in the modelling process; 1) Create a detailed geological and structural map of the metamorphic basement geology based on all available geophysical data, historical drilling and interpretations; 2) Define a stratigraphic pile in Geomodeller; digitize the unconformity surface as a plan map; 3) Import drill-hole constraints to the model and adjust the model accordingly; 4) Create regional and grid scale cross-sections to constrain behaviour at depth. Select sections of the completed 3D model can be viewed in figures 2, 3 and 4. Once complete, the 3D model can be applied to current exploration drilling to map and confirm target drill-holes, adjusting targeting or the model accordingly to new information. The block 3D model encompasses a volume of 15640m x 14300m x 1600m with cell size varying depending on the input resolution.

3 Forward modelling and target advancement

3.1 Preliminary modelled results

To provide suitable data for forward modelling, physical property sampling was implemented across the project areas over the 2016 drilling season and the results have been added to the 3D model. Geomodeller has the capability to forward model the gravimetric and magnetic responses. The resulting forward gravity model is presented in figure 5b.

Validation of the forward model can solely be completed on zones of analogous observable geophysical anomalies. Regional magnetics surveys have been amalgamated in 2010 (Card 2015) and completely cover the project area. A gravimetric survey completed in 2016 across most of the Getty-Russell property can be used as a direct comparison to the forward modelled response. Presented in figure 5, the normalized comparison to the observed and forward modelled responses shows reasonable correlation with notable differences between the scale of the northern low zone and a high zone in the north-east of the observed response. Causes of the differences are likely related to minimal constraints on the geology as exploration drilling is limited in this area. Terrain effects are also suspect in the modelled response as some of the anomalies match up very well with the morainal topography.

3.2 Targeting advancement

Once a working model has been advanced and strengthened by forward modelling reconciliation, it can be beneficial to examine exploration targeting in the context of the model. Proposed drill targets across the two project areas for the 2017 drilling program within the Martin and Getty-Russell projects have been added to the model for target confirmation and several examples of plotted target locations within the 3D model are shown in figure 6.
Differences between the conductor location within the model and the planned target are points of interest for additional examination to be evaluated at the end of the drilling program. If drilling confirms the model interpretation that a conductor is displaced, the model can then be used as additional perspective for follow up drilling and ideal targeting of the graphitic horizon at its discordant sub-crop.

4 Perspectives and limitations

In conclusion there are many strengths and weaknesses developed throughout the modelling and analysis process. Strong geological interpretation of the project area is needed for a reasonable interpolation of the 3D geometry. As drill-hole constraints are the only definitive information on the basement in the area, a significant amount of interpretation is necessary and drawing hypotheses based on historical studies is necessary. Studies have been done to determine that the outcropping basement rocks north and south of the Athabasca basin limits along the WMTZ are analogous compositionally, metamorphically and structurally to the basement under cover (Annesley et al. 2005; Tran 2006; Jeanneret et al. 2016) with the exception of the silicified gneiss unit which does not appear to outcrop south of the Athabasca basin margin. It has been discussed in Card (2014) that the silicified gneiss unit represents a regional alteration corridor which may change towards the south.

Margins of error with respect to the forward models can often be attributed to limitations of interpretation, data density and unknown variables. Overburden thickness varies significantly across the project from four to 70+ metres. Overburden thickness must be interpolated across the project area as sparse drill holes provide the only constraints. The resulting interpolation will significantly affect the forward modelled gravity. For this basic modelling, the Athabasca sandstone has been amalgamated into one unit. Variations in the sandstone due to grain size, alteration, dissolution and structure will have a significant impact on the geophysical signature and thus on the forward model accuracy. This same homogenization of lithology necessary for ease of modelling within the metasediments and granites will account for some difference between the modelled and observed anomalies. A large difference between the observed data and the model response will also be related to alteration. This affect is not currently taken into account in the model but will be integrated as the project advances. The statistical size of the data pool on some lithologies is an issue and can be improved by subsequent programs. Model evolution continues as additional drilling is completed throughout the year.
Figure 4. Clipped and zoomed 3D geological model with sandstone cover and drill-holes plotted along the CS (Martin Lake) conductor looking north-east.

Figure 5. Normalized gravimetric grids across the overlapping zone of the 2016 Getty-Russell airborne gravity survey (linear transformation). a observed, b forward modelled, c calculated difference.

Figure 6. Select 2017 drill targets for the Getty-Russell project plotted within the 3D model sections.

References


Radiation induced alteration of Permian uraniferous coal (Rybníček deposit, Czech Republic)

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Abstract. The effects of uranium mineralization on organic components of coal have been studied at the former Novátor mine (the Rybníček coal and uranium deposit, Intrasudetic Basin, Czech Republic) in order to characterize physical and chemical properties of mine wastes as a basis for further environmental studies. Disseminated uranium minerals caused local radioactive alterations in the uranium-enriched coal matrix. The radiation-induced haloes around uranium mineral grains displayed higher reflectance (Rr = 1.52–1.75%) compared to radiation unaffected bulk coal (Rr = 0.72–0.86). Structural changes in radiation-induced haloes are characterized by low values of Raman D band disorder, fewer aliphatic C–H bonds and higher levels of oxygenated functional groups in micro-infrared spectra. Zones of higher reflectance are also confined to veinlets of epigenetic chalcopyrite, galena, and sphalerite mineralization, thus indicating uranium remobilization.

1 Introduction

Since uranium is a common chemical element associated with coal seams, the effect of α-radiation-induced coal alteration was studied by Dill (1983), Halbach et al. (1984) and Dill et al. (1991). They concluded that radiation-induced alterations are observable by the development of anisotropic haloes surrounding accumulations of uranium minerals (coffinite, uraninite, brannerite or sooty pitchblende). Smieja-Król et al. (2009) found a direct correlation between an increase in the maximum reflectance of carbonaceous materials and the concentration of U in the Witwatersrand deposit in South Africa. The impact of radiation on organic matter (kerogen) and migrabitumens was also studied in uranium deposits in black shales, gold-uranium deposits in conglomerates, unconformity-type or vein-type uranium deposits (Leventhal et al. 1986; Lewan and Buchardt 1989; Landais 1993, 1996; Kříbek et al. 1999).

2 Geological setting – study area

Coal and uranium were mined in the Upper Stephanian-Lower Permian sediments of the Upper Paleozoic Intrasudetic Basin (ISB) located at the boundary between the Czech Republic and Poland (Fig. 1). At the former Novátor mine (the Rybníček coal and uranium deposit) mineralization was composed of “uranium blacks”, coffinite, uraninite and formed small stratiform lenses from 0.1 to 0.3 m thick (Arapov et al. 1984; Bernard 1991). Uranium was associated with elevated contents of Cu (up to 1.8 wt.%), Mo (0.6 wt.%), Pb (0.5 wt.%) and Zn (up to 0.9 wt.%). Uranium mining took place at the Rybníček deposit from 1952 to 1957. Roughly 300,000 tons of coal and 40,000 tons of radioactive material were extracted. Uranium contents ranged from 0.008 to 2 wt.%.

Figure 1. Location of the abandoned Rybníček coal and uranium deposit.

2 Samples and methods

Samples of coal and coal claystone were taken from shallow pits from the mine heap. Determination of the mineralogical identity of inorganic components in coal and claystone with organic admixture was attempted using a CAMECA SX 100 electron microprobe in the wavelength dispersion mode. Maceral analysis of coal and the measurement of random reflectance of vitrinite as a rank parameter were carried out on collected samples. Sample extraction and GC/MS analysis were conducted as described in detail by Havelcová et al. (2014) using the following oven temperature program: 40 °C (2 min) to 140
°C at a rate 20 °C/min, and continued at a rate 5 °C/min to 300 °C (5 min). Raman spectra of organic matter were collected from polished samples using a Thermo Scientific DXR Raman microscope equipped with a 532 nm line laser. Locations of interest were positioned using a motorized XY stage and an optical camera. The spot size of the laser focused by the 50× objective was ~1 μm in diameter. The laser power and time of sample excitation were adjusted to obtain high quality Raman spectra allowing the production of spectral maps. Infrared microspectra of the individual coal macerals were measured with a Bruker IFS 66 FTIR spectrometer combined with Hyperion IR microscope using a microATR objective equipped with a germanium crystal (diameter of 150 μm). Concentrations of chemical elements in coal samples were studied in the accredited Central Laboratories of the Czech Geological Survey in Prague.

2 Results

2.1 Mineralogy of mineralization

The mineralization of studied coal samples consisted of: (1) grains of framboidal or euhedral pyrite, coffinite and uraninite scattered in coal matter (Fig. 2A,B) and, (2) base metal mineralization bound to fissures in coal matter (Fig. 2C). The fissures were filled with carbonates, quartz, kaolinite, chalcopyrite, sphalerite and galena. In several fissures, uraninite occurred in association with base metal minerals.

2.2 Radiation induced alteration of coal

The anisotropic radiation induced haloes surrounding the uraninite and coffinite grains were found in many positions in the U-enriched coal. The occurrence of bright zones of haloes was associated predominantly with vitrinite-rich detrital layers. Halo diameters ranged from 35 to 100 μm. Zones with increased reflectance also appeared along some cracks filled with sulphides, kaolinite and carbonates. The average reflectance of vitrinite in haloes (R_r =1.52–1.75%) were higher compared with radiation non affected vitrinite (R_r = 0.72–0.86). This corresponds with lower values of Raman D band width in half peak height (FWHMD) of organic matter within radiation haloes (Fig. 3). A suitable rectangle halo area with dimensions 126 × 93 μm was chosen for Raman microspectroscopy mapping. The map of this area based on Raman spectral features in the range 1800–900 cm⁻¹ (Fig. 4) shows that the halo surface is not homogenous, but the intensity of radiation-induced coal alteration generally decreases from the central part of the halo to its peripheral area.

Using ATR-FTIR micro-spectroscopy, structural differences between the halo and its surroundings were studied. From the different spectral features it is obvious that the organic structure of the halo contains a smaller content of aliphatic C–H bonds (negative bands at 2927, 2855, 1447 cm⁻¹) and higher content of oxygenated functional groups (positive features at 3432, 1747, 1686, 1400, 1332, 1238, 1043 cm⁻¹).

Figure 2. Photomicrographs of mineralized coal from the Rybníček deposit (Novátor mine). a: Stratabound uranium mineralization in the coal seam. Mineralization consists of disseminated grains of euhedral or framboidal pyrite, uraninite and coffinite. b: Close-up of the radiation-induced halo surrounding the grain of coffinite. c: Galena-sphalerite-carbonate mineralization with minute grain of remobilized uraninite confined in fissures of coal. Note radiation halo around uraninite grain.
3 Discussion

3.1 The origin of mineralization

The distribution of uranium minerals in coal revealed that two types of mineralization occur in the studied samples: (1) Stratabound, syngenetic or early diagenetic uranium mineralization, and (2) epigenetic, base metal mineralization.

(1) In the stratabound, syngenetic or early diagenetic mineralization, the concentrations of uranium correlate with concentrations of $C_{\text{org}}$ and P. Uranium minerals are not accompanied by the base-metal mineralization. Scattered grains of uraninite and coffinite occur predominantly in thin laminae of vitrinite-rich material together with common accumulations of frambooidal pyrite. It is well known that uranium can be adsorbed onto humic-type organic matter (Jennings and Leventhal 1977; Borovec et al. 1979) at an early stage of diagenesis. As the amount of humic acids decreases with an increasing intensity of diagenetic processes and subsequent coalification, uranium is released to form separate mineral phases (Bouška 1981; Ketris and Yudovich 2009; Seredin and Finkelman 2008). This corresponds to the results of microprobe mapping of samples from the Rybníček deposit, where uranium concentrations were not detected by microprobe in any individual coal macerals outside of the radiation haloes.

(2) In contrast to the previous mineralization type, the concentrations of Pb, Zn and Cu in epigenetic, veinlet-type mineralization correlate with $S_{\text{tot}}$, $C_{\text{carb}}$ and Fe concentrations. The origin of veinlet-type base metal mineralization from the Rybníček deposit is difficult to explain because the time period of deposition of this type of mineralization is not known. In the study area, up to 800 m of Autunian volcanic rocks form the hanging wall in the Rybníček deposit and small manifestations of base-metal, mostly chalcopyrite mineralization were observed at the basal part of this volcanic rocks pile (Bernard 1991). Therefore, it is believed that the base metal hydrothermal mineralization and partial remobilization of the stratabound uranium mineralization may be related to the younger volcanic and related hydrothermal processes.

3.2 Radiation induced alteration of organic matter

Results of our study revealed that the radiation damage on carbonaceous matter is manifested by an increase of reflectance and structural ordering of carbonaceous matter. Yield of chloroform extracts decrease with increased radiation-induced alteration of carbonaceous matter and the aliphatic to aromatic compounds ratio in extracts increases. It indicates that the radiation has an impact on the chemical composition of organic matter similar to coalification.

In contrast to coalification, however, the content of
oxygen-bearing groups in the structure the coal increases with increasing radiation damage. It corresponds to the results by Landais (1996), who reported an increase of the Rock-Eval O/C values in radiation affected coal. We have no explanation for this phenomenon. It can be only speculated that the increase of oxygen is due to a metamict decomposition of uranium oxides structure, and a short-distance diffusion of oxygen to the surrounding organic matter.

2 Conclusions

Coal and coal claystones deposited at the waste heap of the former Novátor coal and uranium mine attain up to 0.1 wt.% of uranium. Two types of mineralization were detected in the studied coal and uranium deposit. The syngenetic or early diagenetic, stratabound uranium mineralization, and the epigenetic, veinlet-type base metal mineralization with remobilized uraninite and coffinite. Uranium minerals in both mineral assemblages caused local radiation-induced alteration of the coal matrix. Radiation haloes are not homogeneous but generally display higher reflectance and lower values of Raman organic matter band disorder (D-band) in contact with the uranium mineral grains relative to radiation-unaffected organic components of coal. The infrared spectroscopy revealed lower amounts of aliphatic C–H in haloes, relative to the radiation-unaffected coal matrix.

Mineralized coal has a low amount of solvent-extractable material (0.01–1.33 wt. %). The MNR in extractable part of organic matter of the uranium-rich coal samples increases in mineralized coal as is characteristic of coal thermal alteration (coalification), and corresponds to the uranium concentration in individual bulk coal samples.

Considering relatively high contents of U in studied coal waste materials, their leaching potential and possible surface water pollution should be evaluated with a long-term monitoring of water and stream sediments chemical composition at the vicinity of the former mine.

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The effects of deformation bands on uranium-bearing fluid migration in sedimentary sequences, Flinders Ranges, South Australia

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Abstract. Deformation bands are well known in petroleum geoscience for their petrological characteristics. However, their effects on sedimentary-hosted uranium systems are unknown. Four Mile Creek provides a natural laboratory to study the interplay between deformation bands and palaeofluid roll front deposits at the Dead Tree section. Two-dimensional face-maps of the Dead Tree section were produced to study the temporal evolution and spatial distribution of deformation bands within the Eyre Formation sandstone, which hosts the Four Mile uranium deposits 500 metres to the south. Structural analysis of 239 deformation bands is used for palaeostress reconstruction modelling. The analysis results show that a group of dilatational deformation bands are acting as uranium-bearing fluid conduits, supporting fluid flow from the Mt Painter Domain sources to the Four Mile uranium deposit. This indicates that permeability contrast between the deformation bands and host rock is sufficient to support the flow of uranium-bearing fluids via deformation band pathways, bridging the gap between the local structural history and fluid flow history of the Eyre Formation sandstone.

1 Eyre Formation deformation bands

Deformation in porous sedimentary rocks (>10% porosity by volume) is often accommodated in discrete zones of localised strain, known as deformation bands. These bands form as a result of compaction or dilation due to sediment loading, or high horizontal or vertical stress (Fossen et al. 2007). While deformation bands can act as conduits for fluid flow during their early growth stages, they can also reduce permeability in their later stages of development, baffling fluid flow and leading to reservoir compartmentalisation. Thus, the petrophysical properties of deformation bands are an important factor when investigating the flow properties of petroleum reservoirs (Fossen and Bale 2007). Until now, deformation bands have not been considered important features to sediment-hosted mineral systems of the brittle upper crust. Similarly, fluid migration pathways related to sedimentary-hosted uranium deposits worldwide are poorly constrained and understood.

2 Geology of the Dead Tree section

Deformation bands have recently been recognised within Eocene–Palaeocene sediments of the Frome Basin adjacent to the Four Mile uranium deposit, arguably Australia’s most prospective region for sandstone-hosted uranium. The Four Mile uranium deposit is located on the eastern flank of the northern Flinders Ranges, proximal to the NE-SW striking Paralana Fault, and 500 m south of the Dead Tree section. The study area (Dead Tree section) is situated downslope, immediately between the Mt Painter domain uranium source and the Four Mile uranium deposit. The uranium deposits are hosted within the Eyre Formation, which is exposed in the Dead Tree section. The formation is composed of kaolinized terrestrial sandstone, abundant in thorium- and uranium-rich oxidised palaeo-fluid fronts (Hore and Hill 2009).

