The theme for this 15th edition is “Life with Ore Deposits on Earth”.

**Suggested citation for the entire volume:**

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**Volume 1**
Advances in understanding hydrothermal processes

**Volume 2**
Magmatic sulfide and oxide systems
Gold - from orogenesis to alluvial
Supergenes, gems and non-metallic ores

**Volume 3**
Magmatic-hydrothermal systems: from Porphyry to Epithermal
New discoveries – new views - Advances in the science of mineral exploration
New Techniques for ore discovery

**Volume 4**
Co-evolution of Life and Ore Deposits
Economics of ore deposits
The changing face of metal extraction - geology, biology and geometallurgy
Sustainable development of ore deposits
Mineral resources for green growth
Open Session

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A digital version of these volumes is available from the SGA website at [www.e-sga.org](http://www.e-sga.org)
Welcome to Glasgow, and the 15th Biennial meeting of Society for Geology Applied to Mineral Deposits – the SGA. Once again, the SGA Biennial has attracted delegates from around the world (57 countries), and across academia and industry, to take part in one of the largest meetings dedicated to Mineral Deposit research ever held in Europe. This is the first time the Biennial will be held in Scotland. Glasgow - and its people: Glaswegians – pride themselves on their particularly friendly, informal welcome to visitors, extending back to its earliest foundations by St Mungo in the 6th century. The meeting will be held in the University of Glasgow, founded in 1451. Amongst many famous people who have taught, worked and studied at the University are Adam Smith, James Watt and William Thomson, Lord Kelvin, whose peerage (and temperature unit!) is named after the river which flows in front of the University’s classic Gothic edifice.

The Local Organising Committee and the Mineral Deposit Studies Group of the Geological Society (MDSG) from which the LOC emerged, presents an exciting Scientific Programme consisting of more than 300 talks and 200 posters, arranged over 13 themes, in 5 parallel sessions. Of course, we thank all of you who submitted an abstract for a talk or a poster for your efforts – together with 3 Plenary, 24 Keynote and 9 Invited talks dispersed over the four days of talks, covering the full spectrum of “Life with Ore Deposits on Earth”, there will indeed be something for everyone at the meeting! Our 7 Short Courses and 4 Field Trips book-end what we hope will be a most memorable experience for you all!

SGA Glasgow 2019 would not have been possible without the dedication of volunteers from Universities and Institutions across the UK and Ireland, and the input of the Glasgow Convention Bureau, Glasgow City Council, the University of Glasgow and our Professional Conference Organisers Abbey Conference and Events, and of course the SGA Council. I thank them, and our many sponsors for their most generous support.

Welcome to Glasgow – welcome to the 15th Biennial meeting of the SGA!

Adrian Boyce
Chair, SGA Glasgow 2019
No one can seriously doubt the challenge over the coming decades for the urgent need to cut CO\textsubscript{2} emissions to secure the future of our planet - but this has enormous implications for our natural resources, for example, to produce green technologies such as electric cars and to keep them charged. Over the next few decades, the global supply of raw materials must drastically change to accommodate this transformation to a low carbon economy for the whole world. Society needs to understand that there is a raw material cost of going green and that both new research and investment is urgently needed for us to evaluate new ways to source these. For example, if we are to achieve targets of making all cars electric worldwide by 2035 (as many governments state) - a projected estimate of two billion cars - the annual production for neodymium and dysprosium would have to increase by 70%, copper output would need to more than double and cobalt output would need to increase at least three and a half times for the entire period from now until 2050 to satisfy the demand.

**Life with Ore Deposits on Earth**, our Biennial tagline, directly addresses many of the underpinning geoscience issues related to this new future. It is both exciting and daunting – but it must start with leading-edge research on understanding our Earth’s natural resources, and how we can responsibly explore for, and extract them to securely deliver the future we all want to see for our children. We are therefore delighted to present to you, in the 4 volumes of the 15\textsuperscript{th} Edition of the renowned “SGA Abstracts”, 492 conference papers totalling almost 2000 pages. Many papers directly address metals related to the electrification of vehicles, and the transformation of energy technologies to our greener future – emerging from initiatives like the UK’s ambitious NERC SoS Minerals Programme. Others address issues of sustainability and economics related to the mining/extraction and exploration industries. There are also, of course, many other papers relating to metals and processes which are delivering new ideas as to the very nature of our planet, including how life itself may have emerged from chemosynthetic hydrothermal processes in the most ancient of oceans.

The SGA Biennial meeting is also a celebration of the cross-fertilisation of ideas between academia and industry which brings a special flavour to the event. And so, the Scientific Program Committee are deeply grateful to the many authors – both from academia and industry – for their contributions. All of these extended abstracts – actually little papers! - are fully peer-reviewed, and of course this takes an enormous effort from a team of dedicated reviewers and editors, to whom we express our sincere gratitude. We also thank theme convenors who inspired colleagues and our plenary, keynote and invited speakers to use SGA as an international platform to share their state-of-the-art research and knowledge. As a result, the meeting is host to >300 talks and 200 posters – a record for the SGA Biennial event. As ever, our meeting is also a truly global celebration of our science with around 700 delegates from around the world – it will be a privilege for us to welcome them all to listen to some of the very latest ideas in Geology Applied to Mineral Deposits in its broadest sense.

Finally, we want to express our gratitude to our Professional Conference Organising company - Abbey Conference and Events, and its devoted staff for their work in preparing the 15\textsuperscript{th} SGA Biennial Meeting Scientific Program and the SGA Abstracts Proceedings.

Gawen Jenkin, Chair
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Richard Herrington – Natural History Museum

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Magmatic sulfide and oxide systems
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Iain McDonald – Cardiff University

Gold - from orogenesis to alluvial
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Rob Chapman – University of Leeds
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Economics of ore deposits
Simon Jowitt – University of Nevada, Las Vegas
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The changing face of metal extraction - geology, biology and geometallurgy
Gawen Jenkin – University of Leicester
Shaun Graham – ZEISS Research Microscopy Solutions
Chris Bryan – BRGM, France

Sustainable development of ore deposits
Anita Parbhakar-Fox – University of Queensland
Karen Hudson-Edwards – Camborne School of Mines

Supergenes, gems and non-metallic ores
Frances Cooper – University of Bristol
Gaston Giuliani – CRPG-CNRS, France

Open Session
Martin Smith – University of Brighton

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We express our gratitude to all the following for their efforts in reviewing the SGA extended abstracts:

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New occurrence of Ag-Hg-Cu mineralization in the Tassafte area, NE edge of the Saghro inlier, Ediacaran-Cambrian transition (Eastern Anti-Atlas, Morocco)

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Abstract. The Tassafte Ag-Hg-Cu mineralization, located about 20 km to the East of Imiter Mine (Ag, Hg), at the NE edge of Saghro inlier, Eastern Anti-Atlas, represents a key zone to study and understand the mineralization history in the Anti-Atlas belt. It exposes E-W-oriented polymetallic mineralization veins hosted within Ediacaran formations and throughout Cambrian formations. The main metallic minerals are represented by argentite, amalgam of Ag-Hg and rarely native silver; copper minerals mainly comprise chalcopyrite, chalcocite, covellite, bornite, and copper oxides. The gangue minerals are mainly constituted by quartz and barite. Preliminary results of our finding show that the Ag-Hg-Cu mineralization in the NE of the Saghro inlier is presumably younger than what has been assumed previously. The mineralization is probably related to the Variscan to Alpine orogenies.

1 Introduction

The Anti-Atlas in Morocco consists of Paleozoic cover overlying Precambrian basement which is exposed within several inliers: Bas Draâ, Ifni, Kerdous, Tagragra-Akka, Agadir Melloul-Iguerda, Igherm, Zenaga, Sirouva, Bou Azzer, Saghro and Ougnat (Fig. 1-A). These mountains are considered as a large metallogenic province for mineral exploration and exploitation (Bouchta et al. 1977; Mouttaqi et al. 2011), positioned at the NW margin of the West African Craton. Its evolution was related to a poly-phase tectono-magmatic history (from Eburnean to Alpine orogeny). In the Eastern Anti-Atlas, the Saghro inlier is composed of meta-sedimentary Cryogenian basement that crops out in restricted areas know as Imiter-, Sidi Feleh-, Bou Skour-, Kelaa Megouna sub-inlier. The Ediacaran Ouarazzazate supergroup consists of volcano-sedimentary successions overlying the basement (Gasquet et al. 2005; Tuduri et al., 2018). This supergroup itself is overlain by Cambrian sedimentary series. The Saghro inlier contains several ore deposits of precious and base metals, such as Imiter- (Ag-Hg), Tiouit- (Cu-Au), Thaghassa- (Au-Ag), and Bou Skour mine (Cu) (Mouttaqi et al. 2011; Tuduri et al. 2018). The mineralizations are hosted within Cryogenian meta-sediments and Ediacaran volcano-sedimentary rocks (Fig.1-B).

Previous studies argued that the mineralization events in the Eastern Anti-Atlas are linked to the extensional regime during late Ediacaran magmatic activities (Levresse 2001; Cheilletz et al. 2002; Gasquet et al. 2005; Bouabdellah and Slack 2016). However, recent data reported from the Imiter mine indicate a younger age for the silver mineralization and it is assumed to be related to the CAMP (Central Atlantic Magmatic Province; Triassic-Jurassic transition) magmatism during the opening of the central Atlantic ocean (Borisenko et al. 2014; Essarraj et al. 2016).

The current work reports for the first time on an Ag-Hg-Cu mineralization in the Tassafte mining district (Eastern Anti-Atlas belt), where the mineralization is hosted within both, Ediacaran and Cambrian formations.

2 Results

The Tassafte mining district is located at the NE edge of the Saghro inlier, about 25 km to the South of Tinghir city and 20 km to the East of the Imiter mine. In this area, two lithostratigraphic units were distinguished (Fig. 2), which correspond to the Ediacaran complex in the southern sector and to Cambrian formations in the northern part.

2.1 Country rocks

In the Tassafte area, the ore veins are hosted within Precambrian to Cambrian formations. The Precambrian is presented by Ediacaran volcano-sedimentary succession in which different lithofacies are identified that comprise rhyolitic ignimbrite, basalt to andesite lava, fallout deposit and a hydroclastic complex. These rocks are unconformably overlain by Cambrian sediments. The lower Cambrian comprises the Igoudine Formation, composed of polygenic conglomerates, the Imoussiekllissafene Formations that consist of alternating carbonates and shales, and fine quartzite beds that represent the Asrir formation. The Middle Cambrian is
composed by greenish shale that represents the Jbel Wawrmast Formation showing interbedded lenses of carbonates and sandstone; the top is characterized by white massive quartzitic sandstones of Jbel Afrou Formation (Fig. 2).

2.2 Ore structures

In the Tassafte area, the ore deposits formed along an E-W shear system, in which the veins are oriented from N80 to N120. These ore structures are hosted in Ediacaran units and continuing within the Cambrian successions. The veins exhibit a thickness varying from some centimeter to decameter and they extend along 1 to 2 Km. They are generally dipping to the south about 55° to 90°, except the main major fault which marks the cartographic limit between the Ediacaran basement and the Cambrian cover and which is dipping to the North (85 to 70°N).
Figure 3. A- BSE image shows amalgam Ag-Hg mineral with different proportion of Ag and Hg that is confirmed by EDX analyses displayed on the right (Number 1 and 2 in circles). B- BSE image shows chalcopyrite and grey copper and their EDX analysis on the right. (Number 1 and 2 in circles). C- Thin section in reflected light image shows galena (gn) mineral within barite (ba) gangue. D- Malachite (mala) and azurite (az) mineralization within microcrystalline quartz gangue (qz).

2.3 Mineralization

Our preliminary results about the mineralization on the Tassafte mining area show a polymetallic mineralization within barite and quartz gangues. In the following, we present a brief description:

-Ag and Hg mineralization
The silver minerals are represented as argentopyrite, argentite, native silver and as an Ag-Hg amalgam (Fig. 3-A). The silver is also associated with grey copper.

-Cu mineralization
The copper minerals are largely present as copper sulfide (mainly chalcopyrite, chalcocite, covellite, bornite) or as a sulfosalt (grey copper) (Fig. 3-B, D). In addition, copper carbonate hydroxides are present as azurite and malachite.

-Zn mineralization
Is represented mainly by sphalerite or also within the
oxide stage in the form of zinc oxide.

-Pb mineralization
The Pb is present mainly as galena (Fig. 3-C).

-Gangue minerals
The gangue is represented by quartz that formed within several generations. They are microcrystalline quartz and geodic ones. Second gangue mineral is barite that show different texture such as massive and colloform.

Conclusions and prospective
The Tassafte mining area is located at the NE part of the Saghro inlier, about 20 km to the East of the Imiter mine. In this district the mineralization are formed in veins with centimetric to metric thickness. They are E-W-trending and they are hosted within Ediacaran and Cambrian successions. The mineralization is represented by copper minerals in the form of sulfide (chalcopyrite, chalcocite, covellite, bornite) or as carbonates hydroxide (malachite and azurite). In addition, the Ag mineralization forms an amalgam of Ag and Hg, or it is present as argentite and argentopyrite. This mineralization is also associated with galena and sphalerite.

Previous studies about the Ag-Hg-Cu mineralization specifically in the Imiter mine considered the mineralization to be restricted to the late Ediacaran age (Levresse 2001; Gasquet et al. 2005; Bouabdellah and Slack 2016). We present data indicating that at least part of the Ag-Hg-Cu-Pb-Zn mineralizations are younger and probably related to Variscan to Alpine orogenies.

Our prospective concerning the mineralization of the Tassafte area, consist of a deep study of the mineralization including fluid inclusions, isotopes, in order to understand the source and the genetic model of this mineralization. A comparison with Imiter mine and similar mining areas in the Anti-Atlas will be also carried out.

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The Xiasai vein-type Ag–Pb–Zn deposit in the Yidun Terrane, SW China: source and timing of magmatism and mineralization

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Abstract. The Xiasai-Lianlong metallogenic belt in the central Yidun Terrane hosts numerous Sn–Ag and (Sn–) Ag–Pb–Zn deposits, which are spatially associated with Cretaceous granites. The Xiasai Ag–Pb–Zn deposit (0.27 Mt Pb+Zn, 1028 t Ag, and 20000 t Sn), is the largest deposit in the belt and is related to a monzogranite intrusion. The deposit consists of (quartz-) sulfides in veins, resulting from three successive mineralization stages (I–III). Rb–Sr isochron dating of sphalerite samples yielded an age of 99 ± 3 Ma and zircon U–Pb LA–ICP–MS dating of the monzogranite gave ages between 102 ± 1 and 101 ± 1 Ma. The δ34S values of eleven sphalerite separates range from −9.7 to −3.1‰ and those from nineteen galena samples from −10.5 to −4.9‰. The estimated δ34S value of the ore-forming fluid is −8.5‰, using the sulfur isotopic fractionation of sphalerite-galena pairs that are assumed to be in equilibrium. Eighteen sulfides from sub-stages II-2 and II-3 have relatively homogeneous Pb isotopic compositions, which are similar with the ones of K-feldspars from the Xiasai monzogranite. Geochronological and isotope data support a magmatic-hydrothermal origin for the Xiasai Ag–Pb–Zn deposit.

2 Geology of ore deposit

The YDT lies between the Qiangtang and the Songpan–Garze terranes and is separated by two oceanic suture zones, i.e., the Jinshajiang suture to the west, and the Garze–Litang suture to the north and east (Wang et al. 2013). Three types of ore deposits belts have been recognized in the YDT: volcanogenic massive sulfides (VMS), porphyry–skarn Cu–Mo, and Sn–Ag polymetallic belts (Hou et al. 2007). The Sn–Ag belt (Xiasai–Lianlong metallogenic belt) is located in the central YDT, and is composed of four large deposits, two medium-sized deposits and numerous smaller Ag polymetallic deposits.

The Xiasai Ag–Pb–Zn deposit (0.27 Mt Pb+Zn, 1028 t Ag, and 20000 t Sn) is controlled by NNNW-trending faults and is located in the northern part of the Xiasai monzogranite (XSM) (Fig. 1). The XSM has a weakly peraluminous A-type granite composition, with high SiO2, alkalis, and FeOt contents, and low CaO, MgO, and TiO2 contents. The host-rocks consist of grey slates, sandstones, intermediate to felsic volcanic rocks, and tuffs, belonging to the upper part of the Triassic Tumugou Formation.