3 Results: deformation band sets 1 – 6

We have produced a two-dimensional face map of the Dead Tree section, highlighting the spatial relationship of 239 deformation bands within the Eyre Formation (Fig. 1). Five sets of shear-enhanced deformation bands were identified, defining a range in $\sigma_H$ orientations between WNW-ESE to ENE-WSW. One set of pure compaction bands (DBS 6) was identified, which formed concurrently with DBS 1–5 indicated similar maximum horizontal stress ($\sigma_H$) orientations (Fig. 2). The deformation bands show a stress state regime progression, which evolved from a normal fault stress regime dominated tectonic setting to the present-day reverse fault stress regime. Deformation Band Set 1 (DBS 1) formed first under a normal fault stress regime. DBS 2 and 3 formed next in sequence under a strike-slip dominated fault stress regime. DBS 4 and 5 formed last during the most recent stage of northern Flinders Ranges uplift, as the local palaeostress regime evolved into the present-day reverse fault stress regime c. 10 Ma (Célérier et al. 2005). Finally, Thorium- Uranium-rich palaeo-fluid roll front deposits formed post deformation, and are associated with DBS 4 and 5.
4 Discussion: dilatational deformation bands conduits supporting uranium-bearing fluid migration

Palaeoredox roll fronts are abundant within the Eyre Formation located at the Dead Tree section, and we make the critical observation that the presences of thorium- and uranium-rich roll front deposits are associated with DBS 4 and 5. DBS 4 is the first set of deformation bands in sequence to require partial unfolding, indicating that DBS 4 initiated formation concurrently with the tilting of Eyre Formation. DBS 4 and 5 formed as conjugate dilatational deformation features within the Eyre Formation, resulting in increased deformation band porosity and permeability. These dilatational deformation bands act as preferential fluid conduits supporting uranium- thorium-bearing fluid flow downslope from the Mt. Painter source towards the Frome Basin. The palaeoredox front in figure 3 is segmented by a dilatational deformation band, indicating that the deformation bands highlighted in this study have influenced the small-scale migration of uranium-bearing fluids. Deformation bands are extremely sensitive to discrete changes in the local stress regime, and thus are proven here to be a reliable indicator for constraining the temporal evolution of palaeostress and palaeofluid flow, that is proximal to the Four Mile uranium deposit, critical
for modelling and reconstructing the dynamics of fluid pathways related to the Four Mile uranium deposit.

**Figure 3.** Photograph of a uranium-thorium-rich palaeoredox fluid front supported by a dilatational deformation band (after Hore and Hill, 2009)

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Classification of bedrock and till at the Kiggavik uranium district (Nunavut, Canada) by combined multivariate statistical analysis of iron oxides chemistry

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Abstract. Iron oxides from bedrock samples collected at the Kiggavik uranium district were examined petrographically and analyzed to determine trace element compositions to develop discrimination models classifying the origin of iron oxides in unconsolidated sediments covering the Kiggavik deposit and the surrounding area. Petrographic observations such as mineral association, inclusions, and textural relationships indicate that in Kiggavik igneous basement rocks magnetite is a late forming magmatic phase that is replaced by hydrothermal and/or weathering related hematite. Kiggavik metamorphosed basement mainly includes hydrothermal hematite, whereas Kiggavik quartz arenite contains detrital iron oxides grains that are partly or entirely replaced by weathering-related and/or diagenetic hematite. In Kiggavik till, the surface of detrital iron oxides is coated by layers of supergene iron oxides (1 to 10 μm thick). Principal component analysis (PCA) and linear discriminant analysis (LDA) were used to classify the Kiggavik bedrock, and to identify the bedrock sources of iron oxide grains in till. The PCA-LDA separate hydrothermal hematite in metagreywacke from other bedrock samples because of its elevated concentration of U (450 ppm). PCA-LDA demonstrates that a high proportion of iron oxides in Kiggavik till were sourced from local bedrock lithologies.

1 Introduction

Magnetite and hematite are able to incorporate a large number of minor or trace element cations in their structure. This ability makes these minerals a sensitive record of magmatic, metamorphic and/or hydrothermal processes, and important tracers of various mineral deposit types (Dare et al. 2014). In recent years, the chemistry of magnetite has been widely studied for determining sediment provenance or in support of exploration for various mineral deposit types (Dare et al. 2014). Many studies have shown concomitant occurrence of U and Fe oxides in various environments and on a variety of geologic time scales (Stewart et al. 2009), yet iron oxides from U deposits have not been widely investigated. In U-rich settings, there is a strong correlation between hematitization and U mineralization, as hematite commonly forms a characteristic alteration halo around the majority of the UO₂ settings. Under alkaline conditions, hematite and goethite are able to incorporate a significant proportion of U(VI) into their crystal structures (Stewart et al., 2009). In this study, magnetite and hematite from the igneous (granite, leucogranite, and syenite) and metasedimentary (metagreywacke, and quartzite) basement, sedimentary (quartz arenite) bedrock, and from local till in the Kiggavik uranium district were characterized for their morphology, surface and boundary textures, and minor and trace element compositions. The datasets obtained by analyzing iron oxides by various analytical techniques were investigated by standard and multivariate statistical methods to establish classification diagrams for separating iron oxides from different bedrock sources and to distinguish the source of iron oxides in Kiggavik till.

2 Methodology

Eight bedrock and ten till samples (Fig. 1) containing iron oxides, collected by the Geological Survey of Canada (GSC) in the Kiggavik area (Robinson et al. 2016), were investigated in this study. The Kiggavik area is located in the NE Thelon region of Nunavut (central Kivalliq Region; Fig. 1), and has been explored for uranium since the 1970s because of its similar geology to the eastern part of the Athabasca Basin (Fuchs et al., 1985). Till samples were collected in various distances up and down ice from the Kiggavik Main Zone (KMZ) in the direction of the main ice flow direction (NW & WNW; Fig. 1).

Following Makvandi et al. (2015), iron oxides morphology and textures were examined using an optical microscope and a JEOL JSM-840A scanning electron microscope (SEM) at Université Laval. Following the analytical protocols developed by Boutroy et al. (2014), major and minor elements in iron oxides were measured by a Cameca SX-100 Electron Probe Micro-Analyzer at Université Laval, whereas a RESolution M-50 193 nm Excimer Laser Ablation system coupled with an Agilent 7700x ICP-MS at Université du Québec à Chicoutimi (UQAC) was used to measure the concentration of trace elements.
Geochemical censored data (values below detection limits) were imputed using the robCompositions R-package (Hron et al. 2010). The imputed data were transformed by centered log-ratios to overcome the closure of compositional data (Wolter 1985). The maximum variation in the geochemical datasets was investigated by principal component analysis (PCA), and linear discriminant analysis (LDA) of PCA factors was carried out to predict the sample classes (James et al. 2013).

3 Results and discussion

In Kiggavik igneous basement, magnetite is a late forming magmatic Fe oxide phase that formed by replacing primary ilmenite (Fig. 2a). In these rocks, hematite is mainly hydrothermal formed at the expense of pre-existing Fe-Ti oxides (Fig. 2a), though a small proportion must be the result of lateritic weathering affecting the Kiggavik area prior to hydrothermal mineralization. Magnetite rarely occurs, or is absent, in metagreywacke, quartzite, and quartz arenite, whereas hematite is the dominant Fe oxide mineral. In Kiggavik quartzite, hematite is specular and formed in situ by replacing precursor magnetite and/or filled porosity remained after dissolution of preexisting minerals. Kiggavik metagreywacke, however, includes rounded hematite grains replaced by clay alteration along edges and fractures (Fig. 2b). The rounded hematite grains can be detrital in origin. In the Kiggavik quartz arenite, a component of Thelon Formation overlying the igneous and metamorphosed basement, hematite is a lateritic weathering or diagenetic product (Davis et al. 2011). Detrital magnetite and ilmenite in quartz arenite are variably replaced by quartz arenite hematite.

The mineral association and textures of a large proportion of iron oxides in the Kiggavik till samples resemble that from the Kiggavik igneous and metasedimentary basement, as well as sedimentary bedrock. The study of till grains by SEM indicates that the surface of the majority of iron oxide grains are imprinted by mechanical textures that are diagnostic of transportation by glaciers such as crater, arc-shaped steps (Fig. 3B), conchoidal fractures, troughs, and crescentic gouges. These mechanical textures on the surface of 70% of detrital grains are masked by iron oxide coating (Figs. 3a & b). The porous nature of the iron oxide coating (Fig. 3A) indicates it formed under unstable physicochemical conditions (Makvandi et al. 2015).

The integrated EPMA--LA-ICP-MS data of iron oxides from Kiggavik rocks were analyzed by PCA (Fig. 4a). Hematite from metagreywacke and quartzite form distinct clusters because of higher U and Si values respectively. The anomalous U content (450 ppm) and detrital origin of metagreywacke suggest that these grains were eroded from uranium-rich lithologies in which they had incorporated U into their crystallographic structures (Stewart et al. 2009). LDA of PCA factors was carried out to classify iron oxides in Kiggavik rock samples (Fig. 4b), and use the classification model to predict the sources of iron oxides in the till samples (Figs. 4c & 5).
Figure 4. a Principal component analysis (PCA) of iron oxides chemical data from Kiggavik bedrock samples. b Linear discriminant analysis (LDA) of PCA factors for Kiggavik bedrock data. c Projection of till iron oxides geochemistry onto the model defined by LDA of bedrock data. Colored polygons limit the field for various Kiggavik bedrock samples from b. Abbreviations: M: magnetite; H: hematite; Gr: granite; Qzr: quartz arenite; Lg: leucogranite; Ms: mafic syenite; Mt: Martell syenite; Qz: quartzite; Mg: metagreywacke. T replaces prefix 10-MPB- in till samples names.

The LDA shows that 10% of hematite grains from quartz arenite share similar chemistry with hematite from Kiggavik granite (GrH) or leucogranite (LgH), consistent with the evidence of Kiggavik igneous basement in the overlying sedimentary basin. LDA-PCA of chemical data indicates that hematite and magnetite from leucogranite and martell syenite share similar chemistry (Figs. 4a &b). The chemical data of Kiggavik till iron oxides were projected into the models defined by LDA-PCA of iron oxides in Kiggavik bedrock (Fig. 4c). The results summarized by the histograms in Figure 5 show that the majority of till iron oxides were derived from the local bedrock lithologies at the Kiggavik area, whereas 2% are from unclassified sources.

However, the chemical signature of hematite in metagreywacke is not evident in till grains that are 0.5 to 2.0 mm in size because of its fine-grained nature in the metagreywacke. This absence suggests that to use oxides for provenance studies using Kiggavik till samples, investigating smaller size fractions of the till is essential. As shown in figure 5, quartz arenite is the source of 60% of iron oxide grains in Kiggavik till.

Figure 5. Histograms summarize sample classes predicted by LDA for iron oxides in Kiggavik till. Till- replaces prefix 10-MPB- in till samples names.

Conclusions

This study indicates that iron oxides morphological, textural and chemical data can be used for provenance studies and for mineral exploration in glaciated terrains and uranium rich settings of Canada and worldwide. Combining PCA and LDA is a robust method to discriminate different bedrock lithologies, and distinguish the origin of iron oxides in unconsolidated sediments.

Acknowledgements

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References


A mineralogical characterisation of the A1, A5 and UE1A reefs at the Cooke 3, Sibanye gold mine, Randfontein, South Africa

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Abstract. Cooke 3-shaft in the West-Rand of Johannesburg is characterised by conglomerate-reefs and quartzite layers of the Witwatersrand Supergroup, deformed into an east-west trending anticline. These occur as one band (UE1A) on the western-limb of the anticline, which subdivides into multiple conglomerates (A5-A1) on the eastern-limb. This study aims at discriminating reefs using mineralogy and provides deportment information for gold (Au), uranium (U) and thorium (Th). Thirty-one minerals were detected using the MLA (Mineral Liberation Analyser). Similarities were seen in the UE1A and A5-reefs as both are relatively depleted in all major minerals, in comparison to the A1. The A1 and UE1A-reefs were investigated for the nature and distribution of Au, U and Th, using grading analysis, heavy liquid separation (HLS) and examined using a FEI (600 F MLA). Analysis indicates a fine-grained deportment for the minerals of interest with a pronounced upgrading of U and Th into the fine-grained fractions. HLS effectively upgrades the Au and sulphur (S), whilst the U and Th are lost to the slimes and sinks fractions. The native-gold and electrum found in sinks are associated with sulphides and quartz with uraninite and brannerite both associated with quartz, muscovite, pyrite, pyrophyllite, xenotime, monazite, zircon and arsenopyrite.

1 Introduction

The mine properties where the samples were collected from are located in the Cooke section; a region situated about 35 km south-west of the city of Johannesburg South Africa, at the town of Randfontein.

Discussions with then, Rand Uranium geologists revealed that a correlation between some of the reefs that are associated with the anticline at Cooke 3, still remains a problem. Geologists at Rand Uranium had difficulty in determining whether the UE1A-reef on the western limb of the anticline is a correlative of any of the A-reefs on the eastern limb of the anticline, and macroscopic characteristics of the reefs have proven to be an unreliable tool for discrimination purposes. It was therefore suggested that a mineralogical discrimination study be undertaken in an attempt at differentiating the various reefs within Cooke 3.

An extension to this study entailed investigating the mineralogical associations of Au- and U-bearing reefs through gravity based HLS and grading analyses. This was done so as to provide further details on the behaviour of the reefs and their mineralogy when subjected to common recovery/upgrading methods in the metal extraction phase of mining, within the metallurgical plants.

The use of mineralogy to discriminate between the reefs at Cooke Section has been attempted before in a preliminary manner through e.g. optical methods and X-ray diffraction (Tucker, 1980 and De Waal, 2009), with encouraging results obtained and this present study build on to the studies of Tucker (1980) and De Waal (2009) with the application of more modern technology.

2 Methods

For mineralogical analysis, 13 channels were sampled using the conventional chip sampling method, used by the mine. The samples were crushed and split. 30 mm grain mounts were produced from aliquots derived from the split samples. These mounts were subjected to mineralogical abundance quantification as possible through quantitative MLA-based modal abundance protocols such as XMOD.

A standard file on the various mineralogical phases encountered was created on the MLA and complemented by quantitative XRD (X-ray diffraction) data. Mineral identification and abundances were quantified using integrated backscatter electron (BSE) images and energy dispersive spectrometry (EDS) analyses. The average atomic number determines the number of backscatter electrons emitted by the mineral and hence is directly proportional to the grey level registered in the BSE image (Fandrich et al. 2007).

For deportment studies, channel samples of four reef panels weighing approximately 10 kg each were chosen. Reef types collected comprise of the A1 (samples Lethu 1 and Lethu 4) and the UE1A (samples Lethu 2 and Lethu 3) ore horizons. These panels were composited, crushed and milled using a cone-crusher and a ball mill, to 80% passing a 75 μm for the best Au and U liberation. These samples were reweighed and put through several splitting rotations before assaying.

Polished flat grain mounts were prepared from the sinks fraction of the HLS. These samples were analysed under two measurement modes, the SPL_DD_Lt routine (SPL_Lt) as well as the XBSE routine on the MLA. Au
and U deportments, modal abundances, BSE images were obtained. Head chemistry assays were conducted through X-ray fluorescence (XRF) for the major elements. The total sulphur and carbon was analysed using Leco, a combustion infrared detection technique. For the trace elements (Cu, Ni, Pb, Zn, Sh, Te, Hg and Bi), an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used. The grades for arsenic and silver were ascertained from Atomic Absorption Spectroscopy (AAS) and the Au assays were determined by fire assay.

Grading analysis was conducted by screening the material into 6 size fractions, +150 μm, 106 μm, 75 μm, 53 μm, +25 μm and -25 μm, with each fraction assayed for its Au, S, U, and Th content. A portion of the sample aliquots were split and deslimed at 25 μm and treated with TBE, at 2.96 g/cm³ SG. In the dense medium separation the Au, S, U and Th distributions were calculated for the slimes, floats and sinks of each of the samples.

### 3 Between-reef mineralogical discrimination

The minerals detected within the reefs are listed in table 1 below. Amongst these minerals, only a few are relatively more abundant than all the minerals associated with Au and U. Modal abundance data from all three reef types suggest that albite, chlorite, muscovite, pyrite and pyrophyllite are relatively most abundant within the A1-reef. Albite, muscovite and pyrite are least abundant within the A5-reef. Quartz, uraninite and zircon are most abundant within the A5 and least abundant within the A1-reef. The UE1A-reef occurs in between the A1 and A5-reefs in mineral abundance with the exception of pyrophyllite and chlorite, in which it is found to be the least abundant. All three reef types are depleted in all other minerals relative to the major minerals. A5 and UE1-reefs are more similar in mineralogy when compared with the A1 reef by means of discriminant function analysis a tool in multivariate statistics.

### Table 1. Average modal abundances in approximate wt. %, of all the minerals detected within all reef types. Weight of Unknown = mineral not present in the standard file – probably a mixture of fine grained minerals which cannot be resolved under the beam. Invalid = EDS counts too low to allow for mineral classification.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>A1</th>
<th>UE1A</th>
<th>A5</th>
<th>Mineral</th>
<th>A1</th>
<th>UE1A</th>
<th>A5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>0.279</td>
<td>0.097</td>
<td>0.087</td>
<td>Iron metal</td>
<td>0.0453</td>
<td>0.0237</td>
<td>0.0414</td>
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<td>Apatite</td>
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<td>0.0086</td>
<td>Muscovite</td>
<td>0.0904</td>
<td>0.0033</td>
<td>0.0081</td>
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<td>Arsenopyrite</td>
<td>0.0734</td>
<td>0.0729</td>
<td>0.0719</td>
<td>Monazite</td>
<td>0.0914</td>
<td>0.0028</td>
<td>0.0066</td>
</tr>
<tr>
<td>Biotite</td>
<td>0.0035</td>
<td>0.0033</td>
<td>0.0066</td>
<td>Muscovite</td>
<td>0.7729</td>
<td>0.0587</td>
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<tr>
<td>Biotite</td>
<td>0.0075</td>
<td>0.0145</td>
<td>0.012</td>
<td>Pyrite</td>
<td>1.0609</td>
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<td>1.1434</td>
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<tr>
<td>Bramante</td>
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<td>0.0768</td>
<td>Pyrochrocite</td>
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<td>7.9862</td>
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<tr>
<td>Hornblende</td>
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<td>0.0491</td>
<td>Pyrochrocite</td>
<td>0.0685</td>
<td>0.0781</td>
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<tr>
<td>Carbon</td>
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<td>0.0046</td>
<td>0.0062</td>
<td>Quartz</td>
<td>0.6714</td>
<td>7.2064</td>
<td>7.5253</td>
</tr>
<tr>
<td>Calciopyrophyllite</td>
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<td>0.0145</td>
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<td>Rutile</td>
<td>0.1353</td>
<td>0.0832</td>
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<tr>
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<td>0.1471</td>
<td>0.3327</td>
<td>Sc-Cr-Borneoite</td>
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<td>0.0927</td>
<td>0.1310</td>
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<tr>
<td>Chromium</td>
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<td>0.0824</td>
<td>0.0757</td>
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<td>0.0242</td>
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<td>0.0486</td>
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<td>Dolomite</td>
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<td>0.001</td>
<td>0.0002</td>
<td>Xenotime</td>
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<td>0.0252</td>
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<td>Magnesite</td>
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<td>0.0002</td>
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<td>Zircon</td>
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<td>Unknown</td>
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<td>0.191</td>
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<tr>
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<td>0.0005</td>
<td>0.0004</td>
<td>Irmax</td>
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<td>0.1786</td>
<td>0.1775</td>
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<tr>
<td>Irmellite</td>
<td>0.0007</td>
<td>0.0011</td>
<td>0.0014</td>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

### 4 Au, U and Th deportment

#### 4.1 Heavy liquid separation and grading

Figure 1. Results from the heavy liquid separation analysis for gold, uranium, sulphur and thorium in Lethu 1 to Lethu 4.

The results of the HLS analyses are depicted in figure 1. These results indicate that the Au is successfully upgraded into the sinks with exception to the Lethu 4 in which the floats show almost 50 % upgrading. U and Th behave in a different manner to that observed in the Au and S. The majority of the U and Th report mainly to the slimes and floats fractions and a lesser proportion to the sinks. This is the instance with three of the four samples analysed. Lethu 3 shows better upgrading of U into the sinks (74%).

#### 4.2 Modal mineralogy and Au and U speciation – HLS sinks

The modal abundances reveal that the sinks are predominantly pyrite-rich. The silicates constitute a small proportion of the sinks wt%; this is to be expected, with lesser oxides in all the samples.

Two Au alloys are present in the sink samples, native Au (Au) and electrum (Au,Ag), with ~95% of the Au detected to be native Au. Two uranium-bearing phases were detected, uraninite (UO₂) and brannerite ((U,Ca,Fe,Y,Th)₃Ti₅O₁₆). Illustrated in figure 2 are gold and uranium particles observed in the concentrated sink samples.
4.3 Liberation and particle associations

Mineral liberation by particle composition data for gold indicates that almost 80% of the gold mass recovery has gold particles which are 70-75% liberated. The recovery rates then steadily decrease until about only 5% of the recovered mass is 100% liberated gold (Figure 3). The uraninite recovery is variable for Lethu 1 and 2, 80% of uraninite particles are seen to be in the 60-65% liberation class, whereas Lethu 3 and 4 perform differently and have a lower compositional liberation state of about 50% of the recovered mass at 35-40% liberation (Figure 3b). For the brannerite, ~70% of the cumulative recovered mass has compositional liberation of 50-55% for all the samples.

The MLA maps the particles and details the mineral locking state according to the associations of the minerals of interest. The minerals of interest which are not completely liberated are classed as either binary, implying that the mineral of interest is enclosed within or attached to one other mineral phase, or classified as a ternary+ particle, where two or more phases are associated with the mineral of interest (Figure 4). Ideally, with grinding and milling the aim is to liberate the particles completely; however this is not always achieved.

The ternary+ locking of gold particles accounts for less than 16wt% of the sink samples. Gold is associated with sulphides as well as the silicates, with a minor proportion of gold associated with uranium bearing phases and oxides. The uraninite particles are to a greater extent locked in particles consisting of brannerite, sulphides, silicates and all four samples indicate a locked state with carbon as well as the phosphates.
5 Discussion and conclusion

The application of statistics to mineralogical discrimination of the reefs proved to be successful in that minerals with discriminative powers were identified and to which discriminant function analysis was applied for the various reefs and sampling locations. Distinct grouping of the various reefs and sampling locations was achieved with respect to the variation in mineralogy. Discriminant function analysis was able to provide an understanding of the mineralogical variation within the various samples with respect to the minerals which showed discriminative powers. These minerals were determined by statistical techniques in the present study and similar previous studies, to be quartz, muscovite, pyrophyllite, chlorite and pyrite. Two mineralogical enrichment zones or domains were obtained and they are the chlorite enrichment zone/domain as well as the pyrite, pyrophyllite, quartz and muscovite enrichment zone/domain. Samples that were more abundant in chlorite were less abundant in pyrite, pyrophyllite, quartz and muscovite and vice versa. The majority of these samples were from the A1-reef. Some samples are depleted in the minerals that are used to define the enrichment zones. This is seen mostly within the A5 and UE1A samples. This could suggest that there are more similarities in mineralogical enrichment/depletion within the A5 and UE1A samples than there are between the A1 and A5 as well as between the A1 and UE1A samples. This could mean that the UE1A on the western limb of the Cooke 3 anticline could be the equivalent of the A5-reef on the eastern limb of the anticline.

As is known to be the occurrence, the gold in the Witwatersrand reefs occurs as native gold and electrum, while the uranium is deport ed in the uraninite and refractory brannerite.

The liberation data provides information on the state of the particle compositions and percentages of the external surface which is available for leaching and flotation, and based upon these findings, extra milling time, can further liberate the gold, however, the same may not be the solution for the uranium phases. Between the HLS and the screening of the material, HLS proves the superior pre-concentrator of gold, whilst screening is more effective with uranium and thorium upgrading.

Further metallurgical test work on the recovery of gold and uranium, particularly leaching tests, need to be conducted in order to gain better insight into the effects of the refractory nature of the gold and uranium to confidently report on the nature of the department of minerals of interest within the Cooke reefs in its entirety.

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References


Timing of uranium mineralisation from Mesozoic Nong Son Basin, Central Vietnam and its implication for regional sandstone-hosted uranium metallogeny

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Abstract. The geology, mineralogy and geochemistry of a uranium occurrence in the Nong Son Basin support the presence of roll front type mineralization. The special attention was given to coffinite, as a target for chemical age dating. WDS analyses show minor concentration of V2O5 up to 0.435 wt.% FeO up to 0.576 wt.% and P2O5 up to 1.395 wt.%. Four different stages of coffinite precipitation have been distinguished. The older one took place at 144 Ma. This episodic stage was followed by 122-86 Ma, 73-51 Ma and quite young ranging between 44-and 14 M years.

1 Introduction

The main part of this study has been conducted on the drill core collected from a drill hole (GK26604) located in the southwestern margin of the Nong Son at a depth of 80.4-81.4 m (Figure 1), which is stored at the Radioactive and Rare Minerals Division, General Department of Geology and Minerals of Vietnam. The samples collected from the coarse-grained sandstone members that interlayered with siltstone, mudstone, and shale.

2 Regional geological setting

The east central portion of Indochina Block (terranes derived from Gondwanaland in the Devonian) comprises complex lithotectonic entities, which formed during a long-lived, multi-episode tectonic history (Tran et al. 2014). The ‘core’ block, generally known as the Kontum Massif, consists of dominantly high-grade para- and ortho-gneissic rocks of Precambrian ages (e.g., Tran and Vu 2011; Tran et al. 2014). The Kon Tum Massif adjoins dominantly Early-Middle Paleozoic, low-grade, strongly deformed sedimentary rocks of the Truong Son fold-thrust belt in the north by a major tectonic break, namely the Tam Ky – Phuoc Son Suture, which formed during late Silurian-Early Devonian time (Usuki et al. 2009; Tran et al. 2014). These are intruded by numerous magmatic complexes of varying age and origin, from Late Silurian to Triassic and affected by Permo-Triassic (i.e. ‘Indosinian’) thermotectonism (Tran and Vu 2011 and Tran et al. 2014) for detail discussion.

Within the northern margin of the Kon Tum Block, a Mesozoic, subcontinental basin infilled by mostly grey molasse deposits was formed, namely the Nong Son Basin (Nguyễn Văn Trang 1986; Cat et al. 1991; Fig. 1). Current available geological data (Nguyen 1986; Cat et al. 1991; Tran and Vu 2011) show that the Nong Son Basin is an open, northeast-southwest trending syncline, which include 2 subbasins that are separated by a fault-bound horst structure (Fig. 1). The basin is surrounded and underlain by numerous rock types, including highly metamorphosed Precambrian gneisses, Early Paleozoic supracrustal siliciclastic, volcanicogenic and carbonate assemblages, Middle Triassic siliciclastic and felsic volcanic sequences; all of which are intruded by numerous magmatic complexes ranging in age from Ordovician to Early Triassic (e.g. Nguyen and Tran 2016).

The basin is covered by several thick sequences of Mesozoic continental deposits: the lower part comprise Norian-Rhaetian grey molasse deposits comprising dominantly polymictic conglomerate, gritstone, siltstone, thin layers or lenses of carboniferous shale and antracite coal seams that form part of the Nong Son Formation (T3n- r ns; Fig. 1; Nguyen 1986). These in turn are unconformably overlain by the Early Jurassic continental deposits of the Tho Lam Formation (J1 tl) consisting of conglomerate, gritstone, sandstone in the lower part and pebbly gritstone, dark-grey and marly mudstone in the upper part.

Recent structural interpretation (Tran et al. 2014) demonstrated that the currently tectonic configuration of the Nong Son Basin and its underlaying basement were consequence of multiphase thermotectonic history in which the Paleozoic assemblages have under gone several phases of ductile deformation and associate high-grade thermal heating during regional orogenesis. The Mesozoic assemblages, including Nong Son and Tho Lam formations on the other hand were affected by folding and several phases brittle faulting, which led to the modification of the basin in to the syncliroria and subsequent fracturing with numerous fault systems, creating complex regional interference pattern (Fig. 1). Within the Nong Son Basin, numerous uranium showings have been identified and investigated during the last 20 years. They are hosted within the sandstone uranium showings commonly occur in medium to coarse-grained sandstone layers and lenses.
that are interbedded with shale/mudstone units. Locally, the host rocks contain variable amounts of carbonaceous materials, pyrite, and chlorite in the reduced sandstone units. The mineralizations commonly occur as pods, pockets, small lenses, veinlets and stockworks that host pitchblende, coffinite and some other secondary uraniferous minerals. The uranium showings normally occur along the contact zones between the oxidized reddish rocks and the reduced grey sandstones, indicating a typical roll-front type mineralization. In addition, tabular type, and tectonic/lithology type mineralizations are also observed, the later occurs along permeable fault zone that cross-cut the mineralized zones.

3 Analytical methods

The chemical analyzes of coffinite were performed using a JEOL SuperProbe JXA-8230 electron microprobe (EMP) at the Laboratory of Critical Elements at the University of Science and Technology. The EMP was operated in the wavelength-dispersion mode at an accelerating voltage of 15 kV, a probe current of 40 nA, focused beam with a diameter of 3 μm. Counting times peak/background (in sec.) were as follows: Si 10/5, Al 10/5, S 20/10, U 120/60, Y 45/15, P 20/10, Ti 20/10, Th 120/60, Ca 20/10, Pb 180/90, V 10/5, Fe 20/10 and As 20/10. The following standards, lines and crystals were used: albite (SiKα, TAP; AlKα, TAP), anhydrite (Skα, PETJ), UO2 (UMβ, PETJ), YPO4 (YLA, PETJ; PKα, PETJ), rutile (TiKα, LIF), ThO2 (ThMa, PETH), wolastonite (CaKα, PETH), Crocoite (PbMa, PETL), V (VKα, LIFH), Fayalite (FeKα, LIF) and GaAs (AsLa, TAPH). Data were corrected to the ZAF procedure using an original software.

The procedure of age determination was based on JEOL software Monazite Age Dating using age equations from Suzuki et al. (1991, 1994). Raman spectroscopy was used to confirm presence of OH group in analyzed coffinites.

4 Mineralogy and geochemistry

In the investigated samples coffinite occurs as a cement in altered sandstone. Together with coffinite, carbonate,
phosphate, clay, pyrite, galena and clausthalite have been identified. Coffinite formed rims surrounding clastic grains, and was heterogeneous, confirmed by the differences in reflectivity of this mineral, porosity and chemical composition.

![Figure 2](image1.png)

**Figure 2.** WDS contour maps showing distribution of Ca in coffinites and apatite crystals (red-white)

Phases characterized with lower reflectivity contain higher amounts of Ca, and lower value of SiO₂ and usually also UO₂ (Tab. 1).

![Figure 3](image2.png)

**Figure 3.** WDS contour mas showing distribution of U in coffinites (red spots)

### Table 1. WDS composition in wt. % of some coffinite points

<table>
<thead>
<tr>
<th>No.</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>UO₂</th>
<th>FeO</th>
<th>SiO₂</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.12</td>
<td>1.75</td>
<td>71.89</td>
<td>0.14</td>
<td>16.19</td>
<td>91.09</td>
</tr>
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<td>9</td>
<td>0.94</td>
<td>3.28</td>
<td>75.60</td>
<td>0.24</td>
<td>11.51</td>
<td>91.57</td>
</tr>
<tr>
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<td>1.81</td>
<td>72.87</td>
<td>0.11</td>
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<td>4</td>
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<td>15.76</td>
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<td>11.37</td>
<td>91.14</td>
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### Table 2. Ages of coffinites calculated from each individual data point.

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<thead>
<tr>
<th>no</th>
<th>ThO₂</th>
<th>UO₂</th>
<th>PbO</th>
<th>Age (Ma)</th>
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<td>61</td>
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<td>18</td>
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<td>0.43</td>
<td>44</td>
</tr>
<tr>
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<td>0.71</td>
<td>73</td>
</tr>
<tr>
<td>6</td>
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<td>0.36</td>
<td>37</td>
</tr>
<tr>
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<td>0.50</td>
<td>51</td>
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<td>86</td>
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<tr>
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<td>0.69</td>
<td>72</td>
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</table>

n.d.- not detected
Relationship of Ca, Si and U contents are visible of WDS quantitative contour maps (Figs. 2, 3, 4). Based on WDS quantitative analyses (Table 1) and Ca WDS map (Fig. 2) it can be concluded that at least two different varieties of coffinite occur in the deposit. Some heterogeneity is also visible on WDS images (Fig. 3, 4). Total ions sum of coffinites range from 88.42 wt.% to 93.38 wt.%; a function of OH group content incorporated in the crystal structure or contamination with other light elements which are difficult to be measured using WDS techniques, e.g. carbon. The presence of OH was confirmed using Raman spectroscopy techniques. Weak and broad band at the region of 3300-3100 cm⁻¹ suggest the occurrence of some amounts of water in the coffinite structure. Analyzed grains of coffinites contain also some P₂O₅ ranging between 0.60 and 1.40 wt.%. Some apatite crystals associated with coffinite show high content of F ranging between 3.8 and 4.53 wt.% and low content of SiO₂ - 0.06-0.54 wt.%, SrO - 0.12-0.43 wt.%, up to 0.26 wt.% of REE sum and up to 0.15 wt.% of Fe (seven measurements). Three analysed points of this mineral showed also presence of small amounts of U and Th up to 1.23 wt.% and 0.08 wt.% respectively. During routine ore microscopy and EDS observations, grains of claushtalite have been recognized containing some admixtures of Bi, S, Fe and Te.

5 Discussion and conclusions

Based on both quantitative WDS measurements and microscopic observation it can be concluded presence of two different varieties of coffinite. The first one is low calcium content ranging between 1.11 and 1.96 wt.% The second is characterized with much higher Ca content ranging between 3.00 up to 5.28 wt.%. Presence of F-

apatite containing some admixtures of U and Th and claushtalite in association with the coffinite suggests precipitation of all these minerals in a low temperature digenetic environment with participation of hydrothermal waters that interacted with volcanic and volcanoclastic rocks (Nguyen and Tran 2016).

Calculations of an absolute age (Table 2) show wide range of crystallization of the uranium mineral assemblage. Based on these data, four stages of deposit formation can be proposed. The older one is about 144 Ma. This episodic stage is followed by 122-86, 73-51 Ma and quite young ranging between 44-and 14 Ma (Table 2). The first three are probably connected with tectonic activity, but the last one is of roll front origin.

Acknowledgements

The authors are grateful to MSc eng. G. Kozub from Critical Elements Laboratory of the Faculty of Geology, Geophysics and Environmental Protection UST-AGH Krakow for the WDS analyses. The authors are also grateful to UST-AGH Krakow for financial support, grant no 11.11.140.320.