Two types of mineralization, i.e., Sn-bearing veins and Ag–Pb–Zn-bearing veins occur in the Xiasai deposit. The Sn mineralization consists of cassiterite-quartz veins in a proximal location within 800m of the XSM. The Ag–Pb–Zn mineralization is hosted in (quartz-) sulfides veins that are located distal and to the north of the XSM with distance of ~500–3500 m (Fig. 1). Nine Ag–Pb–Zn ore bodies have been recognized and they commonly occur as lodes, lenses, and disconnected pods. The Ag–Pb–Zn mineralized veins exhibit horizontal and vertical zonation in the mineral assemblages. It can be divided into three zones from south to north, i.e., a Sn rich zone, a Zn–Cu-rich zone, and a Pb–Ag-rich zone (Fig. 1). A horizontal and vertical alteration zonation is developed. Three alteration zones are recognized from south to north, i.e., epidote+actinolite+garnet zone, quartz+cassiterite+chlorite zone, and weak quartz+cassiterite zone. Three hydrothermal stages are recognized in the Xiasai deposit, i.e., stage I (quartz-cassiterite veins), stage II (Cu–Zn–Pb–Ag), and stage III (quartz+carnite veins). In addition, the stage II can be further divided into three sub-stages, i.e., sub-stage II-1 (Ap+yPo), sub-stage II-2 (Ccp+Sp), and sub-stage II-3 (Gn+Ag-bearing minerals).
3 Geochronology and isotope geochemistry

3.1 Ages for mineralization and ore-related monzogranite

Rb–Sr isotopic dating were performed using a Thermo TRITON thermal-ionization mass spectrometer (TIMS) at the Wuhan Isotope Laboratory, Chinese Academy of Geological Sciences. More details about the method and procedure can be found in Duan et al. (2014) and Yang et al. (2015). Eight sphalerite samples have Rb contents of 0.022–2.215 ppm and Sr contents of 0.173–7.143 ppm. Their $^{87}$Rb/$^{86}$Sr ratios vary from 0.029 to 6.303 and $^{87}$Sr/$^{86}$Sr values from 0.71051 to 0.73367. The data of seven samples constitute a good linear array on $^{87}$Sr/$^{86}$Sr vs. $^{87}$Rb/$^{86}$Sr correlation diagram with Rb–Sr isochron age of 99 ± 10 Ma ($R^2 = 0.992$). The $^{87}$Rb/$^{86}$Sr ratios for the ZnS phase of samples K18-1S and 4755-1S are 26.51 and 19.09, and $^{87}$Sr/$^{86}$Sr values are 0.76130 and 0.75226. Nine samples, including seven sphalerite phases and two ZnS phases, also constitute a good linear array on $^{87}$Sr/$^{86}$Sr vs. $^{87}$Rb/$^{86}$Sr correlation diagram with an age of 99 ± 3 Ma (Fig. 2). This data is interpreted to represent the age of the Cu–Zn mineralization in the Xiasai Ag–Pb–Zn deposit.

Two samples (XS–5 and XS–1) from the XSM were selected for LA–ICP–MS U–Pb dating of zircon at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences in Wuhan. Eighteen analyses have been carried out on the sample XS–5. Most data plot (n = 14) on or near the concordia curve, and some (n = 4) are shifted to the right side of the concordia curve (Fig. 3), which is probably generated by the analytical uncertainty of $^{206}$Pb.

3.2 Sulfur and lead isotopic compositions

The $\delta^{34}$S values of five sphalerite separates range from −7.6 to −3.1‰ with an average of −6.0‰, and those for five galena samples range from −10.1 to −6.7‰ (mean = −8.2‰) (Fig. 4). The measured $\delta^{34}$S values of sphalerite and galena are similar to those from six sphalerite (−9.7 to −5.5‰) and fourteen galena (−10.5 to −4.9‰) samples found in previous studies (Liu 2003; Ying et al. 2006; Zou et al. 2008). Meanwhile, $\delta^{18}$O values of six
pyrite and four pyrrhotite separates are comprised between –6.4 and –1.2‰, and –7.1 and –6.5‰, respectively. Pyrite has higher δ34S relative to sphalerite and galena. Combined with literature values, the δ34S values of 41 sulfides from the Xiasai deposit range from –10.5 to –1.2‰, with an arithmetic mean of –7.0 ± 3.5‰.

**Figure 4.** Histogram of δ34S values for sulfides from the Xiasai Ag–Pb–Zn deposit

Five galena samples have Pb isotopic ratios of 206Pb/204Pb = 18.711–18.748 (average = 18.727), 207Pb/204Pb = 15.711–15.752 (average = 15.730), and 208Pb/204Pb = 39.104–39.225 (average = 39.158). In addition, thirteen other sulfides including ten galena, two sphalerite, and one pyrrhotite samples have 206Pb/204Pb = 18.687–18.920 (average = 18.767), 207Pb/204Pb = 15.675–15.956 (average = 15.770), and 208Pb/204Pb = 38.979–39.851 (average = 39.331) (Ying et al. 2006; Zou et al. 2008). The lead isotopic compositions of galena samples analyzed in this study and previous sulfides (206Pb/204Pb = 18.711–18.748, 207Pb/204Pb = 15.711–15.752, and 208Pb/204Pb = 39.104–39.225) are similar to those at the Lianlong skarn Ag–Sn deposit, which has 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb ratios of 18.618–18.710, 15.630–15.738, and 38.199–39.176, respectively (Fig. 5; Qu et al. 2001).

Five K-feldspar separates from the XSM have 206Pb/204Pb, 207Pb/204Pb, and 208Pb/204Pb of 18.702–18.731, 15.680–15.718, and 39.000–39.128, respectively, and are distinctly lower than those of the whole-rock samples from the RYCI granite (Fig. 5). Compared with the two types of samples from granites, the ore sulfides from the Ag–Pb–Zn deposit tend to have similar lead isotopic compositions to K-feldspar from the XSM.

**Figure 5.** 206Pb/204Pb and 208Pb/204Pb vs. 207Pb/204Pb plots for ores and monzogranite from the Xiasai Ag–Pb–Zn deposit

with the ages of the Genie biotite monzogranite (LA–ICP–MS U–Pb age on zircons of 105 ± 2 Ma, Wang et al. 2008) and the Chuershan granite (LA–ICP–MS U–Pb age on zircons of 104 ± 1 Ma, Reid et al. 2007) in the YDT. Therefore, it is suggested that the crystallization age of the granites is between 105 to 101 Ma. The younger Ar–Ar and Rb–Sr ages obtained likely reflect post-crystallization episodes related to hydrothermal alterations. The Rb–Sr dating method for different phases of sphalerite was applied to obtain constraints on the age of the Pb–Zn mineralization (Duan et al. 2014; Yang et al. 2015). The Rb–Sr isochron age of 99 ± 3 Ma obtained for sphalerite from sub-stage II-2 is interpreted as the age of Ag–Pb–Zn mineralization. The age for sphalerite is identical within uncertainty to zircon U–Pb age of the XSM in the Xiasai district, thus indicating that the mineralization and the granitic magmatism are coeval.

**4 Discussions**

**4.1 Albian-Cenomanian magmatism and Ag–Pb–Zn mineralization**

Cretaceous granites in the central YDT have been dated at 93–60 Ma by Ar–Ar on biotites and K-feldspars separates, as well as whole-rock Rb–Sr isochron (Qu et al. 2002; Ying et al. 2006). The U–Pb ages for the XSM are between 102 ± 1 and 101 ± 1 Ma, which are coeval with the ages of the Genie biotite monzogranite (LA–ICP–MS U–Pb age on zircons of 105 ± 2 Ma, Wang et al. 2008) and the Chuershan granite (LA–ICP–MS U–Pb age on zircons of 104 ± 1 Ma, Reid et al. 2007) in the YDT. Therefore, it is suggested that the crystallization age of the granites is between 105 to 101 Ma. The younger Ar–Ar and Rb–Sr ages obtained likely reflect post-crystallization episodes related to hydrothermal alterations. The Rb–Sr dating method for different phases of sphalerite was applied to obtain constraints on the age of the Pb–Zn mineralization (Duan et al. 2014; Yang et al. 2015). The Rb–Sr isochron age of 99 ± 3 Ma obtained for sphalerite from sub-stage II-2 is interpreted as the age of Ag–Pb–Zn mineralization. The age for sphalerite is identical within uncertainty to zircon U–Pb age of the XSM in the Xiasai district, thus indicating that the mineralization and the granitic magmatism are coeval.

**4.2 Source of ore-forming materials**

41 sulfides from the Xiasai deposit have δ34S values ranging from –10.5 to –1.2‰ (arithmetic mean = –7.0 ± 3.5‰) with an overall disequilibrium of sulfur isotopes among sulfides during the evolution of the deposit. The sulfur isotopic compositions for the Xiasai deposit are slightly higher than the ones of sulfides from the adjacent Lianlong skarn-type Sn–Ag deposit in central YDT (~10.5 to 9.5‰, Qu et al. 2001). The δ34S value of the estimated ore-forming fluid for the Xiasai deposit is – 8.5‰, using the sulfur isotopic fractionation of sphalerite-galena pairs that are assumed to be in
equilibrium. It is similar to the $\delta^{34}$S value of one whole-rock sample from the Lianlong granite which was associated to skarn-type Sn–Ag mineralization (~8.1‰; Qu et al. 2001). The result indicates that the sulfur may be derived from the XSM. In addition, Wang et al. (2015) proposed that the low $\delta^{34}$S values for hydrothermal Ag–Pb–Zn veins and skarn type Sn–Ag deposits in the central YDT were interpreted as magmatic in origin resulting from partial crustal melting of A-type granites.

The Pb isotopic compositions for ores from the Xiasai Ag–Pb–Zn deposit are identical to those of K-feldspar from the XSM. This probably indicates a common source of Pb and a possible genetic relationship between the XSM and Ag–Pb–Zn mineralization. The controversy regarding the discrimination diagrams for Pb isotopes indicates complex Pb sources for sulfides and granitic intrusions (Wang et al. 2015). Ores and K-feldspar from the XSM in the Xiasai deposit share the same linear relationship in the $^{206}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb diagrams (Fig. 5), which could suggest a two-component mixing model involving crust and mantle components. This conclusion can be corroborated by Lu–Hf isotope on zircons from the XSM ($\epsilon_{Hf}(t) = -2.7$ to 0.6 and $T_{DM2} = 925–1095$ Ma).

5 Conclusions

Zircon U–Pb dating of the XSM and the Rb–Sr isochron age for sphalerite confirms that the granitic magmatism and the formation of hydrothermal Ag–Pb–Zn mineralization were coeval during the Lower to Upper Cretaceous (Albian–Cenomanian). The S isotopic composition is similar to the $\delta^{34}$S value of the LL granite, indicating that the sulfur may be derived from the Albanian granitic intrusions. The Pb isotopic composition of sulfides from the Ag–Pb–Zn mineralization is consistent with the ones of K-feldspar from the monzogranite, suggesting a common origin.

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References

Hydrothermal native element-arsenide (five-element) mineralizations

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Abstract. The hydrothermal native element-arsenide mineralization (five-element) type comprises native Ag and/or native Bi as well as Ni-, Co-, and Fe-arsenides and -sulfarsenides. Due to the current surge in Co-demand, this mineralization type has regained recent economic interest. Thus, it is of interest to further understand the paragenetic and possible spatial relation of Co-bearing minerals and the formation mechanism/process of this mineralization type. This is achieved through an extensive literature review in combination with newly calculated stability relations.

The mineralization is host rock independent, but spatially linked to sources of reducing agents (as this is the cause of precipitation). This reduction process results in a thermodynamically controlled characteristic Ni- → Co- → Fe-diarsenides sequence, as well as a transition from native elements to mono- to di-arsenides. The temporal Ni → Co → Fe trend has also been described to occur on a special scale, and since it is ubiquitous, it may be used as a tool in constraining Co rich sections of a deposit. The formation of this mineralization is, however, not only thermodynamically, but also kinetically controlled, as is evident by the abundant dendritic textures. Kinetics favor a sulfate-sulfide disequilibrium which enables an aqueous sulfide poor system that allows for arsenide formation.

1 The mineralization

Hydrothermal ore deposits that are dominated by Ni-Co-arsenides ± native elements have been labeled "five-element vein type", "five element association", "nickel-cobalt-native silver ore type", "Bi-Co-Ni-As-U-Ag-Formation", and "Ag-Co-Ni-As-Bi type" (e.g., Bastin 1939, Baumann et al. 2000, Kissin 1992, Kissin et al. 1988, Markl et al. 2016, Müller 1860). We propose that this mineralization type should better be termed "Ni-Co-Fe-arsenide type" or "native element-arsenide mineralization", as it always contains hydrothermal Ni-, Co-, and Fe-arsenides and/or sulfarsenides together with variable quantities of native elements (silver, bismuth, arsenic, antimony), metal alloys and in rare cases gold, uranium, antimonides and Cu arsenides (e.g. Bagheri et al. 2007; Hiller and Schuppan 2008; Staude et al. 2007).

The hydrothermal native element-arsenide mineralization has been subject to centuries of exploration and mining. Although economic interest has decreased over time, the ever-increasing recent demand for Co due to in large part the renewable energy industry, this mineralization type has sparked new economic interest. Furthermore, the arsenides are commonly associated with other economically interesting elemental enrichments (such as Ag, Cu, Au; e.g., Bouabdellah et al. 2016, Bagheri et al. 2007) Their current economic importance is evident for example the Bou Azzer mine (Slack et al. 2017) and the recent exploration in Slovakia (Dobšiná and Kolba deposits) by European Cobalt Ltd (Kumova 2017).

The following description (Fig. 1) of the mineralization is compiled, evaluated and generalized by Scharrer et al (in review) from publications on a large number of localities worldwide. These among others include: Anārak, Iran (e.g., Bagheri et al. 2007); Belorechenskoe deposit, Russia (Pekov et al. 2010); Black Hawk district, USA (e.g., Gillerman and Whitebread 1953); Bou Azzer, Morocco (e.g. Bouabdellah et al. 2016); Cobalt-Gowganda, Canada (Bastin 1949; Petruk 1968; Petruk 1971; Marshall and Watkinson 2000); Dobšiná, Slovakia (Kiefer et al. 2017); Great Bear lake, Canada (e.g., Robinson and Ohmoto 1973); Kongsberg, Norway (Kotková et al. 2017); Odenwald, Germany (Heimg 2015; Burisch et al. 2017); Ore mountains Germany and Czech Republic (e.g., Hofmann 1986; Baumann et al. 2000; Lipp and Flach 2003; Hiller and Schuppan 2008); Pyrenees, Spain (e.g., Fanlo et al. 2006); Schladming, Switzerland (Paar and Chen 1979); Schwarzwald, Germany (Staude et al. 2007; Staude et al. 2012); Spessart, Germany (Wagner and Lorenz 2002) ; Valais, Switzerland (Kreissl et al. 2018); Zálesí, Czech Republic (Dolniček et al. 2009).

Figure 1. Simplified Paragenetic sequence of the arsenide and sulfide stage.

The native element-arsenide assemblage (arsenide stage) forms an intermediate stage within a polystage, polymetallic mineralization sequence. The typical dendritic growth of the initial minerals native silver,
native bismuth and niccolite (Ni-monoarsenide), which act as crystallization nuclei to subsequent minerals, define the overall characteristic rosette type texture of the ores. Niccolite typically forms subsequent to the native elements and is in turn overgrown by the generalized consecutive sequence of Ni-, Co-, and Fe-diarsenides (Fig. 1). This mineral sequence has also been reported to be spatially resolvable (Petruk 1968).

Several generations of tri- and sulfarsenides are common and crystallize at random intervals and in variable abundance, but are generally more common towards the end of the arsenide stage (Fig. 1). The Ni→Co→Fe sequence is at times also visible for the tri- and sulfarsenides, but the data on this in the literature is scarce. The arsenide minerals and native elements commonly occur in a gangue of carbonates (typically calcite, dolomite, ankerite or more rarely siderite; Markl et al. 2016), where fluorite, barite, and quartz may be present, but are generally much rarer (Bastin 1939).

There is a gradual transition from the arsenide stage to the subsequent sulfosalts-bearing and base-metal sulfide- mineralization stages. Typical minerals of this stage are Ag-, Sb-, As-bearing sulfosalts together with native arsenic, and base-metal sulfides. These are present in the form of overgrowth and/or replacement textures producing a complex and locally variable mineral succession. This generalized mineralogical succession is very similar (independent of localities), and only the absolute abundance between minerals varies. It should, however, be noted that this mineral sequence is only generalized and may not always be visible in individual samples.

2 Genesis

2.1 Precipitation mechanism

The formation temperature (fluid inclusion data) of the arsenide stage varies greatly between localities (50-400 °C) and no systematic cooling has been observed (e.g. Bouabdellah et al. 2016, Markl et al. 2016; and references therein), which indicates a principally temperature-independent formation mechanism. The fluids are highly saline (up to 50 wt% NaCl eq. containing dominantly NaCl and CaCl₂ (e.g., Bouabdellah et al. 2016, Markl et al. 2016). The fluid source has been strongly debated, between and for individual localities (e.g., Bou Azzer: Bouabdellah et al. 2016; e.g., Cobalt-Gowganda: Petruk 1968, Echo-Bay: Robinson and Ohmoto 1973) and there seem to be several fluid sources. Thus, the source is irrelevant for the formation of this mineralization, as long as the fluid carries the necessary metals.

The conspicuously similar mineralization sequence implies common formation conditions/mechanisms for this mineralization type, independent of location. However, several different formation mechanisms have been proposed in the past (Burisch et al. 2017; Kissin 1993; Kreissl et al. 2018; Markl et al. 2016; Ondrus et al. 2003a; Robinson and Ohmoto 1973). Most of these differ to some degree, but involve some sort of redox change. The abundant minerals, native bismuth, native silver, arsenides and native arsenic are only stable under reduced conditions, whereas their constituent elements are soluble under more oxidized conditions, Markl et al. (2016) and Burisch et al. (2017) related the formation of native element-arsenide assemblages to a process of strong and rapid reduction. Furthermore, hydrocarbons have been identified in fluid inclusions, also indicating very reduced conditions (e.g., Odenwald: Burisch et al. 2017; Cobalt-Gowganda: Kerrich et al. 1986; Bou Azzer: Essarraj et al. 2016 and Imilet: Levresse et al. 2016). Lastly, a close spatial association of ores and reducing agents such as siderite, sulfide, and/or graphite-rich host rocks and organic-rich shales has been described for several localities (e.g., Cheilletz et al. 2002; Kissin 1993 and references therein, Kreissl 2018; Lipp and Flach 2003). From an exploration point of view, this signifies that the hydrothermal native element-arsenide mineralization is spatially independent of the host rock or specific fluid source, but is constrained to the presence of various reducing agents.

3 Methodology

Thermodynamic modeling was done using the Thermomod database of 2017 (Blanc et al. 2012) with internally consistent additions and the Phase 2 application of the Geochemist’s Workbench 12 ® (Bethke 2007). For thermodynamic modeling procedures, thermodynamic data selection and estimation, as well as fluid composition compilation and constraints see Scharrer et al. (in review).

4 Genetic model

4.1 Mineral sequence

According to thermodynamic predictions, the initial minerals that precipitate during fluid reduction are native silver and native bismuth (Fig. 2). This is in perfect agreement with petrographic descriptions (see above). The subsequent formation of Ni-monoarsenide and then Ni-, Co- and Fe diarsenide (that is present in nearly all localities) is also in accordance with thermodynamic predictions at mildly basic to acidic conditions (Fig. 2). Ni-monoarsenide only forms at neutral to basic pH, which enables the formation of Ni-diarsenide without abundant initial Ni-monoarsenide. The arsenide sequence (Ni→Co→Fe) is determined not only by the decreasing stability of the minerals, but also by the increasing thermodynamic stability of the aqueous Cl- and O-complexes from Ni to Co and followed by Fe. Thus, during reduction, the fluid is successively depleted in elements (e.g., Bouabdellah et al. 2016) due to this precipitation sequence. This sequence, but not the absolute abundance of the arsenides, is largely independent of Ni, Co and Fe concentration in the fluid, as it would require a three order of magnitude difference in concentration to change. A nearly complete miscibility is present between the diarsenides in natural samples (not considered in the thermodynamic calculations).
Thus, such a large difference in concentration would result in some minerals not forming.

Figure 2. Thermodynamic model of the Ni-Co-Fe-As (top) and Ni-Co-Fe-Pb-Zn-As-S system (bottom) modified from Scharrer et al (in review).

4.2 Sulfide enigma

Concerning liberations and extraction during processing, it can be vital to understand the mineralogy and their textural occurrence. Although normally, arsenides dominate, some occurrences present a predominance of sulfarsenides over arsenides (e.g., Dobšiná: Kiefer et al. 2017; Kongsberg: Kotková et al. 2017; Valais: Kreissl et al. 2018). Thus, at these locations the Co/As ratio of the ore is expected to be significantly larger, since the undesired arsenic is replaced by sulfur.

Sulfarsenides become thermodynamically stable even at low sulfide concentrations (<<10 mg/kg S) until the present aqueous sulfide has been precipitated as sulfarsenides. At these conditions, they form co-genetically with the arsenides which is featured in natural samples as sulfarsenide or sulfide-rich arsenide bands within arsenide rosettes. Thus, it is likely that these textures represent a local and short-lived increase of the sulfide activity in an otherwise sulfide-deficient solution.

If, however, more sulfide is present, the sulfarsenides become predominant over the arsenides and no arsenides would form (Fig. 2). The only exception is the Ni-monoarsenide that is stable at higher oxidation states than the Ni-sulfarsenide. Furthermore, Ni-, Co-, and Fe-sulfides as well as base metal sulfides and sulfosalts become stable. These minerals are however, all absent in the arsenide stage and only, in part, become relevant in the subsequent sulfide stage. Thus, the sulfide content of the mineralizing fluid has to be low in order to form the arsenide- and native element-dominated mineralization at hand. For sulfide to be scarce, either sulfur has to be limited or a disequilibrium between sulfide and sulfate is present during reduction. Although both scenarios can occur in nature, the thermodynamic disequilibrium is certainly an important factor since sulfate-sulfide kinetics are very sluggish at low temperatures (<200 °C; Ohmoto and Lasaga 1982) and some localities show cogenetic sulfate in the form of barite together with arsenide (Lipp and Flach 2003; Stuewe et al. 2012). Thus, our proposed slower reduction of sulfate to sulfide than arsenate/arsenite to arsenide might also be relevant at temperatures well above 200°C.

The transition to the sulfide stage is indicated by the formation of sulfosalts and base metal sulfides. This and the typical reaction textures of native silver and native bismuth to sulfosalts indicates the increase in sulfide at the transition from the arsenide to the sulfide stage. This can be attributed to either the delayed reduction of sulfate to sulfide or by an influx of sulfide/mixing of a sulfide bearing fluid.

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A new look at the geology of the White Pine Cu-Ag deposit and the Midcontinent Rift System

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Abstract. The White Pine Cu-Ag deposit in the Midcontinent Rift System (MRS) is one of the archetype sediment-hosted stratiform copper deposits, with an initial resource of ~10Mt contained Cu metal. A reinterpretation of reflection seismic data shows the basin lacks many features characteristic of rifts such as syn-sedimentary faults and alluvial fans. Mineralisation is hosted in the ~1.1 Ga Oronto Group, between braided fluvial sandstone and conglomerate of the Copper Harbor Formation, and siltstones and shales of the Nonesuch Formation deposited in an estuarine setting during a marine transgression. New stable isotope and petrographic data reveal the ingress of seawater into the Copper Harbor Formation aquifer that facilitated the leaching of metals from basaltic detritus during diagenesis. The mineral paragenesis suggests that rapid burial compaction of the aquifer, in tandem with incipient inversion, drove fluid flow. Formation waters reutilised earlier petroleum migration pathways, flowing towards the margins of the sag basin where they were focused by faults on the margins of a paleo-topographic high. Metals were deposited in a zoned sequence during thermochemical sulphate reduction across a redox front of liquid petroleum and in situ organic matter.

1 Introduction

Sediment-Hosted Stratiform Copper (SHSC) deposits are one of the major sources of Cu worldwide. They are believed to form in rift basins containing evaporite sequences, from the interaction of moderate temperature, highly saline, oxidised and metal-bearing brines with reduced lithologies such as organic-rich shales or liquid hydrocarbon traps (Hitzman et al. 2005). The Midcontinent Rift System (MRS) of the American Mid-west is anomalous to other rift systems containing SHSC deposits as it contains an unusually large volume of mafic rocks, no known evaporite sequences, significant native copper mineralisation, and is hosted in shales of lacustrine origin rather than marine (Elmore 1989). Previous interpretations of reflection seismic data identified syn-sedimentary and syn-volcanic faults on the basin margins (Cannon et al. 1989; Dickas & Mudrey 1997). The sedimentary fill of the basin was interpreted as early alluvial fans shedding conglomerates into a half-graben subsequently filled by lacustrine siltstones and shales (Daniels 1982).

Prevailing models for the formation of SHSC mineralisation at White Pine, Copperwood and nearby prospects suggest fluids were driven by volcanism (Brown 2014a), gravity compaction (Swenson et al. 2004), meteoric recharge (Brown 2014b) or a combination thereof. A second phase of mineralisation is interpreted to have formed around thrust faults during subsequent (Grenville orogeny) basin inversion at 1047 ± 35 Ma (Ruiz et al. 1984; Mauk et al. 1992). Here we present new interpretations of reflection seismic data, new data on core and outcrop including C-O isotopes on carbonate rocks, sulphur isotopes on sulphide minerals and H-O isotopes on authigenic clays. A detailed paragenesis is compiled from petrography and drill core observations with peak temperature estimates and characterisation of alteration minerals derived from X-Ray Diffraction (XRD). We combine these data into a holistic understanding of the mineral system, the geodynamic and structural evolution of the basin, the stratigraphic framework for the Oronto Group, the changing nature of the pore fluids within these rocks and the factors that influenced the timing of fluid flow.

2 Geological setting

The MRS is a c. 2000 kilometre-long arcuate feature of dense and magnetic rocks in the eastern portion of the Laurentian continent, interpreted commonly as a failed rift (Cannon 1994; Stein et al. 2014). That is based on reflection seismic data in which basin-margin, syn-volcanic and syn-sedimentary faults have been inferred.
The basin fill consists of a lower sequence c. 20 km thick of basaltic volcanic rocks and an upper sequence c. 10 km thick of sedimentary rocks that constitute the Keweenaw Supergroup (Ojakangas et al. 2001). Volcanic rocks are overlain by the Oronto Group, which from the base upwards includes the Copper Harbor, Nonesuch and Freda formations. The Copper Harbor Formation contains lithic arenites and conglomerates interpreted as alluvial fans (Elmore 1989) with multiple minor volcanic units (Baumann et al. 2018). The Nonesuch Formation conformably overlies the Copper Harbor Formation (Daniels 1982), comprising siltstones and shales including organic-rich and micritic beds and is interpreted to be of a lacustrine origin (Elmore 1989), although organic geochemistry studies have highlighted evidence of marine influences (e.g. Hieshima and Pratt 1991). The Freda Formation is a brown-coloured alluvial sandstone of greater textural and compositional maturity than the Copper Harbor Formation (Daniels 1982). In the western Lake Superior sub-basin, the Oronto Group is unconformably overlain by the sub-arkosic Jacobsville Sandstone (Kallikoski 1982). Placed within the context of a rift basin, the Copper Harbor Formation alluvial fans were shed into half grabens filled subsequently with lacustrine siltstones and shales of the Nonesuch Formation (Daniels 1982). Contrasting explanations for why the MRS failed to extend to develop oceanic crust include compression related to the Grenvillian Orogeny (Cannon 1994) or extension accommodated elsewhere on the margin of Laurentia (Stein et al. 2014).

3 Results

3.1 Basin architecture

A total of 21 reflection seismic lines have been collected across Lake Superior, imaging the subsurface to a depth of up to ~30 km (e.g. Behrendt et al. 1988). Our interpretation of the seismic data shows that the volcanic rocks, including the Portage Lake Volcanic (PLV) flows, display a draped geometry with units thickening towards the centre of the basin. An unconformity surface truncates the top of the volcanic units, cutting deeper into stratigraphy at topographic highs and at the margins of the basin. The low resolution of the seismic data prohibits the identification of individual formations above this unconformity. Clinoforms within the lower Oronto Group show clear onlap of units onto this unconformity surface and infill a pre-existing topography. Clinoforms within the lower Oronto Group, interpreted to be Copper Harbor Formation, prograde systematically northward into the basin centre. The uppermost units imaged in the seismic data lie above an unconformity although it is unclear if the surface is the base of the Freda Formation, Jacobsville Sandstone or another unit. Late reverse faults are present on the northern and southern margins of the basin. The faults ramp up through stratigraphy becoming steeper near the surface and displaying offsets of 10-20 km. All volcanic and sedimentary units show constant thicknesses across faults.

3.2 Stratigraphy and sedimentology

The surface at the top of the PLV is a gentle undulating surface with a locally-developed paleosol, overlain unconformably by a relatively well-sorted sandstone unit. The Copper Harbor Formation varies from 115 m to ~1400 m in thickness and its lower part is dominated by conglomerate with well-rounded cobble to boulder-sized clasts of mostly basalt reworked from the underlying PLV Group. Beds are 2-3 m thick and display imbrication and subtle upward fining. Upwards, the conglomerate becomes interbedded with trough and planar cross-bedded sandstone, in upward fining channelized beds. The topmost units are dominated by sandstone that locally fines up into shale and contains stromatolites, evaporite minerals, flaser bedding and features indicative of a sabkha. The distribution of these facies extends over tens of kilometres laterally, with grain size fining vertically and laterally away from basement highs. The Copper Harbor – Nonesuch Formation contact is conformable and is commonly interbedded over several meters. The basal Nonesuch Formation contains abundant organic-rich shales, microbial mat textures, syneresis and desiccation cracks, flat-top ripples and heterolithic bedding. These units are overlain by a more homogenous fine-grained, dark siltstone recognisable across the basin. The unit also contains abundant flaser bedding. A third unit at the top of the Nonesuch Formation contains coarser-grained sands and silts with hummocky-cross stratification and evidence of cyclical flow reversals. Brown fluvial sandstones of the Freda Formation lie unconformably above the Nonesuch Formation on an erosional surface which cuts downward through stratigraphy towards the southwest.

3.3 Mineral paragenesis

Approximately 200 thin sections were examined with a focus on the paragenetic sequence and spatial distribution of authigenic minerals. Framework grains in the Copper Harbor Formation show hematite coatings that appear coeval with early tangential anisopachous smectitic rims. The smectite content varies from zero to completely filling pore throats. The upper Copper Harbor Formation from the White Pine and Copperwood areas shows evidence of widespread hematite destruction resulting in a colour change from red-brown to grey or beige across an area of ~25 x 25 km. A zone of neoformed isopachous chlorite rims is present in the lower Nonesuch and uppermost Copper Harbor formations beneath White Pine. Chlorite rims overgrew and possibly replaced earlier smectite rims. The zone of chlorite alteration attains a maximum thickness of up to 10 m on the southwest side of the White Pine fault. Pyrobitumen (solidified petroleum) fills many interstitial pores, post-dating chlorite rims, with which it displays a close spatial association. Native copper commonly mantles pyrobitumen in interstitial pores and copper sulphides replace pyrite that has nucleated on the surfaces of detrital and authigenic chlorite grains.
Syntaxial quartz overgrowths commonly fill pores and post-date copper mineral grains. Quartz cements are particularly well developed in quartz-rich sandstones and around grains that are not rimmed by smectite or chlorite. Grain dissolution textures, including framework quartz grains, are commonly infilled by a late poikilotopic calcite cement.