References

Clay mineral host-rock alteration at the Bong basement-hosted uranium deposit, Kiggavik area, Nunavut

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Abstract. Hydrothermal host-rock clay mineral alteration at the Bong uranium deposit (Kiggavik area, Nunavut) displays similarities to the illite-chlorite alteration assemblages associated with Athabasca unconformity-type ingress-style basement uranium mineralization (illite, sudoite chlorite, Mg-chlorite, alkali-deficient dravite, APS). The mineralized zone is associated with a strongly illitic alteration halo, with sporadic Mg-rich sudoite, and minor B enrichment and APS minerals. Mg-rich sudoite ± illite occurs exterior to illitic alteration and grades progressively into background retrometamorphic Fe-Mg chloritic material. Compositionally, Bong illite resembles illite around Athabasca basement mineralization, although displaying much greater range in (Fe+Mg) content, widely variable Al, Si, K contents, and phengitic to non-phengitic compositions. However, the 1Mc illite lath polytype is dominant, with moderate amounts of "hairy" 1Mt polytype, a function of illite replacement of metamorphic mica/sericite and K-feldspar.

The chlorite is Mg-sudoite that contains significantly more Mg and less Al than the near-stoichiometric, strongly aluminous, sudoite present around Athabasca mineralization. Formed through replacement of biotite and retrograde metamorphic Fe-Mg chlorite, this inheritance is reflected by the Mg-rich composition of the sudoite. Neoformation of (aluminous) sudoite does not appear to have occurred at Bong.

B-enrichment is present at Bong, but discrete dravite is only rarely observed on a microscopic scale.

1 Introduction

The Athabasca sedimentary basin (Fig. 1) is host to some of the largest and richest uranium resources in the world (e.g., McArthur River, Cigar Lake). The mineralizing processes of these structurally-controlled unconformity-related deposits comprised complex hydrothermal systems associated with episodic fault movements and fluid flows along major brittle structural features. These structures intersect the unconformity between Archean-Paleoproterozoic metamorphic crystalline basement rocks and overlying sandstone strata present in the Paleo- to Mesoproterozoic intracratonic Athabasca Basin (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Jefferson et al. 2007; Dahlkamp 2009; Fayek 2013).

There are two styles/sub-types of unconformity-related uranium deposits (Quirt 2003; Jefferson et al. 2007; Fayek 2013). (1) Sandstone-unconformity deposits, or egress-style unconformity-related deposits (e.g., Cigar Lake, Midwest, Collins Bay B), in which the mineralization is dominantly located immediately above, or straddling, the unconformity and is associated with large, broad clay mineral alteration halos. (2) Basement deposits, or ingress-style deposits (e.g., Eagle Point, Millennium, Cluff Lake, Sue C), in which the mineralization is hosted by the metamorphic basement rocks, consists of breccia- and fracture-hosted mineralization, and displays host-rock alteration closely located to the structural features.

The uranium mineralization textures include disseminated and vein uraninite/pitchblende in fractures, breccia matrix, and host rock replacement. The diagenetic-hydrothermal metallogenic model attributes the precipitation of the uranium minerals to redox reactions and the formation of the associated host-rock clay alteration minerals to hydrolytic acid-base reactions (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; 1987; Fayek and Kyser 1997).

The uranium deposits of the Kiggavik area, western Nunavut, including the Bong deposit, have been historically attributed to ingress-style, basement-hosted unconformity-related metallogenesis (Fuchs and Hilger 1989) and are located in the NE Thelon Basin region (Fig. 1).

2 Geologic setting

The Paleo- to Mesoproterozoic Thelon Basin of western Nunavut contains dominantly alluvial siliciclastic strata that developed in the interior of the western Churchill Province of the Canadian Shield after the Paleoproterozoic suturing of the Rae and Hearne cratons (Hoffman 1988) (Fig. 1). It is strongly analogous to the Athabasca Basin.

The basement to the Thelon Basin contains Archean granitoid gneiss, Neoarchean supracrustal rocks of the Woodburn Lake group (Pipedream and Marjorie Hills assemblages), and Snow Island Suite (Peterson et al. 2015), and the early Paleoproterozoic Ketyet River group (Hadlari et al. 2004; Pehrsson et al. 2013). These were unconformably overlain by the Paleo- to Mesoproterozoic Dubawnt Supergroup during and following the Trans-Hudsonian Orogeny (Rainbird et al. 2003; Hiatt et al. 2003).

The circa 15 km-thick undeformed Dubawnt Supergroup contains three sedimentary sequences that fill the Baker Lake and Thelon Basins: Baker Lake Group, Wharton Group, and Barrenland Group. The circa 1.5 km-thick Thelon Formation (Barrensland Group), comprising three dominantly alluvial upward-fining siliciclastic sequences (Hiatt et al. 2003), is the dominant unit filling the Thelon Basin, unconformably overlying the older sequences. In the western part of the basin, the Thelon Formation is capped by <10 m of 1.54 Ga Kuungmi Formation ultrapotassic basaltic flows (Chamberlain et al.
that underlie ~50 m of Lookout Point Formation siliceous stromatolitic dolostone (Gall et al. 1992).

The Kiggavik uranium camp is located ~80 km west of Baker Lake, Nunavut, and lies immediately south of the Aberdeen Sub-basin of the Thelon Basin, just south of the Thelon Fault. This fault is a northeast-striking north-side-down dextral oblique-slip composite fault that juxtaposes the Thelon Formation to the north against metasedimentary basement to the south. There are several uranium deposits/prospects in the camp, including Kiggavik, End, Andrew Lake, Bong, Tatiggaq, and Contact.

The Bong deposit is hosted by Pipedream assemblage psammopelitic metasediments.

Drill core samples were collected from ten diamond drill holes that intersect the Bong deposit or intersected material located outside of the alteration halo. Polished thin sections were prepared for SEM microscopy and quantitative electron microprobe wavelength-dispersive spectroscopy (WDS-EMP) analyses. Rock samples were crushed and ground for lithogeochemical and X-Ray Diffraction (XRD) analyses.

Clay-size fractions of the samples were examined using an automated Philips XRD powder diffractometer. Thin sections were carbon-coated and examined using a JEOL JSM-5900 SEM. Quantitative micro-chemical analyses of the clay minerals were carried out using a JEOL JXA-8600 Superprobe with an EDS detector and five WDS detectors. Beam current was 10 nA and accelerating voltage was 15 kV.

3 Sampling and methods

4 Results and discussion

Optical and SEM microscopy indicate that the clay alteration minerals replace feldspar, biotite, retrograde metamorphic Fe-Mg chlorite, and muscovite in the host psammopelitic gneiss. Desilicification has resulted in a strongly clay-enriched rock due to dissolution of quartz. XRD and WDS-EMP analyses show that the host-rock alteration mineralogy comprises mixtures of illite and Mg-sudoite, with trace amounts of APS minerals (variably goyazite-svanbergite to florencite in composition). Lithogeochemical analyses of background material returned B contents of 10 to 170 ppm, as compared to mineralized material showing B enrichments ranging from 300 to 720 ppm B. However, discrete dravitic tourmaline was only very rarely observed on a microscopic scale and was below XRD detection limit.

Mineral chemical data for Bong illites typically fall into a range similar to that for Athabasca basement alteration illite (Fig 2), however, the presence of illite/sericite from altered feldspar is evident.

However, while Bong illites contain Al and K contents similar to Athabasca equivalents (Figs. 3, 4), they show a much greater range in (Fe+Mg) content (Fig. 3). The additional relict K in illite/sericite from altered feldspar is evident in the data points stretching toward the K apex. Bong illite is widely variable in Si and K contents, with both phengitic compositions and non-phengitic compositions being present (blue symbols; Fig 4). The Bong illites differ from the Athabasca illites in having compositions extending into the phengitic region. Similarly, the Bong illites display a much wider range in Al than Athabasca basement alteration illites. Muscovite (red symbols) shows typical Si and K contents, although there are a number of analyses (not shown) with more variable values that may be illite-muscovite mixtures.
While the 1Mc illite polytype is dominant in the Bong alteration halo, the presence of hydrothermal 1Mt illite (Laverret et al. 2006) is locally significant (Fig 5).

The Al contents in Bong sudoites are significantly restricted (low) relative to the Athabasca basement example (Dawn Lake deposit; Fig 6). No stoichiometric Al-Mg di/trioctahedral sudoite is present at Bong; only Mg-sudoite.

Bong mineral chemical data for biotite, retromorphic chloritized biotite, and hydrothermal chlorite show a relatively restricted range from biotite and chloritized biotite to Fe-Mg retrograde metamorphic chlorite, and to Mg-sudoite (Fig. 2). The Mg-rich composition of the Bong sudoite (lack of sudoite, sensu stricto) reflects the origin of the sudoite through replacement of Mg-chlorite and Fe-Mg chlorite rather than neoformation or replacement of aluminous species, such as kaolin or illite.

The crystal/grain morphology of the coarse-grained alteration illite (platy, lath-like 1Mc polytype) and the finer-grained hydrothermal illite (“hairy”, wispy 1Mt polytype) differ from altered basement metamorphic micas. Relatively little 1Mt illite is present in the Bong basement material, similar to the situation in Athabasca basement alteration.

Bong hydrothermal illite show features similar to Athabasca unconformity-related hydrothermal illite (crystallinity, XRD mineralogy) and the same illite polytypes (1Mc and 1Mt) are present. Bong muscovite is a 2M1 polytype.

There are some mineral chemical differences in contents of Fe+Mg (higher) and Al and Si (wider ranges)
between Bong alteration illites and Athabasca basement alteration illites.

Bong Mg-sudoite shows features similar to sudoite present in Athabasca basement alteration halos, however, stoichiometric hydrothermal sudoite (Al-Mg chlorite), like that found in Athabasca sandstone, in basement below the sub-Athabasca unconformity, and in basement alteration halos, is not present at Bong.

Mineral chemical differences between Athabasca basement sudoites and Bong sudoites include important differences in Al, Mg, and Fe contents. The Bong sudoite is rich in Mg and significantly lower in Al: a Mg-sudoite. This reflects the origin of the sudoite through replacement of Mg-chlorite and Fe-Mg chlorite rather than by neoformation.

However, overall, the illitic and chloritic host-rock clay alteration characteristics at Bong are similar to those observed in Athabasca basement alteration halos and support the premise that the Kiggavik deposits may be of the unconformity-related type.

Acknowledgements

Earlier work on Kiggavik clay mineral alteration was carried out by the author in conjunction with Prof. Daniel Beaufort and PhD student Thomas Riegler, Université de Poitiers, Poitiers, France.

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Exploration of uranium unconformity-related basement hosted deposits based on 3D gravity modelling: A case study from the Contact prospect, Kiggavik, Nunavut (Canada)

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Yoann Richard
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Abstract. In unconformity-related uranium deposits, mineralization is associated with a hydrothermal clay-rich alteration halo that can drastically decrease the density of the metamorphic host rock. In the Kiggavik uranium project, located in the Eastern Thelon basin region, Nunavut (Canada), various basement-hosted shallow deposits were discovered by drilling both airborne and ground geophysical anomalies in the 1970s. In 2014, gravity data was inverted for the first time using the Geosoft VOXI Earth Modelling software to generate three-dimensional (3D) models to assist exploration targeting on the Kiggavik project. For the Contact prospect two 3D gravity models were implemented at two different exploratory phases. An unconstrained model was first computed to produce a 3D density contrast model without any a priori information. A constrained model was computed later using density values measured on core samples collected following the initial drill program. The unconstrained model provided a first approximation of the geometry and depth of the low density body. The constrained model highlights three shallower and smaller low density bodies that match well the geological model. This study case demonstrates that 3D inversion of gravity data is a valuable tool to guide geologists in exploration for shallow basement-hosted uranium deposits associated with alteration halos.

1 Introduction

The Kiggavik uranium project is located approximately 80 km west of Baker Lake in Nunavut Territory, Canada (Fig. 1a). The deposits discovered are attributed to unconformity-related basement hosted uranium types (Miller and LeCheminant 1985; Miller et al. 1989; Riegler et al. 2014; Chi et al. 2016). In this area, the uranium mineralization is associated with pervasive hydrothermal alteration halos around the deposits that extensively alter the original physical property of the rock leading to significant geophysical anomalies (Hasegawa et al. 1990).

Uranium was discovered at Kiggavik by ground truthing an airborne radiometric survey conducted in the mid-1970s by Urangesellschaft Canada Limited (UGC). A series of deposits were subsequently discovered in the late 1970s (e.g., Main, Center Zone and East deposits) and in the mid-1980s with the introduction of EM airborne surveys (e.g., Bong, End and Andrew deposits). The Contact area (Fig. 1b), characterized by a low gravity anomaly, was originally drill tested in 1992. It was re-evaluated in 2013 by a GIS-based mineral prospectivity analysis of the available airborne data (Robbins et al., 2015) and drill tested again in 2014. Drilling continued in 2015 based on initial results and a new geophysical ground gravity survey.

Figure 1. a Location of the Kiggavik uranium project. b Simplified geological map of the southern Kiggavik project (i.e., south of the Judge Sissons fault) showing the location of the Contact prospect and the Andrew and End deposits along the Andrew Lake fault trend.

2 Geological setting

The Contact prospect is located within the hanging wall of the Andrew Lake fault corridor (Fig. 1b). The fault zone is defined by a northwest steeply dipping fault corridor formed by tens of meters-thick quartz-sealed breccia.

The mineralization is hosted in granitic gneiss of Archean age (> 2.65 Ga; Jefferson et al. 2007), locally in Hudsonian granite sills and related lamprophyres dykes and is surrounded by a halo of various degrees of weak to moderate alteration. This mineralization is situated in the hanging wall above a quartz-sealed breccia, and occurs as primary vein-related and disseminated pitchblende replacing/co-precipitating with minor sulphides. Note that no mineralization is within the structure itself.
3 Materials and methods

3.1 Ground gravity data

Ground gravity surveys were conducted in the Contact area (Fig. 2) using Lacoste & Romberg gravity meters with a resolution of 0.01 mGal. Gravity observations were acquired every 50 m using the looping method along profiles separated by 100 to 200 m. Start and end observations for each loop were tied to a temporary gravity base station established on the surveyed grid and tied to the main base station of the Kiggavik exploration camp. The ground gravity data was Free Air corrected, and corrected for latitude, Earth’s tides, instrument drift and an adjustment to the defined base value.

![Ground gravity grid acquired in the Contact prospect. The black frame shows the area modelled with the Geosoft VOXI inversion module. The projected surface traces of the inclined holes drilled in the area are shown by black lines.](image)

The gravity data that was used in the gravity inversion was the Bouguer Anomaly reduced at a Bouguer density of 2.70 g/cc (Fig. 2). The estimation of this density value was based on the Nettleton method (Nettleton 1939; Nettleton 1976).

3.2 Sample density data

A total of 315 drill core samples were collected from 21 drill holes for density measurements. The ~10 cm-long samples were collected systematically every 20 m or less depending on lithological changes. Densities were obtained in-house using the standard Archimedes’ principle based on mass and volume measurements (Quirt and Brulé 1990; Blaise 1998).

The densities of lithologies were grouped into 3 rock units (altered and fresh): Archean granitic gneisses, Hudson intrusives and faulted rocks (Table 1).

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3.3 3D inversion tool and modelling methodology

The gravity inversions have been completed using VOXI Earth Modelling™, a Geosoft Oasis Montaj cloud computing module that allows the inversion of geophysical data in 3D (Geosoft 2016).

Gravity data was inverted in two different ways: (i) an unconstrained inversion was first computed to produce a 3D density contrast model to highlight low density areas and position drilling targets at the first stage of exploration without any a priori information; and (ii) a constrained inversion was performed after drilling, using available density properties measured on dill-core samples.

The constrained inversion requires both a parameter reference model and a weighting model. The first reference model contains the a priori information (i.e., density measured on drill hole samples) while the second reference model provides a confidence level associated with the various regions of the parameter reference model. An additional Iterative Reweighting Inversion (IRI) constraint was applied to refine the model and emphasize both the positive fresh bedrock anomaly and the negative alteration zone responses.

The resulting models present the density variations with respect to the Bouguer density used (i.e., 2.70 g/cc). A voxel with a value of -0.25 g/cc in the resulting voxel mesh represents a rock with a density of 2.45 g/cc.

4 Results

4.1 Unconstrained gravity inversion

The unconstrained gravity inversion creates a massive low density body located beneath the gravity anomaly (Fig. 3a). This "bean"-shape body is oriented along a N045° trend. The depth of the top of the body is about 120 m below the surface in the southwest and 150 m deep in the northeast (arrows nos. 1 and 2 in Fig. 3a).
The constrained gravity inversion shows that the main body splits into three smaller and shallower low density bodies. The first body is approximately 170 m long by 60 m wide, and its top is at a depth of 60 m (arrow no. 1 in Fig. 3b). It is constrained by two adjacent holes characterized by fresh granites and granitic gneisses. The second body is located 200 m to the northeast from previously described body (arrow no. 2 in Fig. 3b). It is approximately 180 m long and 120 m wide. The top of this low density body nearly outcrops. This second body is caused by strongly altered or strongly bleached granitic gneiss containing mineralization. The third body is the northeastern continuation of the previous described body (arrow no. 3 in Fig. 3b). It is approximately 240 m long and 120 m wide. This third body is 40 m below the surface and extends to a depth of 180 m.

A fourth low density body appears 250 m southwest of the three previously described bodies (arrow no. 4 in Figure 3b). It has a conical shape with its apex at 450 m and roots in depth. At 600 m depth (i.e., at the bottom of the modelling workspace) it is approximately 560 x 470 m.

**Figure 3.** a Unconstrained gravity inversion model. b Constrained gravity inversion model. Data cubes clipped for density contrasts below -0.075 g/cc. The arrows show low density bodies that are discussed in the text.

**4.2 Constrained gravity inversion**

The comparison of the three low density bodies with the alteration halo built from drill core logging (i.e., 10 m size blue voxels) shows a good correlation (Fig. 4a). The best fit occurs for pod no. 2 which is the best constrained by a greater number of drill holes or number of samples. The large body located at depth (arrow no. 4 in Fig. 3b), southwest of the three alteration pods (Fig. 4a), can be explained as a response to a strong joint-type fracturing (i.e., fracture corridor) observed on the drill core that prevents systematic sampling and led to the overestimation of high densities values. The anomaly is consequently pushed deeper, just below the two southernmost drill-holes. The validity of this body is questionable as it can be an artefact created by the partial gravity coverage and the inversion process.

**5 Discussion**

The 3D gravity inversion modelling exercise was conducted...
to assist exploration in the Kiggavik project, as part of a set of tools, helping to position the discovery holes of the Contact mineralization and to characterize the 3D geometry (i.e., depth, dip and size) of low density bodies associated with mineralization and related alteration halos. For this case study two types of models were tested: unconstrained without any \textit{a priori} information and constrained by petrophysical data.

The unconstrained model was first computed to produce a 3D density contrast model. This type of modelling provided a first approximation of the geometry and depth of the low density body. Despite the poor accuracy in size and depth of this model, it provided information to the positioning of the discovery drill hole of the Contact mineralization.

The model constrained by drill core density data measured on core samples collected from the drill holes completed on the prospect, brings insights about the currently known deposit footprint. It highlights three shallower and smaller low density bodies that coincide well with the geological model generated from drill hole logging and the geological interpretation. This model allows for adjustment of the geometry of the gravity anomalies in relation to the known deposit footprint.

This study case shows that 3D inversion of gravity data is a valuable tool to guide geologists in exploration of shallow basement-hosted uranium deposits associated with alteration halos and to assess a deposit gravity footprint.

For future inversions, it is recommended to constrain the models taking into account: i) geological information of lithologies and structural features, and ii) \textit{a priori} information obtained from different probing techniques (e.g., borehole gravity, neutron density, and resistivity data).

References


The Thelon Basin, Nunavut, Canada, is similar in age, size, and geology to the uranium producing Athabasca Basin in Saskatchewan, and may share similar economic potential. The Kiggavik project area contains uranium deposits along a ~30 km long NE-SW structural trend; the Kiggavik deposit is a basement-hosted uranium deposit located near the northern end of this trend.

Multiple stages of uranium mineralization were identified at the Kiggavik deposit. Euhedral uraninite (U1; 1255 ± 20 Ma) occurs as disseminated and vein-style mineralization, has elevated Pb contents up to ~15.0 wt.% PbO, and is associated with illite and hematite. A second, Ca-rich (up to 6.3 wt.% CaO) uraninite (U2; 1106 ± 23 Ma) forms fracture-filling style mineralization along carbonate veins, and contains variable Pb contents (0.5 – 7.6 wt.% PbO). Both stages of uraninite are altered to coffinite.

Based on in situ U-Pb geochronology by SIMS, the minimum age of uraninite precipitation at the Kiggavik deposit is 1255 ± 20 Ma, however, this is likely a reset age associated with the Mackenzie dyke event (~1267 Ma). An 1100 Ma age is also observed, and is similar to ages reported for uranium mineralization from the Athabasca Basin and the Kiggavik project area.

Canada is an important global producer of uranium, second only to Kazakhstan. In 2014, Canada produced 16% of the world’s uranium from Proterozoic unconformity-related uranium deposits in the Athabasca Basin, Saskatchewan (OECD 2016). Sedimentary basins of Proterozoic age such as the Athabasca, Thelon and Borden (Canada), Kambolgie (Australia), and Espinhaço (Brazil) are economically important in terms of petroleum and metal (Pb-Zn, Cu, Au, U) production (Kyser 2007). For example, the Paleo- to Mesoproterozoic unconformity-related uranium deposits from the Athabasca Basin are among the highest-grade uranium deposits in the world (e.g., Cigar Lake and McArthur River); their anomalous grade and tonnage has promoted exploration for these types of deposits in other Proterozoic sedimentary basins across the globe.

The Thelon Basin is temporally and spatially related to the Athabasca Basin; the two basins exhibit similar geological characteristics, and may have similar economic potentials for uranium. The sedimentological, metallogenic, and fluid histories of the Athabasca Basin have been extensively studied (e.g., Hoeve and Sibbald 1978; Hoeve and Quirt 1987; Kotzer and Kyser 1995; Fayek and Kyser 1997; Ramaekers et al. 2007; Mercadier et al. 2012; Sheahan et al. 2016). In contrast, the Thelon Basin and associated uranium deposits have not been as thoroughly studied.

While textures and ages of Thelon Basin-related uranium minerals and alteration are similar to those observed in the Athabasca Basin (e.g., Fayek et al. 2002; Cloutier et al. 2009; Sheahan et al. 2016), more work is needed to understand the processes involved in the formation of the Thelon Basin-associated uranium deposits. Therefore, the objectives of this study are to: (1) characterize the uranium mineralogy, (2) determine the ages of uranium minerals, (3) identify the mechanism(s) for uranium mineral precipitation, alteration, and remobilization, and (4) develop a genetic model for the formation of the Kiggavik deposit for comparison with other deposits of the Thelon and Athabasca Basins.

2 Geologic setting

The Paleo- to Mesoproterozoic Thelon and Athabasca Basins are dominantly alluvial siliciclastic repositories that developed in the interior of the western Churchill Province of the Canadian Shield after the Paleooproterozoic suturing of the Rae and Hearne cratons (Hoffman 1988) (Fig. 1).

The basement of the Thelon Basin comprises Archean granitoid gneiss, Neoarchean supracrustal rocks of the Woodburn Lake group, Marjorie Hills assemblage and Snow Island Suite, and the early Paleooproterozoic Keyet River group (Hadlari et al. 2004; Pehrsson et al. 2013; Robinson et al. 2015). These were unconformably overlain by the Paleo- to Mesoproterozoic Dubawnt Supergroup during and following the Trans-Hudsonian Orogeny (Renac et al. 2002; Hiatt et al. 2003; Rainbird et al. 2003).

The Dubawnt Supergroup comprises three undeformed sedimentary sequences (Baker Lake Group, Wharton Group, and Barrenland Group) that fill the Baker Lake and Thelon basins with an aggregate thickness of 15 km. The Thelon Formation of the Barrenland Group is the dominant unit filling the Thelon Basin, has a maximum preserved stratigraphic thickness of 1.5 km, and comprises three dominantly alluvial upward-finining siliciclastic sequences (Hiatt et al. 2003, Davis et al. 2011).
In the western portion of the basin, the Thelon Formation is capped by 1.54 Ga ultrapotassic basaltic flows of the Kuungmi Formation (Chamberlain et al. 2010), which in turn are stratigraphically overlain by siliceous stromatolitic dolostone (~50 m) of the Lookout Point Formation (Gall et al. 1992).

The Kiggavik project area is located ~80 km west of Baker Lake, Nunavut, just south of the Thelon Fault, a northeast-striking north-side-down dextral oblique-slip composite fault that juxtaposes the Thelon Formation to the north against metasedimentary basement to the south. The Kiggavik deposit comprises three ore zones: the Main, Centre, and East. The Main Zone is at the contact between metasediments of Neoarchean age and the Lone Gull granite (~1.8 Ga), with uranium mineralization occurring in both the metasediments and granite, while mineralization at the Centre and East Zones is hosted exclusively within the metasediments.

3 Sampling and methods

Drill core samples were collected from nine diamond drill holes that intersect the Kiggavik deposit; polished thin sections were then prepared for microscopy and mass spectrometry analyses.

A Nikon Eclipse 50i POL polarizing microscope was used to examine polished thin sections to determine textural and paragenetic relationships. Sections were carbon coated and examined at higher magnification using an FEI Inspect S50 Scanning Electron Microscope (SEM). Quantitative micro-chemical analyses of uranium minerals were obtained using a Cameca SX100 Universal EPMA equipped with a Princeton Gamma-Tech (PGT) EDS detector, as well as five Wavelength-Dispersive Spectroscopy (WDS) detectors.

Uranium and Pb isotope ratios in uraninite were measured in situ using the CAMECA 7f ion microprobe at the University of Manitoba. The analytical protocol used was the same as in Sharpe and Fayek (2016). Isotopic ratios corrected for mass bias were used to calculate U-Pb isotope ages using the ISOPLOT program (Ludwig 1993); uncertainties are reported at the 2σ level.

4 Results and discussion

Host rocks for the Main Zone of the Kiggavik deposit include marginal parts of the Lone Gull Pluton, a composite 1.83 and 1.75 Ga granite (Scott et al. 2015) and Neoarchean metagreywacke and epilastic rocks. The East and Centre Zones are hosted solely by Neoarchean strata.

Uranium mineralization in the Kiggavik project area has historically been described as colloform pitchblende, showing alteration to coffinite, with reported U-Pb isotope ages ranging from 1400 to 1000 Ma (Sharpe et al. 2015); associated chlorite, hematite, and illite alteration minerals have also been reported (e.g., Miller and LeCheminant 1985). The uranium and clay alteration phases replace U-Pb-rich fluorapatite and metamorphic minerals (Robinson et al. 2016). Recent studies have shown a complex uranium paragenesis in the Kiggavik camp, with several stages of uraninite precipitation and remobilization, and multiple generations of clay mineral alteration (Riegler et al. 2014). To date, the oldest uraninite in the Kiggavik area (1520 ± 79 Ma) has been found at the Bong deposit by Sharpe et al. (2015). The same study identified two younger ages at 1114 ± 8 Ma and 982 ± 19 Ma, representing later remobilization events. These younger ages have previously been reported at the End Grid deposit for uraninite (U-Pb ages of 1293 ± 6 Ma and 1187 ± 19 Ma; Riegler 2013) and hydrothermal illite alteration at Bong (Ar-Ar age of 1124 ± 9 Ma; Riegler 2013).

Uraninite from the Kiggavik deposit is preserved as disseminated and vein-style/fracture-filling mineralization, with varying degrees of alteration to coffinite. Based on in situ U-Pb geochronology by SIMS, the oldest age of uraninite obtained at the Kiggavik deposit is 1255 ± 20 Ma, however this is likely a minimum reset age related to the Mackenzie dyke event (~1267 Ma). The younger 1106 ± 23 Ma age determined for Kiggavik uraninite is similar to ages observed throughout the Athabasca and Thelon Basin deposits (e.g., Fayek et al. 2002; Cloutier et al. 2009; Boulanger 2012; Riegler 2013; Sharpe et al 2015; Sheahan et al. 2016), and likely represents an extensive fluid event triggered by regional tectonic activity that affected both basins, possibly the Grenville Orogeny and/or Mid-Continent Rift and associated mafic magmatism (Buchan and Ernst 2004).

5 Conclusions

- Multiple styles of uranium minerals were identified at
the Kiggavik deposit: disseminated and vein-style, both associated with illite and hematite, and fracture-filling mineralization along carbonate veins. All styles of uraninite are altered to coffinite.

- The oldest determined age of uraninite at the Kiggavik deposit is 1255 ± 20 Ma; a second age of 1106 ± 23 Ma was also determined.

- An age of ~1100 Ma for uraninite has been widely reported throughout the Athabasca Basin at the McArthur and Sue Zone (1126 Ma; Fayek et al. 2002), Millennium (1091 Ma; Cloutier et al. 2009), Roughrider (1188 Ma; Boulanger 2012), and Shea Creek (1088 Ma; Sheahan et al. 2016) deposits. Studies from the Thelon Basin have also reported this age at the Bong (1114 Ma; Sharpe et al. 2015) and End Grid (1186 Ma; Riegler 2013) deposits.

- The 1250 Ma age is likely a reset age associated with movement of fluids triggered by the emplacement of the Mackenzie dyke event (~1267 Ma), while fluids associated with the 1100 Ma age may be related to mafic and anorthositic magmatism from the Grenville orogenic event and/or Mid-Continent Rift between 1180-1120 Ma.

Acknowledgements

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S05, Iron-ore, Deposit to global scale processes

Convenors:
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Fe-oxide chemistry and ore genesis: understanding the giant BIF-hosted Mt. Whaleback hematite deposit

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Abstract. LA-ICPMS data and SEM mapping on oxides from Mt. Whaleback, Australia’s largest high-grade iron ore body, show that trace element chemistry of magnetite and hematite and elemental maps can be used as tracers for multi-phase and multi-zone fluid-rock interaction during complex hematite ore genesis. It is possible to fingerprint the chemistry of carbonate-silicate alteration, which has been completely obliterated by oxidation and mineralisation. It has been traditionally suggested that iron ore is structurally controlled by the “Central Fault”, and not by the younger “Mt. Whaleback Fault”. However, this may have to be revised: Distinct trace element budgets in hematite across the deposit point to variable fluid chemistry during distinct ore forming stages. Mn-(Ba-Sr)-enriched hematite in Central Fault-controlled ore has a similar chemistry to magnetite from distal carbonate-silica altered BIF. On the other hand, enriched Ni-Mg-(V) in hematite from Mt. Whaleback Fault-controlled ore indicates fluid interaction with mafic rocks. Thus, the importance of mineralisation controlled by Mt. Whaleback Fault is probably larger than previously predicted.

1 Introduction

The present contribution is a proof of concept for unravelling the origin of hematite via mineral chemistry (Laser ablation ICPMS) and SEM element mapping. Particular aims are to identify the chemical types and internal zoning of hematite, link them to ore controlling structures and constrain differences in fluid-rock interaction.

The natural “laboratory” is the Mt. Whaleback deposit, with ~1.8 Gt Fe the world-wide largest banded iron formation (BIF) hosted martite-microplaty (M-mplH) hematite orebody. The genesis of Mt. Whaleback and other Paleoproterozoic M-mplH ore bodies in the Hamersley Province, Western Australia remains a matter of debate. Until early 2000, the widely accepted uniformitarian AMIRA-CSIRO model (Morris 1985; Morris and Fletcher 1987), proposed that martite-goethite formation was driven by giant electrochemical cells in Paleoproterozoic (~2.0 Ga) deep, supergene...
environments. Goethite in the ore is considered to be the direct precursors of microplaty hematite that formed by metamorphic dehydration at 80-100 °C.

Since the late 1990s, delineation of pervasive carbonate alteration zones in BIF located proximal to M-nplH ore at Mt. Tom Price and Paraburdoo, and advances in fluid characterisation, have led to development of hydrothermal models (Barley et al. 1999; Hagemann et al. 1999; Taylor et al. 2001; Thorne et al. 2004). For Mt. Tom Price and Paraburdoo, multistage sequences are proposed: (1) early siderite-phosphorous alteration by infiltration of basinal brines, derived from the stratigraphically lower Wittenoom dolomite, (2) heated ancient meteoric water infiltration with nplH-ankerite mineralisation, and (3) recent supergene modification and final leaching of carbonate and phosphorous. Considering the absence of significant carbonate alteration in BIF at Mt. Whaleback, an alternative hypogene mineralisation models has been proposed for this structurally complex and deep-reaching ore body, involving synorogenic mixing of basinal brines and (ancient) meteoric water (Powell et al. 1999).

2 Working hypothesis and methods

If hematite mineralisation was a hydrothermal replacement product after quartz, silicates, and carbonate, the hematite should inherit specific habits, growth patterns, and trace chemical signatures associated with the precursor phases (and of the mineralising fluid). In addition, martite as a pseudomorphous replacement product after magnetite should inherit some primary magnetite chemistry, which may or may not have been modified by (possibly obliterated) hypogene alteration.

To investigate this hypothesis, several diamond cores that intersect the Dales Gorge Member BIF and related ore in proximity to the ore-controlling, early Central Fault and late Whaleback Fault were sampled (Fig. 1). In addition, unaltered and carbonate-altered BIF from the distal Eastern Ridge deposit were sampled to acquire signatures of (distal) magnetite, in absence of hematite in those rocks. Petrography, SEM imaging and element mapping, as well as laser ablation ICPMS were performed on selected magnetite, martie, and hematite.

3 Petrography and SEM element mapping

The most common ore type at Mt. Whaleback is a high-grade (>65 wt% Fe) laminated M-nplH in the Dales Gorge Member BIF, with mm to cm thick bands of massive martite intercalated with microporous nplH. Interlayered shale macrobands (dm to m thick) are typically oxidised and ferruginised but lack significant nplH mineralisation. Mostly, nplH has homogeneous microspecular habits and, in places, core-rim textures are observed with cores being porous, resembling early, globular hematite, which can be observed in distal BIF throughout the region (Fig. 2a, b).

SEM element mapping of single nplH grains show that those hematite can be compositionally complex (Fig. 2c-f). Silica-rich cores and growth zones that are characterised by Al oscillation or zones of Al-rich grains can be observed. A steady goethite-dehydration appears unlikely, whereas protracted nplH mineralisation induced by variable fluid-flow is compatible with the observed textures.