### 3.4 White Pine deposit geology

The bulk of copper mineralisation is hosted in carbonaceous siltstones and shales of the basal Nonesuch Formation. The zonation of ore minerals, from the base upwards, includes ~0 to 5m of native copper, a chalcolite zone up to ~10m thick, and an upper ~50cm thick zone of bornite, chalcopyrite and greenockite (CdS). Native silver is concentrated in the uppermost ~30cm of the Copper Harbor Formation. Native copper mineralisation is stratigraphically restricted to pyrobitumen-bearing Copper Harbor Formation sandstones and the lowermost Nonesuch Formation. Copper mineral zonation is peneconcordant and stratigraphically highest near the Porcupine rhyolite dome. Copper minerals are most often present in mm-scale sand laminae within the shales, with minor amounts in mm to cm-scale reverse faults. The copper mineral species in these reverse faults shows the same gross zonation pattern as disseminated copper mineralisation. The White Pine fault displays ~200 m of normal offset and evidence of syn-sedimentary movement (down to the southwest) that includes coarser sediments, thickened stratigraphy and erosional scouring in the hangingwall. The fault both focused and partitioned chlorite alteration, interstitial pyrobitumen and native copper mineralisation; the zones of which tend to be thickest in its hangingwall. Irregular, late pyrobitumen veins show a close spatial and genetic relationship to faulting, and are cut by and re-utilised by calcite veins. High angle (~60°) inverted normal faults offset mineralisation by 10s of meters.

### 3.5 Stable isotopes

Stable isotope analyses were completed on sulphide, carbonate and silicate phases from drill core samples across the basin. White Pine, Copperwood and other prospects displaying a similar style of mineralisation show a wide range of δ34S values, of -24.2 to +29.9‰. A prospect containing structurally controlled chalcocite mineralisation displayed a bimodal distribution of δ34S values of ~25 and +15‰. Mineralisation from a stratigraphically lower basalt-hosted deposit and the Mount Bohemia diorite intrusion displays a tight cluster of values close to 0‰, suggesting a different and homogenous source of S. C and O isotopes were analysed in early and late concretions, micrite beds, interstitial cement and several vein generations. The δ18O values varied from ~25‰ for early diagenetic features, ~18‰ for cement and ~15‰ for veins. Calcite cement from mineralised samples contains isotopically lighter C and O of ~9 and ~18‰, respectively. Pre-ore authigenic chlorite coatings on framework grains record the δD and δ18O of pore water shortly before ore formation. Samples were taken from several prospects across the basin and preliminary δDfluid data (~1.4 to 26.2‰) show evidence of a marine-dominated fluid. Oxygen isotope data are pending.

### 3.6 X-Ray diffraction

Copper Harbor Formation sediments onlap an unconformity surface above the PLV Group, infilling an undulating paleo-topography. Sedimentary features within the Copper Harbor Formation are indicative of a braided fluvial deposit and we find no evidence to support the interpretation that it records syn-rift sedimentation. Lithofacies indicative of marine settings that occur in the uppermost Copper Harbor Formation and lowermost Nonesuch Formation suggest deposition in tidally-influenced shallow-marine setting: abundant desiccation cracks, evaporite minerals and sabkha features are evidence of periodic subaerial exposure. We envisage an embayment or estuarine setting in which circulation was sufficiently restricted so as to promote the preservation of organic matter.

The marine transgression that initiated Nonesuch Formation deposition would have resulted in seawater displacing meteoric water in the pores of the underlying Copper Harbor Formation. This is confirmed by the isotopically heavy δDfluid values calculated from authigenic chlorite rims. The presence of evaporite minerals in the lower Nonesuch Formation suggests residual brines may also have percolated down into the Copper Harbor Formation aquifer, thus providing Cl ligands for metal transport.

Isopachous authigenic chlorite in the uppermost Copper Harbor Formation beneath White Pine is absent at grain-grain contacts suggesting formation during mesodiagenesis, after the onset of compaction. Chlorite and smectite rims appear to have inhibited silica cement, and in the case of chlorite, prevented over-compaction and pore collapse. Bleaching of hematite rims at White Pine and Copperwood is interpreted to be the result of iron dissolution at sites of high fluid flux. The attenuation of the aquifer around the Porcupine rhyolite forced ore-forming fluids to higher stratigraphic levels. Thicker shale units in the hanging walls of syn-
sedimentary faults (e.g. White Pine fault) promoted ore deposition lower in the stratigraphy. The top of the native copper zone varies in concert with that of the copper sulphide zones above, and formed in the same paragenetic window, suggesting sulphides and native metals formed coevally under a common redox architecture. Sulphur isotope data imply thermochemical sulphate reduction was the main precipitation mechanism of the sulphides. The presence of minor amounts of ore in small-scale thrust faults that contain exclusively copper minerals suggests that the mineralisation extended into incipient basin inversion.

Paleo-temperature estimates correlate with inferred burial depths (and subsequent exhumation along the Keweenaw fault) and thus call into question interpretations suggesting thermal perturbations being driven by volcanism.

5 Conclusion

The Copper Harbor Formation was deposited on a paleo-topographic surface as a permeable and metal-rich source rock. A marine incursion into the basin resulted in a restricted embayment or estuarine setting that produced carbonaceous shales and brines which percolated into underlying sandstones. Breakdown of volcanic detritus in the Copper Harbor Formation during eo- and mesodiagenesis liberated metals into saline pore waters, initially producing (Mg-Fe) chlorite grain coatings that preserved aquifer porosity. Migrating petroleum was focused towards the edges of the basin and by basin-normal structures at White Pine and Copperwood deposits. Progressively deeper burial and compaction of the Copper Harbor Formation drove oxidised and saline Cu-Ag-bearing brines into these petroleum trap sites where metals precipitated upon reduction of the brines by liquid petroleum or in situ organic matter in shales. Sulphur was sourced primarily from thermochemical sulphate reduction of seawater. Normal geothermal gradients in the basin preclude volcanic thermal inputs as a fluid drive mechanism and meteoric recharge is discounted due to the abundant evidence of seawater influence. The location of ore deposits at topographic highs on the margins of the basin, and the timing of ore deposition (during compaction and sediment loading) suggest burial compaction as the dominant fluid drive mechanism. The process of mineralisation spanned incipient inversion, during which the same redox architecture governed metal zonation in the deposits. Mineralisation likely ceased when sediment-loading decelerated and primary permeability in the Copper Harbor Formation aquifer was degraded by pore-clogging quartz and calcite cements.

Acknowledgements

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References


Textural and mineralogical constraints on the mode of formation of the Bou Azzer Co-Ni arsenide mineralization (Anti-Atlas, Morocco): Tectonic implications.

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Abstract. The Bou Azzer inlier is thought to represent a suture zone within a Neoproterozoic orogeny. The Bou Azzer inlier is composed of an assumed ancient oceanic crust of serpentinitized ultramafic rocks, gabbro and basaltic pillow rocks. This inlier hosts the Co-Ni ore deposit of Bou Azzer with two types of mineralization: i) massive, elongated ore bodies, known as “contact” type mineralization, along the contact between serpentinite, quartz diorite and Precambrian volcanic rocks; and ii) a “cross-cutting” type represented by faults that cut all units, only mineralized at the vicinity of the “contact” type. A detailed mineralogical and textural study brings new arguments on the ore-formation processes at Bou Azzer. First, it appears that both types of mineralization are developed within a progressive and continuous tectono-hydrothermal stage as shown by the mineralogical evolution. Second, the “contact” type exhibits two aspects: i.e., Laminated Contact Mineralization (LCM) and Breccia-Related Contact Mineralization (BRCM) that are related to different initial textures of the pre-mineralization host rocks. Third, Ni-Co mineralization seems to have developed by replacement of spinel/magnetite grains of the serpentinite. All these observations are consistent with ore formation along a tectonic contact which explains the existence of serpentinite fragments slope breccia.

1 Introduction

Various cobalt mineralization styles on Earth cannot be attributed to a single ore-forming model. At least, six major mineralization styles are known: 1) sediment-hosted stratiform Cu-Co deposits (Fay and Barton 2012); 2) ortho-magmatic sulfide deposits (Naldrett et al. 1998); 3) Co from lateritic profiles mainly exploited for Ni (Orloff 1968); 4) Co-rich crusts associated with Mn-nodules within seawater hydrothermal oxidizing venting environment (Hein et al. 2000); 5) hydrothermal/volcanogenic deposits (the Bou Azzer district) (Leblanc 1975; En-naciri 1995); 6) Five elements (Ni-Co-As-Ag-Bi) vein-type deposits (Kissin 1988; Markl et al. 2016; Burish et al. 2017). At Bou Azzer, two types of ore bodies exist – the “contact” and the “cross-cutting” types. Yet, their mode of formation remains unclear, especially regarding their relationship with large-scale geodynamic processes. In this study, we present and discuss: i) mineralogical and paragenetic features that favor coeval processes of formation for the two mineralization types at Bou Azzer; ii) new textural observations helping to discuss the pre-mineralization tectonic context and its implication on the presently admitted classical model of Precambrian ophiolite for the Bou Azzer inlier (Leblanc 1976, Gasquet et al. 2005).

2 The Bou Azzer – El Graara inlier and the deposits

The Bou Azzer – El Graara inlier, oriented NW-SE, is located in the central part of the Moroccan Anti-Atlas, south of Ouarzazate. This inlier is composed of a dismembered but complete sequence of an assumed ancient oceanic crust made of serpentinitized ultramafic rocks overlaid by gabbroic and basaltic pillow rocks (Leblanc 1975, 1976, 1981; Bodinier et al. 1984). This area is thus interpreted as being a suture zone related to the Neoproterozoic orogeny (e.g. Choubert 1963; Leblanc and Lancelot 1980; Saquaque 1992). The tectono-magmatic evolution of this area (Tuduri et al. 2018) involves a first event, associated with the emplacement of large volumes of high-K calc-alkaline magmas in meta-sediments that were deformed under transpressive tectonic control (the Lower Complex). A second transtensive deformational event is associated with intense magmatism, volcanism and deposition of volcano-clastic sediments (the Upper Complex). The Precambrian group of Ouarzazate, characterizing the Upper Complex, is composed of dacitic to rhyolitic ignimbrites and andesitic tuffs (Mifdal and Peucat 1985); all intruded by a calc-alkaline to highly potassic plutonic rocks. All these Precambrian units are covered by the Cambrian sedimentary cover (Pouit 1966; Bouchta et al. 1984).
3 Textural and paragenetic constraints on the mineralization

3.1 The Co-Ni ore deposits of Bou Azzer

Two types of ore bodies occur in the Bou Azzer district, as defined by Leblanc (1975) and En-naciri (1995) (Fig. 1):

i) The massive “contact” type is composed by Co-Ni-Fe arsenides hosted within a siliceous or carbonaceous gangue. This mineralization is developed systematically at the contact between serpentinites and quartz-diorite and/or Upper complex volcanic rocks, located south and north of the serpentinite occurrences, respectively.

ii) The “cross-cutting” type is composed of Co-Fe arsenide mineralization, within K-feldspar, quartz and carbonate veins. These veins intersect all units, and are only mineralized at the vicinity of the “contact” type ore bodies.

A petro-structural model is proposed in order to integrate the six mineralization stages within three main events which lead to the formation of the Bou Azzer deposits (Fig. 1):

1) a Ni-Co-rich arsenide stage composed of nickeline, rammelsbergite and subsequent cobaltite and skutterudite;
2) the formation of the siliceous or carbonaceous gangue associated with the late Co-rich arsenide and the earlier Fe-rich sulfo-arsenide minerals;
3) the formation of the cross-cutting structures mainly hosts the final stage of the Co-rich arsenide mineralization and the Fe-Cu-bearing sulfide minerals, both occurring in veins mainly composed of K-feldspar (minor), quartz and carbonate.

3.2 Textural observations on the massive type

A detailed textural analysis of the "contact" type mineralization led to the following observations:

1. The massive arsenide-rich parts of the mineralization show two distinct textural features:
   - Massive lenses of lamellar nickeline surrounded by skutterudite sometimes alternating with carbonate forming a banded texture (Fig. 2a).
   - Massive lenses of arsenides with isolated nuclei of elongated rammelsbergite surrounded by cobaltite, carbonate, skutterudite and chalcopyrite, all included within large euhedral skutterudite and with late carbonate (Fig. 2b);

2. The gangue of the contact mineralization is mainly carbonaceous and may exhibit several inherited fragments of serpentinite (Fig. 3a), indicating the nature of the host rock (serpentinite) prior to the formation of the mineralized structure;

3. Skutterudite is commonly fractured, with neo-serpentine infilling (Fig. 3b). This demonstrates that the serpentinization was still active during at least the earliest mineralization stages.

4. Spinels and rammelsbergites entirely replaced by spinel are observed within the serpentinite close to the contact (Fig. 3b). Spinels are systematically bordered by magnetite (Fig. 3c) or rammelsbergite (Fig. 3b). In addition, cathodoluminescence imaging shows relics of spinel frequently occurring in the core of the carbonaceous gangue (Fig. 3c). This demonstrates again that serpentinite was the precursor of the mineralized gangue.

5. Cathodoluminescence imaging of the carbonaceous gangue shows that two textures co-exist: i) one dominated by large euhedral crystals evolving
toward, ii) fragmented grains with a lot of space between them. This last texture seems to be related to dilatation breccia formed within a stress-free open space (Fig. 3d) (Jébrak 1997; Chauvet 2019).

The carbonaceous gangue shows two types of texture: brecciated texture of thin carbonates and euhedral texture of large carbonates (image of CL). Carb: carbonate, Co: Cobalt, Mgt: Magnetite, Ni: Nickel, Ram: Rammelsbergite, Serp: serpentinite

4 Formation of the Bou Azzer ore deposit and tectonic implications

We draw two main conclusions from the textural and mineralogical analysis of the Bou Azzer mineralization:
- The mineralogical evolution of both “contact” and “cross-cutting” mineralization types results from a progressive and continuous process that begins with Ni-Co ore formation followed by Co-Fe-Cu-rich stages. The Ni-Co stages are encountered exclusively within the “contact” type while the Co/Fe/Cu stages developed in both structures. This suggests that both mineralization types, i.e. the contact and the cross-cutting ones, are produced during the same tectono-mineralogical event, although the “contact” type ore bodies formed first.

- The textural features within the “contact” type demonstrate that these domains result from replacement and hydrothermal processes that affect a serpentinite rock. Textural constraints indicate that most of the ore bodies derived from serpentinite breccia could form Breccia-related Contact Mineralization (BRCM); although some may have been formed by the transformation of banded serpentinite levels, Laminated Contact Mineralization (LCM) (Fig. 4). It is suggested that such brecciated areas, characterized by high permeability, are favorable domains for fluid circulation.

Figure 2. a. The “contact” type composed of laminated contact mineralization (LCM) of Ni-Co rich arsenide then surrounding by carbonate (image in reflected light). b. Nucleus of Rammelsbergite surrounding by skutterudite, carbonate, chalcopyrite, in a massive gangue of skutterudite and carbonates, indicates a brecciated-related environment of the contact mineralization (BRCM) (image in reflected light). Carb: carbonate, Co: Cobalt, Cp: Chalcopyrite, Ni: Nickel, Ram: Rammelsbergite, Sk: skutterudite

Figure 3. a. Fragments of a previously serpentinite in the carbonaceous gangue (image in polarized light) b. Few information of texture is visible: fractured skutterudite by serpentinite, spinel entirely replaced by rammelsbergite, spinel is observed in the serpentinite host rock (image in polarized light). c. Spinel is included also in the carbonaceous gangue of the “contact” type, is bordered by magnetite (image of cathodoluminescence – CL). d. The carbonaceous gangue shows two types of texture: brecciated texture of thin carbonates and euhedral texture of large carbonates (image of CL). Carb: carbonate, Co: Cobalt, Mgt: Magnetite, Ni: Nickel, Ram: Rammelsbergite, Serp: serpentinite
and subsequent ore formation.

- The occurrence of spinel relics bordered by magnetite and rammelsbergite confirms the hypothesis of replacement of serpentinite levels. It is suggested that spinel and magnetite fragments are at the origin of the Ni/Co-rich arsenides whereas serpentinite ones formed the gangues.

A first hypothesis regarding the tectonic context of ore formation at Bou Azzer is illustrated in figure 4. The brecciated levels, as precursors for the formation of the contact orebodies can result from the activity of normal faults and the geometrical constraints of the inlier. Such normal faults may have helped the exhumation of the serpentinitized mantle in this area. However, they are inconsistent with the obduction scenario.