4 Oxides chemistry in various phases

Consistently detected (> 0.1 ppm) trace elements include Si, Ca, P, Al, Mn, Mg, Ba, Sr, Ti, V, Cr, Zn, Ni, Co, Cu, Pb, Mo, and Ga. The elements Si, Al, Ca, P, may be

![Image](image-url)

**Figure 2** Photomicrographs and SEM Images of oxides from Mt Whaleback. (a, b) two micrographs showing the relationship of early globular hematite in BIF and nplH-cores in ore. (c-f) SEM Fe, O, Si, Al maps of a typical nplH texture in hematite ore at Mt. Whaleback. An Al-Si-zoning within nplH crystals around a spherical nucleation core is recorded.
partly hosted in solid inclusion quartz, silicates, carbonates and apatite. The absence of a strong covariance suggests that all other metals are not significantly affected by inclusions. Magnetite in fresh BIF has generally low trace element concentrations (Si: 1,000-10,000; Ca, Al, Mg, Mn: 100-1,000 ppm; Ti: 10-

Figure 3 Trace element plots: (a) Discrimination plot of Dupuis and Beaudoin (2011) showing the higher Al, Mn, Ti, V trace element abundance in carbonate-altered magnetite and hematite in BIF/ore over fresh magnetite. (b, c) binary plots indicating processes during alteration stages 1 and 2; (d, e) ternary diagrams discriminating samples associated with Central Fault (CF) and Mt Whaleback Fault (WHB) alteration. See text for details.
The Al-Si oscillating core-and rim textures in mplH also provide evidence for hematite formation from a hydrothermal fluid as an alternative to goethite dehydration. Furthermore, mplH veins proximal to the Central Fault, and mplH in the Mt. Whaleback Fault are hydrothermal assemblages that strongly support structurally controlled hypogene models. In summary, these arguments provide a strong alternative model to the supergene-metamorphic model, specifically to iron ore that is located in the weathering horizon.

7 Conclusion

This study shows that microchemistry of magnetite and hematite by LA-ICPMS and elemental maps can be used as tracers for fluid-rock interaction during hematite ore genesis, and is therefore a valid tool for deposit characterisation. It is possible to fingerprint obliterated fluid-rock interaction recorded in oxide. Microchemistry suggests the necessity of revising the traditional genetic models for the Mt. Whaleback deposit.

Acknowledgements

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References


5 Oxides chemistry in deposit zones

Investigating the effect of structural control on oxide chemistry, it is striking that oxides in the vicinity of the Central and Mt. Whaleback faults show different chemical patterns (Fig. 3d, e). Distal magnetite is Zn-Mg enriched, distal carbonate-altered magnetite is Mn-(Ba-Sr) enriched, hematite near and at the Central Fault is moderate to high Mn-(Ba-Sr) enriched, and hematite near the Mt. Whaleback Fault (including samples from D370) is Ni-Mg-(V-Zn) enriched. The extent of the ore zone associated with the Mt. Whaleback Fault is unknown, but probably larger than previously predicted.

6 Synthesis: A multi-stage and multi-source ore formation at Mt. Whaleback

The various patterns of oxide trace metal chemistry supports a two-stage alteration sequence in the Mt. Whaleback deposit. Carbonate-silicate altered BIF, as sampled in the distal Eastern Ridge deposit, was a likely precursor for Central Fault type ore. This is suggested from similar trace element budgets in Eastern Ridge BIF magnetite and ore martite-mplH. Such “proto-ore” has been inferred for other BIF-hosted iron ore deposits in the Hamersley Province (Barley et al. 1999; Hagemann et al. 1999; Taylor et al. 2001; Thorne et al. 2004).

The distinct trace element budgets in hematite across the deposit point to variable fluid chemistry during distinct ore forming stages: Mn-(Ba-Sr) signature in Central Fault-controlled ore (indicating the relics of a carbonate-silica altered BIF signature), and Ni-Mg-(V) signature in Mt Whaleback Fault-controlled ore (indicating interaction of the mineralising fluid with mafic rocks). Because Central (~2.2 Ga) and Whaleback (1.8-1.7 Ga) faults are diachronous, there is a necessity for at least two phases of M-mplH ore formation. This is in agreement to protracted M-mplH ore formation at Mt. Tom Price (Rasmussen et al. 2007).
Geological characteristics, formation age, and geochemistry of the Jiertieke iron deposit in the West Kunlun Mountains, China

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Abstract. The Jiertieke Fe deposit is located in the Taxkorgan West Kunlun Mountains of northwest China. A magnetite-rich unit contains three proven, commercial-grade iron ore bodies that are more than 900 m long and 5 to 30 m thick with a total iron average of 25-65%. The primary iron ores are generally banded and consist of quartz-magnetite. The Fe orebodies are comfortable and interlayered with biotite-quartz schist, metavolcaniclastic rock and marble, which have typical sedimentary Fe deposit characteristics. Uranium-lead analyses on detrital zircons from the biotite-quartz schist, the metamorphic product of a sedimentary protolith, yielded a maximum age of 527.5±3.4 Ma. Geochemical features of biotite-quartz schist indicate a passive margin tectonic setting, which based on the occurrence of the bimodal volcanic rocks in the Taxkorgan terrane, experienced rifting event during the early Cambrian. Under this tectonic regime and compounded by hydrothermal and volcanic activity in the rift basin, anoxic Fe-rich seawater developed in the Taxkorgan region and resulted in the deposition of a BIF during the early Cambrian. This is perhaps the youngest BIF occurrence identified to date.

1 Geological characteristics of the Jiertieke BIF

The Bulunkuole Group located in Taxkorgan-Tianshuihan Terrane, Northwest China recently has been divided into two parts: the previously defined “Paleoproterozoic Bulunkuole Group” and the “Cambrian Bulunkuole Group” (Fig. 1). The Cambrian Bulunkuole Group associated strata consists of metamorphosed sedimentary rocks, metavolcanics and marble, which experienced green-schist to amphibolite metamorphism during Caledonian (Liu et al. 2013). The corresponding protoliths are most likely greywacke, volcanisticlastic rocks, carbonates and sulfates (Zhang et al. 2016). In these Cambrian strata, large scale iron deposits have been discovered in recent years such as Taaxi, Yelike, Kalaizi and Laobing (Dong et al. 2012; Zhang et al. 2016).

The Jiertieke iron deposit is currently being mined and is divided into the western, middle, and eastern belts; the western and middle belts contain over 80% of the Fe ore. The middle and western ore bodies are both over 900 m long and vary in thickness from 5 to 30 m. The eastern orebody can be further sub-divided into three ore bodies, with dimensions varying from 300 to 450 m long and 4 to 16 m thick. All the Fe orebodies trend largely to the NW, and dip to the NE at 35°-75°. The deposit contains total Fe₂O₃(ΣFeO) ranging from 25 to 65 wt% iron ore. The Fe ore bodies have laminated, stratoid, and lenticular structures, mainly interlayered with biotite-quartz schist and metavolcanics.

Figure 1. a Tectonic subdivisions of China, showing the location of the Western Kunlun Orogenic Belt. b Geological map and distribution of meta-sedimentary iron deposits in the south Taxkorgan area. a modified after Zhou et al. (2017), and b after Zhang et al. (2016). Q: quaternary, K,X: Cretaceous, C₂: late Carboniferous, S,W: early Silurian, O-S: Ordovician-Silurian, C₁: early Cambrian, Pt₁/C₁: early Proterozoic or early Cambrian, Pt₁B: early Proterozoic, ζ₁: Himalayan syenite, ζ₂: Himalayan syenogranite, γ₁2: Yanshanian granodiorite, η₁: Yanshanian monzonitic granite, ψ: Pyroxenite.

Quartz-magnetite ore is the primary ore at Jiertieke, with 23-55% magnetite, 20-55% quartz, and <5% calcite and biotite. Most Fe ores are characterized by banded structures of Fe-rich and Si-rich layers. Fe-rich layers mainly consist of magnetite with minor hematite, while the iron-poor layers are consist of quartz, with lesser amounts of calcite, biotite, magnetite, and hematite. The hematite is commonly found within the oxidized ores and locally replaces magnetite crystals in the primary ores.
2 Samples and methods

Samples: Five banded quartz-magnetite ore and four biotite-quartz schist were selected for geochemical analyses; Fe oxides, including magnetite, were further selected from the banded quartz-magnetite ores. The location of the geochronological samples used for dating are indicated in Fig 2b.

X-ray fluorescence: Major elements in the five Fe ores were analyzed using a Phillips Pw 2404 X-ray fluorescence (XRF) spectrometer with a relative standard deviation (RSD) <1% at the Analytical Laboratory Beijing Research Institute of Uranium Geology. Major elements in the four schists were measured on a XRF-1500 spectrometer with an RSD of 0.1-1% at the ALS Minerals – ALS Chemex (Guangzhou).

Inductively coupled plasma mass spectrometry (ICP-MS): Trace element analyses for all lithologies were analyzed on an Element (Finnigan MAT) inductively coupled plasma mass spectrometer (ICP-MS), with a RSD <2.5% at the ALS Minerals – ALS Chemex (Guangzhou). Uncertainties on individual analysis in data are reported at the 1σ level; mean ages for U/Pb (and Pb/Pb) analyses are presented with a 95% confidence interval.

Secondary ion mass spectrometry (SIMS): Twenty-two points of zircons from biotite-quartz schist analyzed Th and Pb isotopes on a Cameca SIMS-1280 ion microprobe at the (IGGCAS). Uncertainties in individual analysis in data are reported at the 1σ level; mean ages for U/Pb (and Pb/Pb) analyses are presented with a 95% confidence interval.

Electron probe micro-analysis (EPMA): The mineral compositions of the Fe oxide minerals (22 points in total) were measured using wavelength-dispersive spectrometry (WDS) on a JEOL JXA8100 electron probe at IGGCAS, with an accelerating voltage of 15kV, a 12 nA beam current, a 5 µm beam spot, and a counting time of 10-30 s. The precision for oxides analyzed by WDS is better than 5%.

Triton Plus multi-collector thermal ionization-mass spectrometry (TIMS): The whole rock Sm–Nd isotopic analysis samples were picked up from biotite-quartz schist. Sm and Nd were separated using the classical two-step ion exchange chromatographic method and measured using a Triton Plus multi-collector thermal ionization mass spectrometer at IGGCAS.

3 Age of ore forming activity

Previous studies on the age of Bulunkuole Group have concluded either a Paleoproterozoic (Ji et al. 2011) or Early Paleozoic age (Yan et al. 2012; Huang 2014). Paleoproterozoic zircons can normally be found within the southern section of the Bulunkuole Group near the Zankan Fe deposit, while Early Paleozoic zircons have been found in several different locations such as the Kalaizi, Taaxi, Yelike and Laobing regions. Zhang et al. (2016) have suggested the controversial zircon ages may be reconciled by dividing the Bulunkuole Group into two parts: (1) the Paleoproterozoic strata in the south, which contains the Zankan and Mokaer Fe deposits, and (2) the Cambrian-aged Kalaizi, Laobing, Yelike and Taaxi formations that run from the southeast to the northwest.

The Fe ore bodies in the Jiertieke deposit is commonly conformable, stratiform and interbedded with biotite-quartz schist. There is also a transition zone between the ore bodies and biotite-quartz schist. Therefore, the maximum depositional age of the metamorphosed schist rocks, which have previously been considered as a metamorphosed greywacke and sandstone, likely represents the age of the ore forming event. Secondary ion mass spectrometry (SIMS) U-Pb dating results indicate that the Jiertieke deposit formation age is up to 527.5 ± 3.4 Ma (Fig 2a), suggesting it was formed in the early Cambrian.

4 Tectonic setting

The biotite-quartz schists in the Jiertieke BIF are thought to be deposited as multicycled sediments or under tropical conditions with low relief and sedimentation rates based on their geochemical features. Moreover, these samples display high Th/Sc (≈1), and high Th/U (>3.8) and evolved major element compositions (e.g., high Si/Al and CIA (>70)) and low εNd(t) values (<0) (calculated at 527 Ma), as low as −3.14, which are most similar to those of the old Upper Continental Crust (McLennan et al. 1995). These characteristics suggest that the source of these metasediments are likely from a stable cratonic setting.

Several immobile elements (e.g., Co, Th, and Zr) are more useful in distinguishing the tectonic environment of the source rock than the major elements (Bhatia and Crook 1986; McLennan et al. 1993). On the Th–Co–Zr ternary diagram of Bhatia and Crook (1986) (Fig. 3) all the biotite-quartz schist (protoliths: greywrack) samples are plotted in the passive continental margin field imply the source of the meta-sediments is from passive continental margin.

Previous research has argued the West Kunlun and the neighboring region were formed by an extensional tectonic event, an assertion supported recently by Gao et al. (2013). Evidence for extensional activity comes from petrological and geochemical data from a suit of bimodal volcanics in the Bulunkuole Group, the meta-basalt (516 Ma) and meta-dacite (521 Ma) in the Taaxi deposit likely represent the formation age of the bimodal volcanics in the early Cambrian (Gao et al. 2013). This is further suggestive of the idea that the region experienced an extensional
tectonic-magmatic event, which may have created a rift basin during early Cambrian.

**Figure 3.** Th–Co–Zr/10 diagram indicate the source of biotite-quartz schist from the Jiertieke BIF (after Bhatia and Crook 1986). A, Oceanic island arc; B, continental island arc; C, active continental margin; D, passive margin.

### 5 Deposit type

The Jiertieke magnetite ore bodies are generally banded and lensoid in shape with alternating Fe- and Si-rich layers that are well-defined and continuous. These structures are conformable and interbedded with both overlying and underlying rocks; all layers were folded simultaneously. The original strata of these iron formation were controlled by multiple sedimentary cycles leading to the deposition of the Cambrian Bulunkuole Group.

The average FeO and SiO₂ of the Jiertieke Fe ore samples are 52.19% and 28.82%, respectively, with very low concentrations of alkali elements and lithogenous elements such as Al, Zr, and Ti (average Al₂O₃=0.64 wt.%; average TiO₂=0.05 wt%; average Zr=0.91 ppm). This suggests that the initial Fe ores were nearly pure chemical sediments (Duhig 1992). The EMPA results for magnetite in quartz-magnetite ore indicate that the Jiertieke Fe ore can be categorized as a metamorphosed Fe-rich sediment. Combine with the geological features, formation age, mineral assembles, host rock protolith and tectonic setting, the Jiertieke Fe deposit share many characteristics with Raptian type BIF. We therefore propose that the Jiertieke Fe deposit is a Raptian style BIF, formed during the early Cambrian, which would make this the youngest known BIF by almost 40 Ma (for a compilation of known BIF deposits see Bekker et al. 2014).

### 6 Source characteristics of the Jiertieke BIF

The iron in Precambrian BIF is normally sourced from a combination of ferruginous seawater and hydrothermal input (Bau and Dulski 1996). In terms of REE+Y characteristics, Precambrian BIF tend to display both positive Eu and Y anomalies, especially for Archean to Paleoproterozoic BIF, as well as HREE enrichment and high Y/Ho ratios (Bau and Dulski 1996; Bolhar et al. 2004). In the Jiertieke BIF, the PAAS-normalized REE patterns are generally flat (La/Yb ~ 1), indicating a lack of enrichment in HREE (Fig 4). Furthermore, two samples display La/Yb <1, and a single sample has a superchondritic Y/Ho ratio. Both are indicative of a characteristic seawater signal (Bau and Dulski 1999). All the samples have positive La anomalies (La/La*=1.13-1.74), and commonly contain positive Eu anomalies (Eu/Eu*=1.61-2.13) that are a typical feature of submarine high-T hydrothermal fluids (Bau and Dulski 1999; Douville et al. 1999).

In summary, the REE patterns of the Fe ores in the Jiertieke BIF show a significant hydrothermal input, however, some evidence of a seawater contribution is present. This suggests that the initial mechanism of deposition for the Jiertieke deposit may be similar to that of Precambrian BIFs.

**Figure 4.** Fe ores REE+Y distributions of the Jiertieke BIF, as well as average South Pacific seawater, average high-T (>350°C) and low-T (<250°C) hydrothermal fluids (data from Bolhar and Van Kranendonk 2007). All values are normalized to PAAS values after McLennan 1989.

### 7 Environmental conditions

The capture and preservation of aqueous REE patterns in the BIF has provided a window into ancient ocean chemistry and redox state. For instance, Ce anomalies in BIF can be used to constrain the redox state of seawater contemporaneous to deposition (e.g., Bau and Dulski 1996; Bolhar et al. 2004). The average Ce/Ce* for the Jiertieke BIF is lower than modern day seawater, but similar to those observed in suboxic to anoxic environments (German et al. 1995). Here, we have calculated Ce/Ce* as Ce/Ce*=Ce_PAAS/(2Pr_PAAS-Nd_PAAS), as per Bolhar et al. (2004). It is evident that the Jiertieke BIF shows no significantly negative Ce anomalies (Ce/Ce*=0.90-1.00, Fig 5), suggesting reducing conditions during deposition of the BIF. However, the samples show a general trend towards a negative Ce anomaly, possibly indicating a depositional environment that may have experienced minimal oxygenation.