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Galena trace element geochemistry of the precious and base metal-rich deposits in the Cyclades District, Greece

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Abstract. The extensional back-arc setting in the Aegean Sea hosts polymetallic ore deposits that are temporally associated with the emplacement of Miocene granitoids and occur adjacent to major detachment systems. Various types of mineral deposits (e.g., carbonate replacement, skarn, vein-type, and low- to high-sulfidation epithermal) formed during different stages of back-arc evolution and can be found in the metamorphic basement, unmetamorphosed hanging wall and Quaternary volcanic units along the active volcanic arc. A comparison of the trace elements in galena from twelve deposits across the Cyclades District was carried out by LA-Q-ICP-MS analyses to identify possible geochemical similarities and differences at regional and local scales. The new trace element data demonstrates the usefulness of galena as an abundant and widespread indicator mineral for ore-forming fluids in the Cyclades. In addition to spot analyses, traverses through galena reveal compositional zoning, which indicates that changes in the fluid chemistry are encountered during crystal growth. Despite these variations, galena from the same deposit show small variations in trace element concentrations that appear to be characteristic of the particular setting and host rocks. Regional differences in trace element concentrations in galena reflect the conditions of mineralization and metal sources in the Cyclades District.

1 Introduction

Precious and base metal-rich deposits in the Cyclades District are temporally associated with different stages of the geodynamic evolution of the arc and back-arc (e.g., Skarpelis 2002). Recent studies by Melfos and Voudouris (2017) and Menant et al. (2018) highlighted the temporal change in mineralization styles and commodities in the Cyclades District. Despite the long mining history and detailed studies of the individual deposits, paragenetic models for many deposit types occurring in the Cyclades District remain controversial. This study compares the geochemistry of the different mineral deposits using galena, a widespread and abundant host for many trace elements, as a guide to the ore-forming fluids and metal sources of the Cyclades District. Recent trace element studies in galena by LA-ICP-MS (George et al. 2015) have shown that galena can contain a large variety of trace elements (e.g., Ag, Bi, Se, Sb, Cd, Tl, Te) that are indicative of the different source rocks, magmatic-hydrothermal influences, and conditions of mineralization.

2 Geological setting

The Cyclades District extends from the Lavrion Peninsula, south of Athens towards Milos and Santorini along the active Hellenic Volcanic Arc. Subduction of the African plate beneath continental Europe created an extensional back-arc setting accommodated by low-angle, crustal detachments. Two major tectono-metamorphic units can be distinguished in the Cyclades: the metamorphic basement divided into the Upper and Lower Cycladic Nappe, which are separated by the Trans Cycladic Thrust (Fig. 1, after Grasemann et al. 2018), and the unmetamorphosed Pelagonian Unit in the hanging wall of the major detachment systems. Intrusion of Miocene granitoids started before 15 Ma (e.g., Tinos) in the north-east, whereas magmatism in the west only started after 11 Ma (e.g., Lavrion, Serifos). Economic mineral deposits occur in all tectono-metamorphic units and are temporally and spatially associated with the detachments and Miocene granitoids as well as Pliocene-Quaternary volcanics along the volcanic arc.

2.1 Cyclades mineral district

The Cyclades mineral district spans the transition from Middle Miocene to modern seafloor hydrothermal systems along the volcanic arc (Fig. 1). The deposits have been classified as carbonate replacement Pb-Zn-Ag-(Au), low- to high-sulfidation epithermal, polymetallic and precious metal vein, skarn and porphyry systems (e.g., Skarpelis 2002; Melfos and Voudouris 2017). Carbonate-hosted replacement Pb-Zn-Ag mineralization is often spatially related to major detachment faults and occurs at Lavrion and on the islands of Syros and Sifnos (e.g., Bonsall et al. 2011; Berger et al. 2013). Skarn deposits occur on the islands of Serifos and Tinos (e.g., Fitros et al. 2017). Low- to high-sulfidation epithermal gold deposits and subvertical detachment- and fault-related base and precious metal vein mineralization are found on Milos, Tinos, Kythnos, Antiparos, and Mykonos islands (e.g., Alfieris et al. 2013; Kevrekidis et al. 2015; Menant et al. 2013; Tombros et al. 2007; 2015). Rapid uplift along the arc front has exposed former submarine hydrothermal systems on the island of Milos. Here, Pb-
Zn-Ba-(Mn-Ag-Au) low- to intermediate-sulfidation epithermal deposits occur primarily in Quaternary volcanic rocks in the western part of Milos (e.g., Kilias et al. 2001; Marschik et al. 2010; Alfieris et al. 2013).

A common low-temperature mineral paragenesis is found in the different deposits in the western Cyclades with sphalerite, pyrite, galena and minor chalcopyrite and sulfosalts. In contrast, precious metal-rich vein-type deposits occur mainly in the northern and eastern Cyclades (e.g., Tinos, Mykonos, Antiparos) which are characterized by a galena-rich, chalcopyrite, pyrite and sulfosalts paragenesis with minor sphalerite and tellurides.

3 Trace elements in galena

To compare the geochemical signature of the mineral deposits in the Cyclades, galena mineral separates were prepared from 31 samples collected at twelve deposits on six islands (from north to south: Lavrion-9, Tinos-1, Mykonos-5, Serifos-3, Antiparos-2, Milos-11). Grain mounts were analyzed at the University of New Brunswick by LA-Q-ICP-MS (Agilent 7700x). Ablations were 30 seconds at 3 Hz with 30 seconds of washout and background collection. For each sample at least ten ablations on a minimum of seven grains were obtained, and a spot size of 45 µm was used. Reference standards include NIST610, MASS-1, GSE-1E, and Broken Hill Galena. Data reduction was performed using the MASS-1 sulfide reference material. In addition to the spot analyses, two trace element profiles were performed on galena from the Profitis Ilias drill core (P012, depth 317.8 m) on Milos and from the barite vein-type deposit on Mykonos (Panormos Bay). The profiles were performed with a 17 µm spot size and a speed of 5 µm/s.

Mineral deposits in the Cyclades District experienced only minor deformation and overprinting, which make galena a powerful indicator mineral of the ore-forming fluids and metal sources. The data support previously suggested potential of galena as host for a wide range of trace metals and metalloids (George et al. 2015), with the following trace elements detected in all of the analyzed galena: Ag, Sb, Cu, Cd, Bi, Ti. The most abundant trace elements are Ag and Sb, which are often correlated with each other (Fig. 2 and Fig. 3).

<table>
<thead>
<tr>
<th>Location</th>
<th>Deposit name (n)</th>
<th>Deposit type</th>
<th>Host rock</th>
<th>Galena trace element concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lavrion</td>
<td>Plaka (4)</td>
<td>Carbonate replacement</td>
<td>Marble, schist (LCN)</td>
<td>Ag, Sb, Sn, Cd, Mn, Cu, Ti, Bi, In, Co (Te)</td>
</tr>
<tr>
<td>Lavrion</td>
<td>Kamariza (4)</td>
<td>Carbonate replacement</td>
<td>Marble, schist (LCN)</td>
<td>Ag, Sb, Cd, Sn, Cu, Bi, Te, In (Co)</td>
</tr>
<tr>
<td>Lavrion</td>
<td>Soumio (1)</td>
<td>Carbonate replacement</td>
<td>Marble (LCN)</td>
<td>Sb, Ag, Cu, Cd, Sn</td>
</tr>
<tr>
<td>Tinos</td>
<td>Panormos Bay (1)</td>
<td>Quartz-veins</td>
<td>Marble (UCN)</td>
<td>Sb, Ag, Cu, Bi, In, Sn</td>
</tr>
<tr>
<td>Mykonos</td>
<td>Cape Eros (2)</td>
<td>Barite-veins</td>
<td>Silica breccia, Miocene intrusion</td>
<td>Ag, Sb, Cu</td>
</tr>
<tr>
<td>Mykonos</td>
<td>Panormos Bay (3)</td>
<td>Barite-veins</td>
<td>Biclastic sediments (Pelagonian)</td>
<td>Sb, Ag, As</td>
</tr>
<tr>
<td>Antiparos</td>
<td>Agios Georgios (2)</td>
<td>Quartz &amp; barite-veins</td>
<td>Schist, marlbit (UCN)</td>
<td>Ag, Sb, Cu, Cd, Ti, Bi, In, Sn</td>
</tr>
<tr>
<td>Serifos</td>
<td>Moutoulas (3)</td>
<td>Skarn</td>
<td>Schist, marble (LCN)</td>
<td>Ag, Sb, Bi, Cd, Mn, Cu, Ti, Sn, In (Te)</td>
</tr>
<tr>
<td>Milos</td>
<td>Triades (3)</td>
<td>IS epithermal</td>
<td>Volcano-sedimentary (dacite)</td>
<td>Ag, Sb, Cu, Zn, Cd, As, Mn, Bi, Ti, Bi, (Te)</td>
</tr>
<tr>
<td>Milos</td>
<td>Galana (4)</td>
<td>IS epithermal</td>
<td>Volcano-sedimentary (dacite)</td>
<td>Ag, Sb, Cu, Cd, Mn, Bi, Te, Ti, Au</td>
</tr>
<tr>
<td>Milos</td>
<td>Profitis illias (1)</td>
<td>IS epithermal</td>
<td>Rhyolite - rhyodacite</td>
<td>Te, Ag, Sb, Cd, Cu, Au, Mn</td>
</tr>
<tr>
<td>Milos</td>
<td>Kondaros (3)</td>
<td>LS IS epithermal</td>
<td>Dacitic domes and lava flows</td>
<td>Ag, Sb, Cu, Ti, Bi</td>
</tr>
</tbody>
</table>

Table 1. Mean concentrations of trace elements obtained by spot analyses of galena of the different deposit types in the Cyclades mineral district. Trace elements are sorted from the most to the least abundant. Elements in bold have mean concentrations above 1000 ppm. Characteristic trace elements are highlighted in blue. n: number of analyzed samples, LCN: Lower Cycladic Nappe, UCN: Upper Cycladic Nappe, IS: Intermediate sulfidation, LS: Low sulfidation.
Figure 2. Major coupled substitution \((\text{Ag,Cu,Tl})^+ + (\text{Bi,Sb})^{3+} \leftrightarrow 2\text{Pb}^{2+}\) occurring in galena from the Cyclades mineral district. Concentrations are shown in ppm on a logarithmic scale.

The previously suggested coupled substitution of \((\text{Ag,Cu,Tl})^+ + (\text{Bi,Sb})^{3+} \leftrightarrow 2\text{Pb}^{2+}\) (George et al. 2015) is likely the main mechanism which incorporates Ag, Cu, Tl, Bi, and Sb into the crystal lattice (Fig. 2). Whereas Ag and Sb concentrations are greater than 100 ppm in galena from most deposits; Tl concentrations are <10 ppm. Mean concentrations for Bi are generally <10 ppm, except for Serifos and Tinos (Fig. 4). Copper concentrations vary significantly from 0.46 ppm to 5030 ppm between the deposits but also within a sample (Table 1).

Galena from the Cyclades has also low concentrations of Hg and Mn. Figure 3 shows the correlation between Ag, Sb, As, and Hg in galena from Mykonos (Panormos Bay). Silver and Sb show similar geochemical zoning, except for one rim of the crystal. The observed positive correlation between Ag and Sb in this profile is in contrast to described zonation patterns showing an inverse correlation of Sb and Ag, Bi, Se, Te, and Tl (George et al. 2015). A similar pattern is observed for Hg and As (Fig. 3), suggesting that pulses of Sb-Ag-Hg-As-rich fluids were encountered during crystal growth.

Figure 3. Profile through a galena from Mykonos (Panormos Bay). Sb, Ag, As, and Hg concentrations are displayed on a logarithmic scale in ppm.

4 Geochemistry of the Cyclades mineral district

Trace element concentrations in galena show systematic differences in the Cyclades mineral district and reflect the range of mineral deposit types (Table 1). Concentrations of Bi in galena are highly variable (Fig. 4). High Bi concentrations in galena from a skarn deposit on Serifos (Moutoulas) are in good agreement with the presence of native Bi reported by Fitros et al. (2017), and elevated Bi concentrations in galena for skarn deposits (George et al. 2015). High Bi concentrations were also detected in galena from the vein-type deposit on Tinos (Fig. 4, Panormos Bay), and together with high Se (average 805 ppm) and Te (average 312 ppm), the low standard deviations suggest these elements are present in solid solution. In general, galena from Tinos has the highest precious metal concentrations, with 707 ppm Ag and 0.04 ppm Au, and mean values of >300 ppm for Se, Sb, Te, and Bi and low mean concentrations of ≤1 ppm for Cu, Hg, Tl, In, and Sn. The abundance of precious metals in galena from Tinos is in good agreement with previously described Au-Ag-Te-rich mineral assemblages (Tombros et al. 2007), although the presence of Bi minerals was not noted. Trace elements in galena of the Panormos Bay vein-type deposit (Tinos) suggest higher mineralization temperatures than for most deposits in the Cyclades mineral district, and support an estimated minimum depth of 1 km and temperatures of 200–320 ºC (Tombros et al. 2007).

Figure 4. Bismuth concentration with respective errors displayed on a logarithmic scale in ppm for 340 different spot analyses in galena of the Cyclades mineral district. Concentrations are sorted from the lowest to the highest value for each analyzed sample.

On Mykonos galena has been analyzed from the polymetallic barite-vein deposits in Cape Evros and Panormos Bay, and generally low concentrations of trace elements have been detected for galena from Cape Evros (Table 1). Galena from Panormos Bay exhibits in contrast high mean concentrations in Ag (1700 ppm) and Sb (3000 ppm), as well as up to a few 100 ppm for As, Cu, and Hg (Fig. 3). High As and Hg
concentrations in galena of Panormos Bay (Mykonos) can be explained by an interaction of the ore-forming fluid with the surrounding clastic sedimentary host rock.

In contrast, galena from the vein-type deposit on Antiparos has the lowest analyzed concentrations of trace elements, with a mean Ag concentration of <250 ppm. This contrasts with microprobe analyses by Kevrekidis et al. (2015) who reported 0.17–2.90 wt.% Ag in galena from Antiparos.

Galena from most deposits has low concentrations of In and Sn, except for samples from the epithermal deposits on Milos. Indium concentrations in galena from the carbonate replacement deposits in the Lavrion District are generally below 1 ppm, but the mean concentrations of Sn are ~20 ppm. Galena from carbonate replacement deposits in Lavrion (Plaka area), skarn deposit on Serifos (Moutoulas) and epithermal deposits on Milos (Triades, Galana, Profitis Ilias) has low concentrations of Mn with a mean concentration of ~4 ppm in all samples. However, the low standard deviation for Mn in the profile through the drill core sample from Profitis Ilias suggests that this small amount of Mn may be present in solid solution in the galena. In addition, gold was detected in the galena samples from Milos (average 0.6 ppm at Triades, 0.05 ppm at Galana, and 5.5 ppm at Profitis Ilias), but have not been detected in samples from Kondaros, likely because of later silicification and metal leaching. Gold concentrations can reach up to 100 ppm in galena from the Profitis Ilias drill core sample, where Au likely occurs in Ag-Au-telluride inclusions, which was observed by a positive correlation between Au, Te and minor Ag in the profile trough a galena crystal. High Te concentrations (average 440 ppm), together with elevated Au concentrations suggest higher temperatures and pressures for mineralization at Profitis Ilias than at other epithermal deposits on Milos (Kilias et al. 2001).

5 Conclusion

Trace elements in galena from different deposits in the Cyclades mineral district are indicative of the deposit types, the conditions of mineralization, and the exposed host rocks. Galena from shallow crustal base metal deposits in the western Cyclades have similar concentrations of trace elements, whereas galena from vein-type deposits in the northern Cyclades have generally higher precious metal contents. Galena from Quaternary and recent mineralization along the active volcanic arc is also enriched in precious metals. These data highlight the potential of trace element geochemistry in galena as an indicator for different mineralization styles throughout the Cyclades mineral district, where only a few occurrences may be exposed.

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References


Relations between matrix type and style of mineralization in sandstone ore, Nowa Sól Cu-Ag deposit, SW Poland

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Miedzi Copper Corp.

Abstract. Five types of cement have been recognized within white sandstones (the BS unit, Weissliegend sandstone) of the Nowa Sól deposit – anhydrite matrix, sulfide matrix, carbonate matrix, clay minerals matrix and silica matrix. A downward cement composition shift from anhydrite and sulfide to clay is visible in Weissliegend sandstones from the Nowa Sól deposit. The pervasiveness of alteration of detrial grains (mainly feldspar, detrial rutile and titanite) increases upwards, reaching maximum range beneath the base of the Kupferschiefer, regardless of its thickness. The uppermost part of the white sandstones contain two types of ore – massive sulfide cement and copper sulfides replacing feldspars, which are associated with ubiquitous anhydrite matrix. Chalcocite predominates within the sandstone ore, but it may be accompanied by other Cu-S-type sulfides, pyrite, galena, sphalerite and Ag-phases at the top of the BS unit, where ore mineral composition sharply increases.

1 Introduction

Sediment-hosted Cu-Ag deposits have been documented on the Fore-Sudetic Monocline and North Sudetic Through, Poland. Polymetallic mineralization is developed within sedimentary rocks ranging from terrestrial red beds to marine Weissliegend sandstones, shales, carbonates and evaporates (the Zechstein Formation) (Borg et al., 2012). The Polish Lower Permian formation is composed of a thick sequence of terrestrial sediments intruded by intermediate volcanic rocks. The Zechstein Formation in Poland is developed in the form of 4 major evaporative cycles (cyclothemes; PZ1 Werra, PZ2 Strassfurt, PZ3 Leine and PZ4 Aller). The oldest cyclopehe, Werra, was deposited directly on the Rotliegend red beds or white sandstones, which are the product of marine re-deposition of terrestrial sandstones. Sediments of the Werra cycle are developed upward as copper-bearing shale (T1), which in some parts of the basin is underlain by the basal limestone (Ca0), the Zechstein limestone (Ca1), the lower anhydrite (A1d), the oldest salt (Na1) and the upper anhydrite (A1g) (Oszczepalski, 1999). The contact between clastic, mainly aeolian, sediments and reduced marine strata is basin-wide and concordant. The Zechstein sequence is covered by Triassic (terrestrial Lower and Middle Bundsandstein, marine Upper Bundsandstein, Muschelkalk and Keuper) and, in eastern part of Fore-Sudetic Monocline, Jurassic sediments of varying thickness. The uppermost part of the Fore-Sudetic Monocline profile consist of Cenozoic sands, silts, coals and clays (Fig. 3).

2 Sediment-hosted Cu-Ag deposits on the Fore-Sudetic Monocline

2.1 Geology

The European Permian basin extends from central Poland to eastern coast of England. It is filled by a sequence of terrestrial – red sandstones (the Rotliegend Formation) – and marine sedimentary rocks – Weissliegend sandstones, shales, carbonates and evaporates (the Zechstein Formation) (Borg et al., 2012). Historically, the richest copper mineralization was recognized within copper-bearing, organic rich shale, known as the Kupferschiefer. Thus, traditionally, sediment-hosted deposits in Europe are called Kupferschiefer-type. However, recently most of the mining operations on the Fore-Sudetic Monocline have focussed on three types of ore – carbonate (the Ca1 and Ca0 units), shale (the T1 unit) and sandstone (the BS unit). As the mining goes deeper, the contribution of the sandstone ore to the copper production in Poland increases. Sandstone ore in the recently discovered Nowa Sól deposit is usually chalcocite-dominated and is restricted to top of the BS unit.

2.2 Types of ore and metal zonation

The north-eastward dipping Fore-Sudetic Monocline is a region of great mineral potential. The base of the Zechstein Formation, which in this area hosts 4 already documented tier 1 stratiform Cu-Ag deposits, is of the main exploration interest. Mineralization in the Polish Kupferschiefer deposits is not restricted to the copper-bearing shale. The position of the ore series is often much wider. Copper sulfides are observed in the upper part of Weissliegend sandstones, basal limestone, copper-bearing shale, Zechstein limestone and in some places also within the lower anhydrite (Pieczenka et al., 2007).

Sediment-hosted deposits located on the Fore-Sudetic Monocline exhibit metal zonation, which is highlighted by the distribution of sulfides within ore series (Oszczepalski, 1999; Alderton et al., 2016). Five zones of different mineralogical and geochemical features have been recognized within all copper deposits in Poland: (1) oxidized copper-depleted hematite-bearing zone (Rote Fäule), (2) Au-PGE-enriched transitional zone, (3) copper-bearing zone, (4) lead-zinc zone and (5) pyrite zone. This continuous transition from hematitic sediments to Cu-Ag-Pb-Zn-mineralized rocks is both vertical and horizontal. High-
grade copper ores are developed in the vicinity of large oxidized fields, where reduced facies hosting copper mineralization contact with hematite-dominated sediments (Oszczepalski, 1999; Borg et al., 2012). The mineral distribution and thickness of the ore zone depends on the position of a transgressive, oxidizing Rote Fäule facies and the composition of the lower Zechstein sediments.

The western part of the Fore-Sudetic Monocline is considered prospective for documenting high grade copper mineralization within the base of the Zechstein at depths exceeding 2000 meters (Speczik, 1995; Oszczepalski et al., 2016). This was proved by the extensive exploration program led by Miedzi Copper Corp. (Fig. 1), preceded by oil and gas industry drilling.

![Figure 1. Location of the Nowa Sól deposit, Lubuskie voivodeship, SW Poland](image)

### 3 Types of ores within the Nowa Sól deposit

An upward transition from white sandstones to evaporites marks the Zechstein sea transgression and a few minor transgressive-regressive cycles, that can be recognized within the Zechstein limestone. White sandstones are interpreted as upper parts of sand dunes that have been flooded by the Zechstein sea. This formerly aeolian sediment was deposited in an arid environment, then rapidly became the seafloor of the Zechstein sea (reducing environment). The Weissliegend unit is not always developed within the Lower Zechstein profile – in some places copper-bearing shale may be deposited directly on the terrestrial red beds, which are sometimes white, due to de-colorization processes.

Drilling program results show that different styles of mineralization can be recognized within the Nowa Sól deposit (Fig. 1). Along the rim of the Zielona Góra Oxidized Field, carbonate ores predominate, while northward, where the base of the Zechstein Formation dips, shale and sandstone ores play more important role. Copper-bearing shale, basal limestone and Zechstein carbonate host mineralization of different styles. Limestone ore is usually disseminated, but may be accompanied by coarse-grained aggregates and sulfide lenses. Shale ore is almost always of the highest grade. Mineralization of the Kupferschiefer unit is usually disseminated, but contains numerous lenses and veinlets parallel to lamination surfaces. Sandstone mineralization is usually disseminated and it is developed in the form of copper sulfides cement. On the top of Lower Permian unit, where sandstones contact with the copper-bearing shale, copper mineralization within sandstone may be massive.

### 4 Results

#### 4.1 Materials and methods

This study is based on examination of thin section petrographic samples from deep exploration boreholes. Its aim is to recognize the main types of sandstone ore within Nowa Sól deposit. All studied mineralized cores have been reexamined and profiled in order to describe CS/BS, BS/T1 and BS/Ca0 contact characteristics. Moreover, macro trends in mineralization style within white sandstone have been studied. All petrographic samples have been examined under polarized light optical Nikon Eclipse E-600 microscope and Zeiss Sigma Field Emission Scanning Electron Microscope.

#### 4.2 White sandstones petrography

White sandstones of the Nowa Sól deposit are gray and light gray, fine-grained and subrounded. The cement is usually blocky and syntaxial. Porosity is always low. Rocks of this unit can contain thin argillaceous laminae, which are usually organic rich. Beneath the uppermost part of the BS unit, sandstones are composed of fine and coarse-grained sand interbeds. Disseminated copper mineralization can often be seen macroscopically. Footwall Weissliegend sandstones are medium and coarse-grained, often exhibit indistinct cross bedding and can be patched with red-colored cement. Thickness of white sandstones does not exceed 10 meters – copper mineralization is restricted only to upper few meters of that unit. The lower limit of sandstone ore is marked by the hematitic zone of oxidizing Rote Fäule.

Quartz is a major detrital mineral in BS sandstones. At the top of the BS unit well-sorted fine and very fine rounded quartz grains are present. Downward, poorly sorted subangular grains start to predominate. Potassium feldspar is the second most abundant detrital phase in the BS unit. It is usually subhedral or anhedral, coarse-grained and exhibits disequilibrium textures – feldspar grains are corroded, contain thin inclusions filled with copper sulfides, galena and anhydrite. While overall rock alteration is usually selectively pervasive or non-pervasive, the alteration of feldspars is usually pervasive (Fig. 2B). Alteration of feldspar to clay minerals is characteristic for the top of the Weissliegend unit. Biotite, zircon, apatite, garnet, ilmenite and plagioclase are present in minor amounts. Ilmenite from white sandstones shows partial to complete conversion into leucoxene-rutile and leucoxene. In the upper part of mineralized interval, conversion of ilmenite into...
leucoxene is complete, while in the distal parts of the sandstone ore ilmenite is partly replaced by the aggregate of rutile and leucoxene (Fig. 2C). In high grade copper zones leucoxene is associated with aggregates of chalcocite grains, whereas in lower parts of mineralized intervals, a leucoxene-rutile association contain pyrite intergrowths.

4.3 Styles of mineralization

Disseminated copper mineralization predominates in the Nowa Sól deposit sandstones. The main ore mineral is chalcocite with minor digenite and covellite. Chalcocite is the major constituent of sulfide cement. It can form large, mono-mineral aggregates, filling voids between quartz grains. Sometimes it is accompanied by framboidal pyrite (Fig. 2A). In the uppermost parts of BS sandstones, chalcocite replaces feldspars, forming lenses and small intergrowths within these mineral phases.

Digenite and covellite are associated with pyrite, in which they are developed in form of thin intercalations. These concentric, rosette-shaped pyrite-covellite-digenite aggregates are ubiquitous in the upper parts of white sandstones, which are enriched in organic matter and contain ubiquitous framboidal pyrite. In the lower part of white sandstones, near the base of the BS unit, pyrite forms independent aggregates, which exhibit similar shape, but lack Cu-S sulfides. Pyrite is the major non-copper sulfide which is recognized throughout the whole profile of white sandstones. Cu-S sulfides are rarely associated with Cu-Fe-S sulfides, mainly chalcopyrite and bornite. Within Nowa Sól deposit such mineral paragenesis is uncommon, contrary to deep Lower Zechstein profiles from the northern part of Fore-Sudetic Monocline.

In boreholes which intersected high-grade mineralization both in Weissliegend sandstones and copper-bearing shale, sandstone ore consists of a range of mineral paragenesis. Chalcocite is the main Cu-S phase. Locally it may form sulfide cement. It is usually associated with minor digenite, covellite and pyrite. Large chalcocite aggregates form intergrowths with Ag-phases and pink bornite. Galena and sphalerite are commonly present. Feldspars may be completely replaced by chalcocite in massive copper mineralization within Weissliegend sandstones.

In the places where copper-bearing shale is present, sandstone ore may be developed in form of rhythmic sulfide bands. Each band is few centimeters wide and its upper limit is blurred, composed of disseminated copper sulfides, while its lower part is sharply-limited. One mineralized interval may be composed of few rhythmic sulfide bands composed of chalcocite.

4.4 Types of white sandstones and their contribution to the style of mineralization

Five types of white sandstones from the Nowa Sól deposit can be recognized: anhydrite-cemented, carbonate-cemented, sulfide-cemented, clay-cemented and silica-cemented. Anhydrite and carbonate cements are the most abundant types (Fig. 3). The former predominates at the uppermost part of the BS unit, while the latter forms matrix beneath the sulfate-dominated zone. Sulfate matrix is present in sandstones regardless of thickness of the copper-bearing shale.

Figure 2. (A) Chalcocite (Cct) mineralization – sulfide cement associated with remnants of framboidal pyrite (Py) and pyrite-covellite-digenite (Py + Cv) rosette-like intergrowths. Upper part of the sandstone ore; (B) Replacement of potassium feldspar (Kfs) detrital grain by chalcocite (Cct) and anhydrite (Anh). Dissiminated chalcocite (Cct) mineralization within illite-kaolinite (Ill + Kln) matrix. Upper part of the sandstone ore; (C) Rutile (Rt) and relict leucoxene (Lx + Rt) associated with very fine-grained Cu-S sulfides (Cct). Distal part of the sandstone ore. SEM images.

Sulfide-cemented sandstones, occur only in the areas of thick T1 unit and are composed mainly of chalcocite. Clay cement is well developed at the lower part of white sandstones unit, but is abundant in subordinate amounts along the whole BS profile. Silica matrix is present only in the most pervasively altered parts of the BS, where sulfides are the main constituent of the
Cement.

In the uppermost part of the Weissliegend unit, which is usually copper-bearing, anhydrite predominates over carbonate, illite-kaolinite cement and silica. Mineralized sulfate-cemented sandstones exhibit pervasive feldspar replacement. Chalcocite is the major sulfide phase replacing potassium feldspar and it is usually associated with anhydrite. Individual chalcocite aggregates exhibit the crystal habit of feldspar. Thin lenses within feldspar grains are filled with chalcocite as well as anhydrite. Corroded feldspar grains are typically rimmed by anhydrite in which chalcocite and minor digenite are disseminated. Feldspars are also pervasively replaced by the clay minerals – mainly kaolinite. Within aggregates of kaolinite and illite anhydrite lenses are being reported. Quartz grains does not exhibit disequilibrium textures, but may be rimmed by silica cement in high grade copper intervals.

Figure 3. Profile of the lower Zechstein copper-silver ore series with particular reference to the white sandstone of Nowa Sól deposit (the BS unit).

Fine grained laminations are commonly reported within coarse-grained sandstone. The style of the copper mineralization is usually dependent on variability of grain size and its spatial characteristics (continuous lenses of fine-grained, sub angular material). Thus, disseminated copper ore exhibit regular patterns in the micro scale. In the coarse-grained zone sulfide phases form small aggregates (<100 μm) which are usually disseminated, while copper mineralization within fine-grained lenses is characterized by more massive habit.

5 Summary

The sandstone ore within the Nowa Sól deposit is almost mono-mineralic – composed almost entirely of chalcocite. However, style of mineralization and grade of copper ore varies throughout the profile of white sandstones. In areas, where Rote Fäule is developed a few meters beneath the T1 unit, copper mineralization is usually disseminated or may be represented by rhythmic sulfide bands. In regions where the top of Rote Fäule is situated tens of centimeters beneath the Kupferschifer, sandstone is chalcocite-cemented and mineralization is massive. The variability of grain size seems to be more important factor determining style of mineralization than the type of cement. However, the fact that anhydrite lenses and intergrowths within potassium feldspars and ilmenite relicts have been documented in all examined samples from the upper BS unit, suggests that the role of cement composition in the formation of ore should be taken into account. Leucoxene formation and the pervasiveness of ilmenite replacement suggests different intensity of mineralizing event (either in terms of time of residence of mineralizing fluids and its thermodynamic properties) at different parts of the BS unit. The pervasive replacement of feldspar and ilmenite by copper sulfides in the uppermost 20 centimeters of white sandstones may be strictly correlated with the part of the BS unit, which has been under the greatest influence of the Zechstein sea reducing conditions.

The major conclusions are: (1) the upper part of Weissliegend was deposited in reducing environment (framboidal pyrite, which is commonly replaced by copper sulfides); (2) organic-rich millimeter-wide clayey interbeds may have acted as first red-ox barrier for the ascending mineralizing fluid (Speczik, and Püttmann, 1987; Speczik, 1994); (3) anhydrite, which is present as a cementing factor, might have been a substrate of thermodynamic sulfate reduction (TSR), that may have generated sufficient amounts of H₂S to promote base metals precipitation (Machel, 1998) and (4) layers of variable grain size within coarse-grained sandstone may have acted as permeable channels for both ascending and descending fluids.

References


Proposed re-Interpretation of hydrothermal alteration, mineralization and host-rock oxidation to form the Keweenaw native copper lodes, Northern Michigan, U.S.A.