The Jiertieke BIF displays either weakly negative or absent Y anomalies (Y/Y*=0.85-0.97; Fig 4). The experimental work of Bau (1999) revealed that precipitating ferric oxyhydroxides tend to have lower Y/Ho ratios than the solutions from which they have precipitated. The REE+Y patterns for the precipitating ferric oxyhydroxides thus have a negative Y anomaly. Scavenging of REE+Y by ferric oxyhydroxides therefore leads to decoupling of Y from REE (Bau and Dulski 1996;
Bau 1999). Bau and Dulski (1996) attributed Y anomalies in BIF to the rate of precipitation based on the REE+Y pattern for modern ferromanganese precipitates. In this regard, slowly forming, modern marine hydrogenetic ferromanganese crusts yield REE+Y patterns with negative Y anomalies, as they are close to exchange equilibrium between the adsorbed and dissolved REE+Y. On the other hand, rapidly precipitated modern hydrothermal ferromanganese precipitates yield REE+Y patterns with positive Y anomalies, because REE+Y have been removed too rapidly to allow for equilibration and significant REE+Y fractionation (German et al. 1990). As a corollary, the negative or absent Y anomaly for the Jiertieke BIF may be attributed to slow rates of precipitation of the BIF precursors.

![Fig 5. Ce/Ce* -Pr/Pr* cross-plot indicating a trend towards negative Ce anomalies for the Jiertieke BIF, after Bolhar et al., (2004).](image)

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Iron-oxide mineralogy of banded iron formations in the Takab region, North Western Iran

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Abstract. Siliceous banded and nodular iron ores intercalated in mica schists and amphibolites of probably Late Proterozoic age, were studied from the NW part of Iran (Takab region). The iron ore is predominately composed of quartz and iron-oxides (magnetite, hematite, maghemite, goethite in different proportions). Magnetite was transformed into maghemite and hematite along fractures and cleavages during a major oxidizing deformation event. Quartz shows undulose extinction. Both quartz and iron oxides partly form 120° triple junctions, but grain boundary migration is also observed. In the nodular ore, grain boundary migration is more pronounced leading also to grain isolation, quartz is partially annealed, and iron oxides are agglomerated, elongated and disrupted. These finding indicate a longer recrystallization episode in the nodular ore. The iron oxide grains contain inclusions of euhedral, zoned and corroded zircons, apatite, uraninite, Mn-carbonate and euhedral monazite. Magnetite contains traces of Al. Hematite and goethite show higher Al, Si and Ca contents than the magnetite. Later hydrothermal solutions precipitated goethite surrounding the magnetite-hematite-maghemite grains and replacing hematite. Barite occurs in fractures of iron oxides, Mn-Ba-Pb oxi-hydroxides and scheelite occur interstitial to iron oxides.

1 Introduction

Iran is the 10th largest iron ore producer and the 9th iron ore exporter in the world. According to forecasts, iron production will triple in the world. It is expected to reach 66.2 Mt of iron ore (Hastorun et al. 2016). Most of the iron ore deposits are located in the northeastern and central part of Iran, while iron ore deposits of the northwestern part are still little studied. We carried out a preliminary mineralogical study on different iron ore samples from the Takab region in northwestern Iran to define iron oxide minerals in their structural and fluid context.

2 Geological setting

The Takab iron ore deposits belong structurally to the Sanandaj-Sirjan Zone (Fig. 1). The study area comprises Precambrian-Early Paleozoic metamorphic rocks, Miocene sedimentary rocks and Quaternary deposits. The Precambrian rocks have been thrust over the Cenozoic sedimentary units. The iron ore deposits of this area are classified as being of volcano sedimentary origin. Their formation might be related to the back-arc extension due to the Prototethys subduction beneath the Cadomian magmatic arc (Ghorbani, 2013; Nabatian et al., 2015). The most important iron deposits, known at present, occur in schists and marbles.

The mineralization forms thin layers and lenses interlayered with quartzite and amphibolites (Nabatian et al. 2015; Fig. 1A). In the study area, west of Zanjan, the iron oxide mineralogy is essentially described as hematite, goethite, with barite as accessory mineral. The age of the iron may be Late Proterozoic, but no geochronological study is performed yet on the iron formation and its host rocks (Ghorbani et al., 2013).

This is the first detailed petrological mineralogical study on banded and nodular iron ores from the Takab region reflecting its complex geological history.

3 Analytical methods

Optical microscopy on polished thin sections was performed in transmitted and reflected light mode, SEM and electron microprobe analyses at the Centre Camparis, Sorbonne Université, UPMC Univ Paris 06, Paris, France. XRD and Curie Balance analyses were carried out at the GEOPS, Université Paris Saclay, Université Paris Sud, Orsay, France.

4 Results

The studied samples are banded and nodular iron ores. Both massive banded and nodular ore occur as decimetric layers within deformed (folded) mica schist (Fig. 1A). The banded iron ore shows coarse and discontinuous banding with interstitial quartz (Fig. 2A). The nodular ore is composed of mm-sized iron oxide agglomerates, partly elongated and disrupted (Fig. 2B).
The banded iron ore is characterized by micro quartz showing 120° triple junctions or slight grain boundary migration of lobate crystal surfaces. Some quartz grains show also 120° triple junctions with iron oxide grains. Quartz grains show undulose extinction. In iron oxide rich bands, poikilotopic textures of iron oxides or quartz grain are characteristic. Iron oxide veins formed perpendicular to the iron oxide bands (Fig. 3A). Pyrite relics are observed in goethite. Barite, interstitial to quartz, is rarely present.

The nodular iron ore shows bimodal iron oxide and quartz grain sizes: some tens of micron and some hundreds of microns in size. Both quartz types show undulose extinction (Fig. 3B). The large quartz grains occur mainly close to iron oxide agglomerates of a few hundreds of microns. They are composed of individual small oriented quartz crystals. Small iron oxide grains show sometimes 120° triple junctions with quartz grains. Grain boundary migration also led to grain isolation (Fig. 3B).

X-ray diffraction on 3 banded and 1 nodular ore samples indicate that all samples contain similar major mineralogy quartz, magnetite, hematite, maghemite, goethite in different proportions. Small peaks are attributed to barite (BaSO₄).

The iron oxi-hydroxide mineralogy is complex. Euhedral magnetite is transformed into maghemite and hematite (Fig. 3C, D, 4A, B).

Trellis structures, which are characteristic for martite,
are also observed (Fig. 4E). Chemical zoned goethite occurs interstitial to the magnetite-hematite-maghemite grains (Fig. 4C). Goethite may also host neoformed hematite inclusions (Fig. 4B). Euohedral, zoned and corroded zircon,apatite, Mn-carbonates, uraninite as well as euohedral monazite are observed as inclusions in magnetite (Fig. 4D, E). In the matrix, a few hundreds of micron large oxihydroxides composed of Mn-Ba-Pb occur (Fig. 4F). Scheelite (CaWO₄) was also observed. Secondary barite occurs in fractures of the iron oxides together with goethite.

Curie Balance analyses show that the material is highly magnetic and magnetite is the dominate phase. In two banded iron ore samples maghemite and/or goethite are indicated.

Electron microprobe analyses were performed on iron oxihydroxides from banded and nodular ores. A special program was designed to analyse oxygen to trace the iron oxide and hydroxide variabilities. The magnetite and hematite contain traces of Al (< 0.5 wt. %). Goethite hosts variable amounts of Al (up to 0.7 wt. %), Si (up to 1.7 wt. %) and Ca (up to 0.2 wt. %). Figure 5 shows the iron versus the oxygen contents of representative iron oxihydroxides and the iron contents versus the total (wt. %). The conversion of Fe²⁺ into Fe³⁺ is accompanied by a decrease of the total iron content and a slight increase of oxygen. Goethite has lowest totals.

Figure 4. Scanning electron microprobe images in back scattered mode. A. Euohedral magnetite partly transformed into hematite and surrounded by goethite; B. Goethite interstitial to magnetite with euohedral hematite inclusions. C. Goethite showing oscillatory zoning; D. Euohedral magnetite with corroded zircon (zr) inclusion; E. Magnetite showing trellis hosting euohedral monazite; F. Mn-Ba-Pb oxihydroxide interstitial to magnetite. Magnetite hosts uraninite inclusion.

Figure 5. Electron microprobe analyses of iron oxides and iron hydroxides of some iron ores from the Takab region. Upper diagram: Oxygen was analysed in particular, to distinguish the different iron-oxide varieties: Fe versus O (wt. %), lower diagram: Fe versus Total (wt. %). Centre Campris, Sorbonne Université, UPMC, Univ Paris 06, France).

5 Discussion and conclusions

This study highlights the complex history of this iron ore and gives useful hints for future research, which will contribute to elucidate the origin of the ore forming elements iron and silica, but also the accessory elements (e.g. Mn, Ba, Pb, U, W, P). Based on the present results, it can be suggested that: (1) The primary iron ore is banded and crystallized statically from an iron and silica rich solution. Zircon, apatite, Mn-carbonates, uraninite and monazite were included during this step in the initial iron oxide, magnetite; (2) Regional deformation led to recrystallization of the iron oxides through grain boundary migration and quartz grain isolation. The micro quartz grains form neoblasts and annealed to the larger quartz grains. The nodular ore represents most likely a highly deformed banded iron ore, where iron oxide bands were disrupted.
recrystallized. Sulfides were present at that state. Oxidizing fluids accompanied this step and transformed the magnetite into maghemite and hematite. (3) Aqueous solutions carrying Mn, Ba, Pb, Ca, W, S, CO₂ led to the formation of goethite and Mn-Ba-Pb oxihydroxides and associated scheelite and barite. This episode is most likely contemporaneous to the W mineralisation in this region (Ghorbani, 2013).

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The nature of late Neoarchean seawater in the ~2.54 Ga Sijiaying banded iron formation in Eastern Hebei, China

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Abstract. The ~2.54 Ga Sijiaying banded iron formation (BIF), the best-preserved and most extensive deposit in Eastern Hebei of the North China Craton (NCC), is intercalated and closely associated with meta-volcanic rocks of the Luanxian Group. Low Al₂O₃, TiO₂ and high field strength elements concentrations show that the BIF is relatively detritus-free. Shale-normalized rare earth and yttrium distributions of individual BIF mesobands exhibit positive La anomalies, enrichment in HREE relative to LREE and MREE and suprachondritic Y/Ho ratios, which are typical features of marine waters throughout the Archean and Proterozoic. The presence of consistently positive Eu anomalies indicates a significant high-T hydrothermal input, while the absence of true Ce anomalies suggests deposition from an anoxic water column. By comparison with other typical BIFs, the Sijiaying BIF is depleted in HREE, and appears to record variations in solute fluxes related to changing intensities of hydrothermal activity. These features, coupled with Sm-Nd isotopic relations and Ge/Si distributional patterns, point to two decoupled sources controlling the depositional environment of the BIF and thus reveal source heterogeneity for silica and iron of the Sijiaying BIF. High Fe fluxes were associated with seafloor-vented hydrothermal fluids; whereas significant amounts of silica were associated with ambient seawater.

1 Introduction

Banded iron formations (BIF) may serve as archives of proxies that provide clues about the composition and redox state of the ancient ocean and atmosphere (Bekker et al., 2010). One of the main issues pertaining to this is that much of the existing dataset of BIFs is based on bulk rock analyses, meaning that high-resolution details in the chemical fabric of the sedimentary rock record are not fully captured.

In China, BIFs occur extensively throughout the Archean-Paleoproterozoic units of the North China Craton (NCC, Fig. 1a), and the Eastern Hebei in the north is considered to be the second largest iron metallic region (Li et al., 2014). Large amounts of BIFs are exposed in this area, such as Shuichang, Shirengou, Erma, Xingshan, Sijiaying, and Macheng BIFs (Fig. 1b), among which the Sijiaying BIF is the largest and laterally most extensive BIF in Eastern Hebei. Previous studies (e.g., Li et al., 2011; Zhang et al., 2012) on geological aspects suggested that the BIFs are Algoma-type (Gross, 1980) because they are closely associated with volcanic rocks, and likely formed in arc/back-arc basins. In addition, based on detailed geochronological studies of interbedded meta-volcanic rocks (e.g., Cui et al., 2014; Zhang, 2014), nearly all of BIFs are Neoarchean in age (2.55-2.50 Ga).

In contrast, giant Algoma-type BIF deposition on other cratons were deposited mainly between 2.85 and 2.70 Ga, and can be found in most greenstone belts (Bekker et al., 2010).

A number of previous studies have focused on the source of the major components of BIFs in Eastern Hebei (e.g., Chen, 2014; Yao et al., 2014). However, there is still only a nascent understanding of the origin of BIFs, given that most previous analyses were focused on major and trace element systematics of scattered bulk samples rather than individual micro- and mesobands. Therefore, we use a combination of major and trace element (including REE+Y) and Sm-Nd isotopic data from individual Fe- and Si-rich layers of a least altered BIF specimen from the ~2.54 Ga Sijiaying BIF (Fig. 1b) to elaborate on the origin and nature of source materials of the BIF and to investigate time-related changes of the relevant depositional environment.

1.1 Subdivisions of the North China Craton (NCC) showing location of Eastern Hebei and distribution of major BIFs (after Zhao et al., 2005).

1.2 Geological sketch map of Eastern Hebei indicating study area (after Nutman et al., 2011). Stars represent typical BIFs.

2 Geological background

Locally exposed strata in the Sijiaying area include Neoarchean metamorphosed volcanic rocks of the Luanxian Group and the middle Proterozoic sandstones and conglomerates of the Changcheng Group (Qian et al., 1985). The Sijiaying BIF and associated supracrustal rocks (i.e. biotite leptynite, biotite plagioclase gneiss and hornblende plagioclase gneiss) have been regionally metamorphosed to lower amphibolite facies with...
temperatures between 350 and 560°C (Chen, 2014). The protolith metavolcanic succession consists of packages of mostly intermediate-felsic rocks up to hundreds of metres thick that are intercalated with the Sijiaying BIF of various thicknesses from less than 10 m to hundreds of metres (Fig. 2) (Qian et al., 1985). The boundary between the BIF and metavolcanic rocks is sharp but conformable. The Changcheng Group rests with an angular unconformity of ca. 15° on these metavolcanic rocks.

Important geochronological work in the region was carried out by Cui et al. (2014), Chen (2014) and Zhang (2014). Cui et al. (2014) reported three SIMS U-Pb zircon dates for metavolcanic rocks associated with the BIF (ZK630, Fig. 2): a meta-dacitic flow (hornblende plagioclase gneiss) near the base of the BIF sequence yielded an age of 2543±14 Ma, another meta-dacitic tuffaceous rock (biotite leptynite) interlayered with the BIF further up in the stratigraphy yielded an age of 2537±13 Ma, whilst a meta-andesite lava flow (biotite plagioclase gneiss) within the upper part of the sedimentary succession yielded an age of 2535±8 Ma. Zhang (2014) also obtained SHRIMP U-Pb zircon ages of 2545±9 Ma and 2545±10 Ma for biotite plagioclase gneiss and interbedded biotite leptynite from different positions in this lithostratigraphic unit. Similarly, Chen (2014) also reported a U-Pb SHRIMP age of 2539±6 Ma for biotite leptynite near the top of the sequence. In addition, the Sijiaying BIF was intruded by a suite of gneissic granites including syenogranite at 2521±12 Ma (Zhang, 2014) and monzonitic granite at 2529±5 Ma (Chen, 2014), which provide a minimum age of deposition for the Sijiaying BIF.

The stratigraphic succession of the Luanxian Group in Eastern Hebei is essentially coherent on a broad scale. On a smaller scale, the defined formations and members comprising multilayered BIF and associated metavolcanic rocks succeed each other with no compelling evidence of major depositional gaps, and in the Sijiying BIF, in particular, the lateral continuity of stratigraphic detail is spectacular. The Sijiaying BIF was deposited most likely during intermittent periods of enhanced volcanic activity. Having regard to the lack of any data constraining the length of possible volcanic hiatuses (i.e. the uncertainty in the time required for deposition of the volcanic tuff interbedded with the BIF) (Fig. 2), reconstruction of depositional rates starts here with an assumption that hiatuses lasted for less than ~1 million years.

Previous age data from the drillhole ZK630 are critical for estimating the CDR of the Sijiaying BIF (Cui et al., 2014; Chen, 2014; Zhang, 2014), both because of its thickness and because of the predominance of typical BIF lithology within it. Our preferred depositional age interpretations from six metavolcanic samples of this drillhole are plotted in Fig. 3, against the stratigraphic depth of each sample below the surface. The lowest depositional rate consistent with all samples is 10.5 m per million years (a line from the uncertainty limit of the oldest age near the base to the youngest uncertainty limit of the youngest age); no upper constraint on depositional rate is provided by these samples. Moreover, the line in Fig. 2 is shown to fit comfortably with the uncertainty limits of all ages. Specially, a CDR here can also be calculated in terms of a relatively small segment. For instance, the best depositional age estimates for the base and the top of the upper part of the BIF are 2537±13 Ma and 2535±8 Ma, respectively. There are approximately 20 m of BIF between these two age spikes. A CDR of 10 m/Ma is thus deduced, in a good agreement with aforementioned results. Therefore, a value of ~9.1 m/Ma (revised again based on the dip angle of strata) is a best approximation for the CDR of BIF. Using this sedimentation rate, the depositional duration of the Sijiaying BIF sample studied here (Fig. 3a) is estimated at ~1.6×105 years and relevant geochemical analyses record relatively small variation of marine basin environments.