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Abstract. Native copper deposition in the Keweenaw district, northern Michigan, is often said to have been accompanied by the destruction of pre-ore hematite. This contribution proposes instead that the pervasive deep-red pigmentsing hematite of the permeable host sediments (and volcanic units) was deposited after native copper deposition and that native copper behaved as a chemical reductant which resisted the deposition of post-ore hematite in the immediate vicinity of native copper. Previous work proposed that native copper was deposited in the Keweenaw rift basin from moderately oxidized hybrid brines formed by mixing of downward infiltrating meteoric water and deep metamorphogenic water. The deposition of late hematite may have occurred as the result of late subsurface circulations of oxygen-rich, highland recharge-driven meteoric water.

1 Introduction

Early descriptions of the native copper ores of northern Michigan have stated repeatedly that widespread deeply reddish host rocks were hydrothermally bleached to salmon-red colors in the immediate vicinity of native copper (e.g., Butler and Burbank 1929; Cornwall 1956; White 1968; Weege and Pollach 1972). As such, the Keweenaw host-rocks would have attained their deep-red colorings before copper deposition. This communication notes however that, in areas of low-grade disseminated native copper mineralization within fine-grained clastic sediments, pervasive hematitic reddening appears to have invaded and enclosed previously native copper-mineralized sediment, and that deep hematitic reddening is absent in aureoles immediately surrounding isolated disseminated grains of native copper. Native copper behaved as a chemical reductant, equivalent to organic matter in red beds containing reduction spots.

2 Prior observations and interpretations

The sequence of Keweenaw hydrothermal alterations, mineralization and reddening may be analogous to that found in red beds showing centimetric-scale reduction spots: e.g., those of the Carboniferous red beds of eastern Canada (Poll and Sutherland 1976; Brown 1976, 1977) (Figs. 1 and 2) and in the fluvial Abo Formation, New Mexico (Bensing et al. 2005). The reduction spots in the Abo Formation have less total iron compared to enclosing reddened (hematitic) fine-grained clastic sediment. Petrographic and SEM analyses indicate that the reduction spots have never been reddened. Similarly, the

Figure 1. Carboniferous red beds of Dorchester Cape district, New Brunswick, Canada, showing abundant centimetric-scale reduction spots with dark-greyish cores centered on organic matter. See Figure 2 for closer details.

Figure 2. Close view of greyish reduction spots shown in red beds of Figure 1 (tip of geologic hammer for scale). Cores of reduction spots contain organic matter (wood debris) and are the sites of base-metal sulfide mineralization (especially copper sulfides, partially oxidized to malachite). See text for further explanations.
matter observed at the centers of reduction spots is interpreted to have maintained surrounding aureoles of reduction where pigmenting hematite could never have been chemically stable, as proposed by Bensing et al. (2005).

3 Observations on Keweenaw native copper

Aureole effects similar to those found in redbeds are recognized in the clastic sediments hosting native copper in the Keweenaw district of northern Michigan, especially where concentrations of native copper are low in fine-grained sediments (Fig. 3); high-grade native copper mineralization in coarse-grained host sediments is more difficult to interpret because massive amounts of native copper tend to mask hydrothermal alterations.

Figure 3 exhibits an apparent finger of “bleached” fine-grained clastic sediment beneath massive native copper in overlying coarse-grained sediment. The “bleached finger” is defined by rusty-red ferric hydroxide alteration immediately surrounding disseminations of native copper, the whole otherwise enclosed by pervasively deeply reddened sediment. In fact, each grain of native copper within the finger defines the center of a hematite-poor “knuckle” of hematite-poor sediment along that finger, separated from surrounding hematite-rich sediment by an approximately ½ cm aureole of unmineralized ferric hydroxide-altered fine-grained sediment.

Earlier reports (noted above) have attributed the so-called bleaching of pre-ore hematite to hot cupriferous hydrothermal solutions which altered the host sandstone-conglomerates during the deposition of native copper; hematite was destroyed by the ore-forming solution. That interpretation has met with skepticism because the cuprous chloride-bearing ore brines should have been mildly oxidizing in order to have carried significant amounts of copper (Brown 1971, 2006; Rose 1976, 1989); i.e., the ore solution should not have been hematite-destructive during native copper deposition.

4 Interpretation of processes and timing of Keweenaw native copper deposition

Most modern interpretations of the genesis of native copper lodes in the Keweenaw district justifyably assume that copper was leached from deep, hot, down-dip extensions of thick rift-filling mafic volcanics and interbedded sandstone-conglomerate host units during or after their northward tilt as a result of Grenvillian compression. Metamorphogenic fluids (Stoiber and Davidson 1959; Jolly 1974; Bornhorst and Mathur 2017), plausibly combined with deep highland-driven meteoric water (Brown 2006, 2008, 2018), ascended along permeable strata (e.g., amygdaloidal flow-top breccias and sandstone-conglomerates) to mineralize cooler, up-dip portions of those same permeable aquifers.
portion of the sample. See text for further explanations. The addition of highland-driven meteoric water to form a hybrid ore solution was proposed principally to explain the transport of copper as chloride complexes in mildly oxidized brines. Otherwise, metamorphogenic fluids generated from mafic source rock should have had low redox levels defined by the ferrous-ferric stability limit, at which the maximum solubility of copper would have been too low to have formed an ore-forming cupriferous solution (Brown 2006).

5 Conclusion

The recommended explanation for the observed native copper mineralization and associated alterations is: (1) deep rift-basin leaching of copper by hybrid evolved meteoric/metamorphogenic waters; (2) ascent of the hot ore solution along Keweenaw aquifers and deposition of native copper lodes at cooler levels (between approx. 280 and 180°C; Livnat et al. 1983), accompanied by partial destruction of mafic minerals and deposition of ferric hydroxides (Walker 1989); and (3) pervasive deep-red oxidation of Keweenaw aquifers by late oxygen-rich highland-driven meteoric waters.

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Dairi: an example of Zn-Pb-Ag sediment-hosted deposit from Indonesia

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Abstract. The Dairi Zn-Pb-Ag deposit is the first SEDEX deposit discovered in Indonesia thus understanding its genesis is key to future SEDEX exploration in Sumatra. Orebodies are hosted in Lower Carboniferous black shales-siltstones (stratiform orebodies) and dolostones (discordant orebodies) representing sag-phase sequence in the Dairi basin. The discordant orebodies are lower in stratigraphy and are conceptually understood as feeder zones to the overlying stratiform orebodies. The reduced and acid ore-forming fluid was moderately saline and warm (18-25 wt% NaCl eq., ~170°C) before being diluted by seawater (3 wt% NaCl eq., ~3°C). A geochemical halo around the stratiform orebodies is accompanied by ankerite and hyalophane. Reduced sulfur in the discordant orebodies is dominated by hydrothermal S isotope signature, whilst there is evidence of bacteriogenic sulfide in the stratiform orebodies.

1 Introduction

Sumatra has long been known as a source of Au in SE Asia. The ancient name of the island was Svarnadvipa which means the gold island reflecting its high Au endowment (Crow and van Leeuwen 2005). Gold occurs in classic epithermal deposits associated with Mesozoic and Cenozoic volcanic terrains covering nearly 75% of the island.

A reconnaissance survey to explore Au and base metal deposits in 1990s encountered an outcrop of stratiform, massive sulfide in black shales and siltstones as its immediate hanging wall and footwall along the Lae Sopokomil, Dairi (Middleton 2003). Although carbonate-hosted veins in North Sumatra were reported to be a source of base metals in the Dutch colonial era (van Bemmelen 1949), and had arrived at the equator by the Early Carboniferous. The Sibumasu Block collided with the Indochina Super-Terrane in the Late Permian. The West Sumatra Block was displaced along the Medial Sumatra Tectonic Zone and emplaced to the west of the Sibumasu Block in the Triassic. The Woyla Arc was thrust over the West Sumatra Block in the Middle Cretaceous completing the tectonic assembly of present-day Sumatra (Metcalfe 2013).

The Dairi Zn-Pb-Ag deposit is located on the eastern flank of the Sopokomil Dome which is a portion of the Lower Carboniferous Kluet Formation (Fig. 1). From the bottom of stratigraphy, the rocks in the Sopokomil Dome consists of massive and brecciated dolostones (the Jehe unit), interbedded black shales and dolomitic siltstones (the Julu unit) and interbedded dolomitic sandstones and siltstones (the Dagang unit). The main composition of the Jehe unit is dolomite while that of the Julu and Dagang units are quartz, dolomite, muscovite, organic matter and K-feldspar. Diagenetic pyrite occurs in trace amounts. These rocks were subject to sub-greenschist metamorphism.

Structures in the Sopokomil Dome are predominantly controlled by NW-SE-trending thrusts and an anticline. NE-SW-trending normal faults are also present. These structures are related to deformation events during collisions of tectonic blocks and the current strike-slip Sumatra Fault System (Reynolds and Geerdts 2012).
3 Dairi basin

Rocks in the Sopokomil Dome (the Dagang, Julu and Jehe units) represent a sag-phase sequence known to be favorable for SEDEX deposition (Lydon 1996). Correlation with Paleozoic stratigraphy in the Indochina Super-Terrane (Metcalfe 2017) suggests that the rift-fill sequence in the Dairi Basin may be similar to its sag-phase sequence. The similarity between the rift-fill and sag-phase sequence in the Dairi Basin is comparable to Phanerozoic SEDEX-hosting basins in North America (e.g. Selwyn, Belt-Purcell; Cooke et al. 2000).

4 Orebodies

Orebodies in the Dairi Zn-Pb-Ag deposit are present in four prospects (Anjing Hitam, Basecamp, Lae Jehe, Bongkaras) extending from SE to NW in a 4-km strike line (Fig. 1). The structurally highest Dagang unit hosts no orebodies. The Julu unit (Fig. 2) hosts stratiform orebodies consisting of three stacked layers: lower (LH), main (MH) and upper (UH) horizons. LH is limited to Lae Jehe and Bongkaras, MH is present in all prospects, and UH occurs as lenses ore horizons in Anjing Hitam, Basecamp and Bongkaras. The maximum thickness of orebodies hosted in the Julu unit is 30 m in Anjing Hitam while 5 m in Basecamp. The maximum thickness of orebodies increases to 20 m in Lae Jehe and decreases to 5 m in Bongkaras. In the Jehe unit, orebodies are discordant, but stratabound at deposit scale.

According to textures and the abundance of ore minerals, the orebodies hosted in the Julu unit are divided into pyrite-rich massive sulfide (PyMs), sphalerite-rich massive (SpMs), bedded sulfide (BS), galena-rich breccia (GnBx) and vein (V-Ju) ore types. PyMs is an ore consisting of abundant cubic hydrothermal pyrite and sphalerite-galena intergrowths filling their interstices. Cubic, hydrothermal pyrite overgrew frambooidal, diageneric pyrite in the NW portion of the deposit. In LH, pyrrhotite occurs as a dominant iron sulfide intergrown with metamorphic pyrite. SpMs is an ore type consisting of abundant sphalerite-galena intergrowths and trace pyrite. As lithic and rock layers incorporated in the orebodies increase toward the NW, the ore type changes from SpMs and PyMs to BS. GnBx is an ore type consisting of abundant galena and large, corroded, euhedral pyrite. Pyrite size is up to 3 mm. Tetrahedrite and bournonite occur as inclusions in galena. GnBx is only present in Anjing Hitam. V-Ju is dominated by sphalerite-galena intergrowths. In LH, V-Ju contains pyrrhotite as well. Gangue minerals consist of quartz, dolomite, hyalophane, trace barite and calcite.

In the Jehe unit, the orebodies consist of vein (V-Je) and disseminated (Ds) ore types. In contrast to V-Ju, V-Je contains significant tetrahedrite, tennantite and chalcopyrite in addition to sphalerite and galena. Trace arsenopyrite coexists with tennantite. In Ds, sphalerite is associated with cubic pyrite. Galena contains Ag-sulfides and Ag-Cu-Pb sulfosalts: acanthite, pyrargyrite, boulangerite, freieslebenite and diaphorite. Chalcopyrite, Ag-sulfides and Ag-Cu-Pb sulfosalts are abundant in the orebodies hosted in the Jehe unit. The presence of Ag-Cu-Pb sulfosalts in Anjing Hitam suggests that the SE portion of the deposit was more proximal to the feeder zone. The distribution of Cu and Ag which are less soluble in low temperature solutions compared to Pb, and that of Pb which is less soluble compared to Zn in low temperature fluids agree with the flow direction of ore-forming fluid from SE to NW in seafloor and sub-seafloor environments (Reed and Palandri 2006). This paleoflow direction is also supported by the decrease of orebody thickness and the increase of abundance of bedded sulfide ore toward NW.
Deformation of orebodies are visible at mega-, hand-specimen and micro-scales. Tilting (15-50°) and disruption of ore horizons indicate deformation at megascales. At hand-specimen scale, the deformation is indicated by folding of ore horizons, presence of sulfide and dachbewung textures. Recrystallization, cataclastic deformation and fracturing of pyrite are microscopic indications of deformation (Gilligan and Marshall 1987; Vokes and Craig 1993). Fractures of pyrite were healed by soft sulfides, such as bornonite, chalcopyrite, galena, sphalerite and pyrrhotite (Barrie et al. 2010).

5 Geochemical halo

A SEDEX Alteration Index (AI) is used to identify geochemical haloes around SEDEX deposits. The equation used in the AI is \( \frac{(\text{FeO} + 10\text{MnO}) \times 100}{\text{FeO}} \). The AI-Ba in the barren area ranges from 8 to 10. In Anjing Hitam, the AI systematically increases from the Dagang unit (AI = 43-53) through the Jehe unit (AI = 51-75) to the stratiform orebodies (AI = 62-99). SEDEX AI of orebodies was added to compare the values in the host rocks and orebodies, although the index was designed for host rocks.

Another indicator was introduced to reveal a geochemical halo in the Dairi Zn-Pb-Ag deposit, i.e. SEDEX AI-Ba. In this indicator, Ba is used as a key enriched element and K as a key depleted element and thus the equation used in the AI-Ba is \((\text{Ba}/1000) \times 100\)/\((\text{Ba}/1000 + \text{K}_2\text{O})\). The AI-Ba in the barren area ranges from 8 to 10. In Anjing Hitam, the AI-Ba increases from the Dagang unit (9-73) to the stratiform orebodies (54-99). The increasing AI coupled with Al-Ba in the immediate hanging wall and footwall suggests that the geochemical halo in the Dairi Zn-Pb-Ag deposit is controlled by compositional change of dolomite and K-feldspar to ankerite and hyalophane, respectively.

6 Ore-forming fluid

6.1 Salinity, temperature and density

Salinity of the ore-forming fluid in the Dairi Zn-Pb-Ag deposit is distributed over three main intervals: 18-25 wt%, 3-7 wt% and 1-3 wt% NaCl eq. The saline fluid (18-25 wt% NaCl eq.) allowed the fluid to leach metals from the rift-fill sequence and to carry them to the depositional site as chloride complexes (Seward et al. 2014). Dilution by seawater reduced salinity (3-7 wt% NaCl eq.) and led to precipitation of metal sulfides and sulfosalfs. The origin of the much-diluted fluid inclusions (1-3 wt% NaCl eq.) remains unexplained.

Homogenization temperatures (Th) of fluid inclusions in the Jehe unit are distributed over a wide range from 110° to 350°C (no distinguishable modes) which may have been affected by metamorphism. Unlike their counterpart in the Julu unit, fluid inclusions hosted in the Jehe unit range from 117° to 195°C with a distinctive mode at 160°-170°C. Probably, higher confining pressures due to deeper position of the Jehe unit could have inhibited the stretching of fluid inclusions (e.g. Leach et al. 2004).

Density of the evolved solution due to dilution was estimated using a formula proposed by Sato (1972). The end-members include ore-forming fluid (T = 170°C, salinity = 25 wt% NaCl eq.) and seawater (T = 3°C, salinity = 3.5 wt% NaCl eq.). The density model suggests that the ore-forming fluid was denser than seawater. The density of the fluid decreased to that of seawater as the fraction of seawater reached infinity. The density of the evolved fluid, which was consistently higher than that of seawater, implies that the ore-forming fluid may have formed a bottom-hugging fluid upon its discharge on the paleo-seafloor. Conceptually, capacity of the fluid to carry metals was maintained as it flowed to a local topographic depression. The density barrier then disappeared due to contact between the stagnant fluid and seawater allowing mixing to occur. The mixing resulted in the precipitation of metal sulfides to form stratiform orebodies hosted in the Julu unit.