3.2 Late Neoarchean ocean environments

The REE patterns of relatively siliciclastic-free BIF have frequently been used as a qualitative proxy of paleoseawater redox conditions (Pepeols et al., 2009; Planavsky et al., 2010). The REE+Y distribution in the mesoband samples from the Sijiaying BIF is very similar to that of other Archean BIFs and marine carbonates which are low in or free from clastic detritus (Bau and Dulski, 1996; Kamber et al., 2004; Planavsky et al., 2010). The REE+Y distribution in the Sijiaying samples to that of modern seawater, which is characterized by (i) a relative depletion of LREE and MREE compared to HREE; (ii) positive La...
and Gd anomalies; (iii) strong negative Ce anomalies, and (iv) suprachondritic Y/Ho ratios (>26) (Bau and Dulski, 1996; Bolhar et al., 2004). Apart from redox-sensitive Ce and Eu anomalies, the general shape of the REE+Y patterns and details are similar to that in modern seawater, supporting the assertion that these Sijiaying BIF samples represent marine chemical sediments that can be used as archives that recorded the evolution of ancient atmosphere-hydrosphere system.

The apparently positive correlation ($R^2=0.82$) (not shown) between Fe$_2$O$_3$ and 2REE+Y in the Sijiaying mesoband data reflects the fact that both iron and REE were derived from a similar source and that the Fe/Nd ratios of the end-members did not change significantly in the Archean ocean. Therefore, the Sm-Nd isotopic compositions of the Sijiaying BIF mesobands can further provide information on the source of REE+Y and iron and detailed characterization of mixing end members. Generally, subchondritic εNd(t) values are found for the Si-rich mesobands and positive εNd(t) values are found within the Fe-rich mesobands (Fig. 3c). Moreover, positive correlation between Fe$_2$O$_3$ and εNd(t) values further indicates that for the Sijiaying BIF the Fe-rich source is associated with a source that is significantly depleted (extrapolated εNd(t) value of +3.0) relative to the Si-rich source (extrapolated εNd(t) value of -1.0). As a consequence, we interpret these two poles to represent the deduced two mixing water masses above (hydrothermal fluids and ambient seawater, respectively) during deposition of the Sijiaying BIF. Moreover, the iron-rich hydrothermal fluids were likely derived from interaction with ~2.7 Ga juvenile oceanic crusts and/or >2.5 Ga mafic rocks stemming from reworking of ~2.7 Ga crusts. By contrast, the source reservoir for ambient seawater is assumed to be dominated by dissolved continental riverine input similar to seawater today. The negative εNd(t) values ($<0$) and older T$_{DM}$ ages ($>2.9$ Ga) of the Si-rich mesobands relative to those of the Fe-rich mesobands imply that the dissolved REE of the surface seawater was derived from weathering of an enriched protocrustal landmass.

Traditionally considered as a "pseudo-isotope" tracer for silica, Ge is an ideal candidate to trace both the continental and oceanic Si cycles (Froelich et al., 1985, 1992; Mortlock et al., 1993; Derry et al., 2005). In particular, it has been suggested that Ge/Si ratio in seawater could help
to evaluate the relative proportion of hydrothermal vs. riverine input of silica to the global ocean. The Ge/Si ratios of the Sijiaying Si-rich mesobands trend to 0.74 μmol/mol as silica content increases (Fig. 3d), which is close to the present-day marine ratio (~0.7 μmol/mol) (Mortlock et al., 1993). This indicates that silica was sourced from the weathering of continental landmass. In contrast, the Fe-rich mesobands have much higher Ge/Si ratios (average 7.06 μmol/mol), similar to those of present-day hydrothermal solutions and sediments (Froelich et al., 1985). This does not necessarily imply the presence of hydrothermal silica, but rather higher concentrations of Ge associated with the iron phases (not shown).

4 Conclusion

(1) The precursor sediments to BIF were deposited during that time at a compacted sedimentation rate of approximately 9.1 m per million years (or >40 m per million years taking limits (e.g., compaction) into account);

(2) High Fe fluxes were associated with seafloor-vented hydrothermal fluids; whereas significant amounts of silica were associated with ambient seawater solutes derived from weathering of an enriched continental landmass.

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Age, tectonic setting and formation conditions of the Neoarchean BIFs in the North China Craton

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Abstract. Banded iron formations (BIF) in the North China Craton (NCC) are predominantly Neoarchean in age, hosted in greenstone belts, with formation ages of BIFs in the NCC showing a peak in the late Neoarchean (2.6–2.5 Ga). The Post-Archean Australian Shale-normalized REE patterns of the BIFs display an enrichment in heavy rare earth elements with positive La, Eu and Y anomalies, indicating that the primary chemical precipitate is a result of solutions that represent mixtures of seawater and high-temperature hydrothermal fluids. The εNd(2.55 Ga) values (4.2–4.5) of BIFs suggest that the Fe was sourced from multiple sources. At the same time, the BIFs lack negative Ce anomalies with consistently positive δ56Fe values (0.12–1.87‰), which suggest that they formed in a low-oxygen or anoxia environment. A possible tectonic setting where the NCC BIFs and associated supracrustal rocks form is a back-arc basin or island arc related to a subducted ocean slab.

1 Introduction

BIF-hosted iron ore deposit are one of the world’s most important iron resource types, with the quantity of both exploitation and resource reserve ranking first in the world (>80%). Proven BIF iron ore reserves account for over 60% of the total iron in China. Numerous large BIF-type iron and high-grade iron orebodies have recently been discovered in the NCC, such as Gongchangling in Anshan, Jining in W. Shandong, Dataigou in Benxi of Liaoning, Macheng and Xingshan in E. Hebei. Given their economic importance, BIFs have been extensively studied, but many aspects of their origin remain enigmatic because modern analogues are unknown. Recent research has focused on the depositional age of these iron formations, with zircon U-Pb ages (obtained by SHRIMP or LA-ICPMS methods) proving important in constraining the time of significant geological events, including crust growth and Great Oxidation Event (GOE), which likely coincided with deposition of BIFs (Zhang et al., 2012; Wang et al., 2015).

In addition, Fe and Nd isotope features can provide constraints on material sources and deposition environment of BIFs. In this paper, we summarize the geochronological, geological and geochemical characteristics of the BIF in NCC in order to decipher the tectonic setting and formation conditions of BIF.

2 Geology of the Neoarchean BIFs

2.1 Geologic features and distribution of BIFs

BIFs occur extensively throughout the Neoarchean units of the NCC, and five major iron metallogenic provinces have been identified (Fig. 1). In the Anshan-Benxi (or Anben) area in the NE NCC, the metamorphic degree is relatively low, BIF-bearing greenstone rocks are distributed as belts in granitic complexes. The main BIFs in E. Hebei have undergone either amphibolites or granulite-facies metamorphism and are hosted in Neoarchean rockd consisting predominantly of hypersthene granulite, biotite-plagioclase gneiss and magnetite quartzite. The Wutai BIF-bearing greenstone belt is located in the central section of the North China Craton. The Huoqiu iron deposit is located on the southern margin of the North China Craton and the orebodies occur in a Neoarchean iron formation with middle-high grade metamorphism. The ore types in the Huoqiu BIF are mainly quartz magnetite (or hematite), silicate magnetite and carbonate magnetite. BIFs in the Guyang greenstone belt are situated in the western NCC and include three large iron-deposits namely the Gongyiming, Dongwufenzhi, and Sanheng deposits.

Figure 1. Geological sketch of major BIF iron deposits in the NCC.

2.2 Mineral composition and evolution of BIFs

BIFs are defined by their unusual mineralogy, which includes mostly silica and a wide range of Fe-rich and Al-poor minerals. The mineralogy of BIFs from the best preserved sequences is remarkably uniform, consisting mainly of quartz, magnetite, hematite, Fe-rich silicate minerals (stilpnomelane, minnesotaite, and riebeckite), carbonate minerals (siderite, ankerite, calcite, and dolomite), and lesser sulfides (pyrite and pyrrhotite). Most of BIF is well banded oxide facies iron-formation composed of alternating quartz-rich and magnetite-rich layers. Some BIFs of wrinkling deformation were seen in Nanfen of Anben area and in Sijiaying of E. Hebei. Some activated quartz veins in BIFs were also observed in W. Anshan. The aain compositional minerals in BIFs are as
follows:

- Magnetite occurs as subhedral grains in BIFs, with some quartz crystals also containing magnetite inclusions. Magnetite is commonly replaced by hematite. Magnetite often formed mostly during late diagenesis and metamorphism.

- Quartz is the most common mineral in BIF (50–65%). It occurs as microbands, alternating with millimeter-thick microbands of Fe-rich silicate and carbonate minerals. The quartz grains are subhedral with 0.06-0.3mm in size.

- Siderite is the most common carbonate mineral in BIFs, typically occurring as minute, single, rhomb-shaped crystals. Small siderite nodules are common in some layers, where they display evidence of differential compaction. This siderite appears to have replaced or overgrown an earlier phase, which occurs in the core of some crystals, indicating a diagenetic origin for the siderite.

Minor or trace minerals include stilpnomelane, ankerite, ferroan dolomite, actinolite, grunerite, pyrite, apatite, monazite, xenotime.

The main minerals now present in BIFs (e.g., quartz, hematite, magnetite, carbonates, and ferrous silicates) in NCC are actually of secondary origin. A diagram showing relative mineral stabilities in BIF, ranging from low to high metamorphic grade is given in Fig. 2. The BIFs in NCC underwent metamorphism of greenschist to lower amphibolite facies, amphibolite facies and granulite facies. Sometimes, some BIFs display shear metamorphic deformation and migmatization features, in which high-grade ores formed in local sections.

3 Geochemistry of the Neoarchean BIFs

3.1 Ages of BIF

In recent years, large amounts of zircon U-Pb ages of metavolcanic rocks associated with the Algoma-type BIFs in NCC have been obtained in order to constrain the formation age of the BIFs, i.e. 2547 Ma of Shuichang BIF, 2553-2541 Ma of Shirengou BIF, 2520–2600 Ma of Sijiaying BIF, 2552 Ma of Nanfen, 2533 Ma of Waitoushan BIF, 2528 Ma of Gongchailing BIF, 2551 Ma of Chentaigou BIF, 2561 Ma of Jining BIF, 2562 Ma of Sanheng BIF in the Guyang area and 2543 Ma of Wutai BIF (Zhang et al., 2012; Wang et al., 2014). Metamorphic or hydrothermal events have been recognized in some BIFs in the NCC, such as the Gongchailing iron deposit, where Li et al. (2014) have recognized a ~1840 Ma hydrothermal event based on the SHRIMP zircon U-Pb age of the garnet-rich altered rocks. Moreover, a ~2.50 Ga metamorphic event has been widely identified in some BIFs, e.g., the Nanfen, Shuichang and Xiaolaihe BIFs. Fig. 3 show formational and metamorphic ages of major Archean BIF-hosting rocks in the North China Craton. It shows that formation ages of BIFs in NCC cover a wide range from Mesoarchean to early Paleoproterozoic, among which the late Neoarchean (2.6–2.50 Ga) is the peak period.

3.2 Major elements

The results of major elements for the NCC BIFs show that the BIFs are mostly composed of SiO₂ + Fe₂O₃T (the average content of 91–93%). The average concentrations of MgO and CaO are 1.95 and 1.95%, respectively. The contents of Al₂O₃(<1.8%), TiO₂(<0.12%), K₂O(<1.0%), Na₂O(<0.4%), MnO(<0.13%) and P₂O₅(<0.23%) are very low, indicating that BIFs are typical chemical sedimentary rocks. It is suggested that the protolith of BIFs are colloid composed of silicious, iron and small amounts of carbonate mud.

3.3 Trace elements

Rare earth element (REE) pattern is generally regarded as a valid method to understand relevant formation conditions of BIFs (Bau and Dulski, 1996; Alexander et al., 2008). All the REE data for the Anshan-Benxi, Eastern Hebei, and Wutai, Huoqui and Guyang BIFs have been normalized to the Post Archean Australian Shale (PAAS) values (Condie 1993). Although the REE data for the NCC BIFs are variable, they are characterized by mild to strong HREE enrichment relative to LREE and distinctly positive Eu anomalies (Eu/Eu*=1.37–6.68). Compared to the E. Hebei,
Wutai and Huoqiu BIFs, the Anshan-Benxi and Guyang BIFs have more hydrothermal contribution (Fig.4). Although the Ce/Ce* ratios are lower (0.77–1.09), the lack of true negative Ce anomalies in all samples indicates that Anshan-Benxi BIFs were formed in an anoxic ocean. The variation range of positive Eu and Y anomalies in the E. Hebei BIFs is not greater than that of the Anshan-Benxi BIFs. In addition, Y/ Ho values of the Anben BIFs vary from 20 to 80 (Fig. 4).

Figure 4. Post-Archean Australian shale (PAAS)-normalized REY distributions of average BIFs from the NCC

3.4 Fe and Nd isotopes

Iron isotopes are typically reported as δ56Fe values with a range of 5‰ in nature (Fig.5). In general, the largest iron isotope fractionations occur during redox reactions. For instance, during Fe(III) reduction and Fe(II) oxidation, there is ~1.5‰ fractionation. Bekker et al. (2013) collected 490 δ56Fe values of BIFs (Fig. 5) and in this paper we have collected 40 δ56Fe values from BIFs in Anben, Guyang, and Yuanjiacun of the NCC (Fig. 5). The δ56Fe values of the Anben and Guyang BIFs are 0.43–1.88‰ and 0.2–1.0‰, respectively, indicating that all Neoarchean BIFs have consistently positive δ56Fe values. These suggest that ancient ocean is under anoxia and reduced condition during BIF deposition. It is worth noting that the δ56Fe values of younger Paleoproterozoic Yuanjiacun BIF is similar to those of Neoarchean BIFs in NCC, which suggest that Yuanjiacun BIF was also formed in anoxia environment below chemocline, although the Proterozoic ocean was redox-stratified, from oxic shallow waters to deeper anoxic waters.

Whether or not components of the BIFs were derived from continental sources, or had its origin in hydrothermal alteration of oceanic crust dominates the Nd flux to ancient seawater. The positive, mantle-like εNd(t) values of the BIFs also contrast obviously with the negative, continental-like εNd(t) values of Phanerozoic and modern seawater. Here we present neodymium (Nd) isotopic data for the ~3.1 Ga Dagushan BIF and ~2.55 Ga Anshan, E. Hebei and Guyang BIFs in the North China Craton (Fig. 6). It is shown that the εNd(3.1Ga) values (3.3–4.0) in the Dagushan BIFs and εNd(2.55Ga) values (3.0–4.5) in Anshan-Benxi BIFs are close to those of the coeval depleted mantle, implying that the iron were most likely derived from the leaching of oceanic crust; the εNd(2.55Ga) values (2.89–2.58) in the Wutai and E. Hebei BIFs suggest that iron is sourced from mixing oceanic and continental crusts.

Figure 5. δ56Fe values for selected BIF in the NCC, plotted against secular variations in the δ56Fe values of Precambrian iron formations (after Bekker et al. 2010)

Figure 6. Neodymium isotopic signatures of the Neoarchean BIF in CNN, plotted against data from other Archean and Paleoproterozoic BIFs (after Bekker et al. 2010)

4 Discussion and conclusions

4.1 Tectonic setting of BIF

The metallogeny in Precambrian was closely related to the evolution of the cratons (Zhai, 1990). The majority of BIFs in NCC were deposited in arc-related basins at ca. 2.55 Ga (Zhang et al., 2012). As Zhai and Santosh (2013) proposed, the Archean basement of the NCC can be divided into seven micro-blocks, which are considered to be
amalgamated through arc-arc, arc-continent and continent-continent collisions during Late Neoarchean. Although the tectonic style and mechanisms were similar to Phanerozoic plate tectonic regime, the scale was much smaller. It is noteworthy that the volcanic and hydrothermal activities during the amalgamation process generated abundant Fe and Si in the seawater, which resulted in the BIF deposition in arc-related basins during the quiescences.

Trace element characteristics of the rocks associated with the NCC BIFs, including amphibolites and leptynites, are all consistent with the geochemical signature of subduction zone. In particular, the geochemistry of amphibolite samples displays a striking similarity with the N-MORB and BABB (Zhang et al., 2012; Wang et al., 2014).

4.2 Formation conditions of BIF

All the Neoarchean BIFs consist predominantly of alternating iron-rich and silica-rich layers and were generally deposited in relatively deep-water environments with the absence of indications for wave or storm effects. The alternating magnetite-rich and quartz-rich bands in the NCC BIFs reflect stable basin conditions, and their precipitation may occur below storm-wave base, about 200m, which is the average depth of modern storm-wave base (Klein, 2005). Large amounts of geochemical studies on BIFs in the NCC indicate that these BIFs lack apparent Ce anomaly and have positive iron isotope values, which suggest that these iron deposits formed in low-oxygen or anoxic environments. The positive Eu anomaly may infer that these BIFs have the same features with high-temperature fluids.

It is generally accepted that the accumulation of large masses of iron requires three conditions: (1) a stable reservoir; (2) a large supply of Fe; (3) low sulfur and oxygen fugacity (Bekker et al., 2010). Based on geochemistry of the NCC BIFs, there have three contrasting REE sources: continental weathering, seawater and high-T hydrothermal fluids. Iron was introduced to the seawater through high-T water-rock exchange (Isley and Abbott, 1999) or anoxic weathering processes (Rye and Holland, 2000) over a certain period of time, ultimately resulting in the formation of a ferrous ocean. Along with appearance of the ~2.55Ga greenstone belts, vigorous hydrothermal activity associated with enhanced submarine volcanism, especially mafic volcanic eruption, would leached silica and iron out of underlying basalt and komatiites in the ocean floor, and subsequently mixed with ferrous seawater.

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