6.2 Redox state and pH

The redox state and pH of the ore-forming fluid were strongly controlled by those of rift-fill sequence (Cooke et al. 2000). The similarity between the host rocks and rift-fill sequence in the Dairi basin may have equilibrated the ore-forming fluid to reduced and acidic conditions. The presence of pyrrhotite in LH and lack of hematite in the orebodies and immediate hanging and footwall rocks also suggest that the ore-forming fluid was reduced. Assuming total S content, dominated by H₂S\textsubscript{aq}, in the ore-forming fluid was \(10^4\) m, the temperature of pyrrhotite and pyrite equilibrium was 125°-175°C. At 170°C, >1 ppm Zn and >1 ppm Pb can be transported by a reduced fluid at pH 3 in forms of metal-chloride complexes.

6.3 Sources of sulfur

Sulfur isotope ratios systematically increased from barren sedimentary rocks (\(\delta^{34}\text{S} = -4.1 \text{ to } +9.7\%\)) to orebodies in the Jehe unit (\(\delta^{34}\text{S} = +3.5 \text{ to } +8.0\%\)), LH (\(\delta^{34}\text{S} = +6.4 \text{ to } +18.1\%\)), MH (\(\delta^{34}\text{S} = +13.5 \text{ to } +28.8\%\)) and UH (\(\delta^{34}\text{S} = +18.7 \text{ to } +26.7\%\)). Sulfur isotope ratios in the barren sedimentary rocks suggest that reduced sulfur in diagenetic pyrite was generated via bacterial sulfate reduction of Carboniferous seawater sulfate. In the stratiform orebodies, the much isotopically heavier sulfides could have possibly resulted in restricted basin and anoxia development prior to mineralization, and more active bacterial systems during the discharge of ore-forming fluid into the seafloor. Distinctive isotopically light sulfides in the orebodies hosted by the Jehe unit may have been influenced by hydrothermal \(\text{H}_2\text{S}\textsubscript{aq}\) carried by the ore-forming fluid.
7 Genetic processes

Genetic processes for the formation of the Dairi Zn-Pb-Ag deposit are divided into precursor and mineralization stages. In the precursor stage, saline ore-forming fluids were generated within the rift-fill sequence and equilibrated with rift-fill sequence in reduced and acidic conditions. On the seafloor, microbes actively reduced Carboniferous seawater sulfate and precipitated dissolved ferrous ions as diagenetic pyrite along with other marine sediments. However, limited ferrous ions resulted in trace amounts of diagenetic pyrite and led to build-up of reduced sulfur concentrations in the bottom waters (anoxia development).

The onset of deeply penetrated syn-sedimentary Carboniferous faults initiated the mineralization stage by providing a pathway for the ore-forming fluid to ascend to the seafloor. The ore-forming fluid encountered descending seawater along the pathway to the seafloor thereby lowering salinity and temperature of ore-forming fluids. This encounter eventually led to the decreased solubilities of metal as chloride complexes in the ore-forming fluid. Reduced sulfur carried by the ore-forming fluid fixed metal ions to precipitate sulfide within the fractures of the Jehe unit. The amount of reduced sulfur transported in the ore-forming fluid had to be low in order for the ore-forming fluid to transport significant amounts of metals. Reduced sulfur served as the limiting reactant in sulfide precipitation within the fractures and therefore excess metal ions were transported to the seafloor by the remaining fluid.

Upon its discharge on the seafloor, the remaining ore-forming fluid, which was denser than seawater (even though it had been diluted), flowed to a local topographic depression on the seafloor. A density barrier preserved the carried metals during the flow. After the fluid was settled on the local depression, heat exchange between the ore-forming fluid and seawater decreased the temperature of the ore-forming fluid. Incorporation of biologically reduced sulfur allowed precipitation of metal sulfides forming stratiform orebodies hosted by the Julu unit.

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References


Coupled control of intra-basinal and deep-seated geologic processes on formation of some super-large uranium and base-metal deposits in sedimentary basins

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Abstract. The largest uranium and base metal deposits in the world are hosted in sedimentary basins. Although intra-basinal processes play important roles in mineralization, the formation of many of these deposits appears to be also related to deep-seated geologic processes. This paper provides two case studies of such coupled control of mineralization.

The unconformity-related uranium deposits in the Proterozoic Athabasca Basin, including several super-large (and high-grade) ones, are closely associated with reactivated basement faults crosscutting the basal unconformity. Despite the involvement of the basement, the mineralization processes have been generally considered of basinal nature (the diagenetic-hydrothermal model), as the mineralizing fluids were basinal brines. However, the elevated fluid temperatures (up to 200 °C) at a relatively shallow burial environment (3 km or less), thus abnormal geothermal gradient, suggests that deep-seated geologic processes were involved in the mineralization.

The super-large Jinding Zn-Pb deposit in the Meso-Cenozoic Lanping Basin (China) displays many geologic characteristics similar to those of Mississippi Valley-type deposits, such as epigenetic features and association with hydrocarbons. However, the tectonically active nature of the basin, evidence of strongly overpressured mineralizing fluids, and mantle-derived noble gas and Pb isotope signatures, suggest that deep-seated processes were also involved in the mineralization.

1 Introduction

Some mineral deposits are mainly controlled by deep-seated geologic processes (e.g., diamond deposits associated with kimberlite), and some are mainly controlled by shallow or surficial processes (e.g., potash deposits in sedimentary basins), whereas some are results of coupled control of both shallow and deep-seated processes (e.g., Cu-Ni sulfide deposits associated with mafic-ultramafic magmatic rocks) (Robb 2005). For mineral deposits hosted in sedimentary basins, it is generally believed that they were formed from intra-basinal processes, although the driving forces of fluid flow may still be from outside the basin (e.g., Mississippi Valley-type Zn-Pb deposits) (Garven and Raffensperger 1997).

However, some mineral deposits in sedimentary basins, including super-large ones, appear to be controlled by both intra-basinal and deep-seated geologic processes. In such deposits, the basinal processes are relatively well manifested, whereas the effects of the deep-seated processes, concealed at great depths, are generally cryptic at the sites of mineralization, requiring careful examination of various geologic, geochemical and geophysical signatures (Fig. 1). The actual deep-seated geologic processes may be variable depending on the tectonic setting, and their contributions to mineralization may include providing fluid, metals, and heat driving fluid flow. The approaches to decipher the relationship between mineralization and the deep-seated processes thus include geochemical, geophysical, structural and hydrodynamic studies (Fig. 1).

Figure 1. A sketch showing potential relationship between mineralization in the basin and deep-seated geologic processes.
Basin in Canada and the sandstone-hosted Jinding Zn-Pb deposit in the Meso-Cenozoic Lanping Basin in China. In both cases, the traditional views are that the mineralization is mainly related to basinal processes, but we propose that deep-seated processes played a critical role in their formation.

2 Unconformity-related U mineralization in the Proterozoic Athabasca Basin (Canada)

The unconformity-related U deposits in the Proterozoic Athabasca Basin, including several super-large ones with reserves of >100 million pounds of U₃O₈ and grades of >10 wt.% U₃O₈ (IAEA 2018; NEA and IAEA 2018), are among the largest and richest U deposits in the world. These deposits have the following common characteristics: 1) they occur near the unconformity between the sedimentary basin fill and the underlying crystalline metamorphic basement rocks (thus the name “unconformity-type” or “unconformity-related”); 2) they are located at the apex of basement-hosted graphitic lithologies or shear zones marked by large low resistivity anomalies at the crustal scale; and 3) they are associated with illite ± chlorite ± tourmaline alteration halos in both the sedimentary cover and basement (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kotzer and Kyser 1995; Fayek and Kyser 1997; Jefferson et al. 2007; Kyser and Cuney 2015).

It has been generally agreed that the mineralizing fluids were basinal brines of evaporated sea water origin derived from the Athabasca Basin (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kyser et al. 2000; Richard et al. 2011, 2014; Mercadier et al. 2012). The uranium is inferred to be sourced either from the basin detritus (Hoeve and Sibbald 1978; Hoeve and Quirt 1984; Kotzer and Kyser 1995; Fayek and Kyser 1997; Kyser et al. 2000), or from the basement rocks (Dahlkamp 1978; Annesley and Madore 1999; Hecht and Cuney 2000; Cuney et al. 2003; Richard et al. 2010, 2016; Mercadier et al. 2013; Martz et al. 2018).

Both fluid mixing and fluid-rock interactions have been proposed as mechanisms for ore precipitation, with graphite and ferrous iron-rich minerals being invoked as the main sources of reducing agents, either in the form of mobile hydrocarbons and dissolved species in solutions, or as solid reactants (Hoeve and Sibbald 1978; Hoeve and Quirt, 1984; Alexandre et al. 2005; Yeo and Potter 2010). More recently, fluid boiling or phase separation has been suggested to have also played a role based on observation of vapor-rich fluid inclusions in many uranium deposits (Chi et al. 2017; Wang et al. 2018). The fluid flow related to mineralization has been inferred to be caused by thermal gradient-induced fluid convection and/or deformation-driven fluid flow (Raffensperger and Garven 1995; Cui et al. 2012; Li et al. 2016, 2017, 2018).

The above geological characteristics and interpretations appear to support a general model in which the ore-forming fluids, the metals and the driving forces of fluid flow are derived from within the basin or its immediate basement rocks, as described in the conventional diagenetic-hydrothermal model (Pagel 1975; Hoeve and Sibbald 1978; Pagel et al. 1980; Hoeve and Quirt 1984; Kotzer and Kyser 1995). It is inferred that the mineralization took place at burial depth >5 km in order to explain the elevated fluid temperatures of > 200 °C, which seems to be supported by elevated fluid pressures (up to 1500 bars) calculated from fluid inclusion data (Pagel 1975). In such a model, the thermal gradient in the basin and basement would be about 35 °C/km, which is normal for an intracratonic basin or foreland basin. The mineralization processes can thus be linked with normal diagenesis within the basin and infiltration of the basinal brines into the upper part of the basement, without the need to invoke deep-seated processes.

However, as discussed in Chi et al. (2018), the high fluid pressures estimated by Pagel (1975) are inconsistent with a hydrostatic fluid pressure regime as predicted for a sand-dominated basin (Chi et al. 2013). Furthermore, based on regional geochronological and stratigraphic data and the interpretation that the ore-forming fluids originated from evaporated sea water (Richard et al. 2011), Chi et al. (2018) inferred that the primary uranium mineralization in the Athabasca Basin took place during the deposition of the stromatolitic carbonates of the Carswell Formation, which contains evidence of development of evaporites (Ramaekers et al. 2007). At this time of the basin history, the burial depth of the basal unconformity was likely less than 3 km (Chi et al. 2018) (Fig. 2).

Based on this shallow-burial hypothesis, and in order to explain the elevated fluid temperatures of > 200 °C (Chu and Chi 2016), the geothermal gradient during the time of mineralization may be up to two times higher than the normal geothermal gradient. This abnormal geothermal gradient is likely caused by some deep-seated geologic processes, although their nature (e.g., magmatic or structural) remains to be investigated (Fig. 2). It is interesting to note that the basement architecture inherited from the Paleoproterozoic orogenes is characterized by steeply dipping, large shear zones separating continental-scale blocks exhumed from the
lower granulitic crust prior to the deposition of the basin. These deeply rooted fault systems have been reactivated several times due to far field tectonic events after the deposition of the basin, and may have served as conduits of crustal-scale fluid flow transferring fluids from deep crustal level to shallow basement structures near the unconformity, some of which host uranium mineralization. In summary, based on the above discussion, it is proposed that the unconformity-related uranium deposits associated with the Athabasca Basin resulted from the coupling of basinal processes (especially development of basinal brines) and deep-seated processes (Fig. 2), the latter of which may have played an important role in driving fluid flow.

3 Sandstone-hosted Jinding Zn-Pb deposit in the Meso-Cenozoic Lanping Basin (China)

The Jinding Zn-Pb deposit is hosted by Cretaceous to Tertiary sandstones and conglomerates in the Lanping Basin in southwestern China (Xue et al. 2007). It has a reserve of approximately 220 million tons of ore grading 6.1% Zn and 1.3% Pb, and represents the largest sandstone-hosted Zn-Pb deposit in the world (Xue et al. 2007).

The deposit shares many geological characteristics with the Mississippi Valley-type deposits, however it differs from the latter not only in terms of host rocks, but also in terms of tectonic setting in that the Lanping Basin is a tectonically active basin linked with tectonic processes at depth, as evidenced by strong deformation of the strata in the basin and development of deep-penetrating faults and mantle-derived magmatic intrusions (Xue et al. 2007).

Fluid inclusion studies indicate that the deposit formed from interaction between hot, metal-carrying brines and H2S generated by bacterial sulfate reduction (BSR) through reaction with hydrocarbons in a reservoir hosted by the Jinding dome (Chi et al. 2017). Although this may appear to be a typical intra-basinal process, noble gas isotopes of fluid inclusions and Pb isotopes of sulfides in the ores suggest that a significant amount of the ore-forming fluid may have been derived from a mantle source (Xue et al. 2007).

Furthermore, fluid inclusion data, coupled with field observations such as sand injection structures (Chi et al. 2007), suggest that the mineralization system was episodically overpressured, which cannot be explained by intra-basinal processes (e.g., sediment compaction; Chi et al. 2006) and requires extra-basinal input (e.g., volatiles from the mantle) (Fig. 3).

In addition, the inference that H2S accumulated in the gas cap of the paleo-oil and gas reservoir participated in the mineralization necessitates that the ore-forming fluids were overpressured and able to penetrate the oil in the reservoir and reach the gas cap (Fig. 3), supporting the hypothesis that the ore-forming fluids were driven by deep-seated driving forces. Therefore, the Jinding deposit represents another example of mineralization that resulted from joint action of intra-basinal processes (development of oil and gas reservoirs and basinal brines), which provide part of the ore-forming fluids and metals as well as geochemical traps, and deep-seated geological process which may have provided additional ore-forming fluids, metals and fluid flow driving forces.

Figure 3. A schematic model showing potential relationship between the Jinding Zn-Pb deposit, intra-basinal processes (especially development of basinal brines and an oil-gas reservoir with a sour gas cap) as well as deep-seated processes, which may have played an important role in driving fluid flow and contributing part of the ore-forming fluid and metals.

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Influence of inherited structures as fluid-thermal conduits applied to the formation of uranium mineralisation in the Athabasca Basin, Canada

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Abstract. Ore deposit formation requires the synchronisation of multiple processes with transportation of fluids and heat. Ancient inherited structures found within the basement of the Athabasca Basin were formed as a result from orogenic processes (i.e nucleation and accretion processes). It is established that their reactivation played a significant role for the formation of the unconformity-related uranium deposits. The time gap between the inherited structures' inception and mineralisation event is sufficient for any traces of hydrothermal systems to reach steady state. The aim of this study is to determine the role for these inherited structures affecting the hydrothermal dynamics, by using a pre-existing tectonic structure generated from a thermo-mechanical study and incorporating fluid-thermal processes until steady-state conditions. The models are then experimented with permeability fields of increasing complexity in three types of tectonic scenarios. Results indicate that deep-seated structures operate as fluid-thermal conduits that bring fluids and heat towards the upper portions of the crust. In addition, thermal convection occurs at favourable permeability conditions. The experimentation of models in different permeability fields provides a general framework for the Athabasca Basin suggesting the transportation of basement-associated fluids and heat to the surface.

1 Introduction

The formation of ore deposits is related to hydrothermal systems at depth in order to precipitate and concentrate minerals (McCuaig and Hronsky 2010 and references therein). One of the known vehicles for fluid-flow, a favourable whole lithosphere architecture, is capable of pre-determining location of future ore deposits (e.g. Catches and Adams 2005, Cox 2005). The extent of these lithospheric-scale structures can be masked from subsequent geological events and would require the use deep sub-surface imaging techniques (see in the Indian orogeny in McCuaig and Hronsry, 2010). These deep-seated inherited structures were formed as the result of orogenic processes (Audet and Bürgmann 2011).

Similarly, the nucleation of the western Canadian Shield and its subsequent Proterozoic accretion (such as the Trans-Hudson Orogeny (THO), Alexandre et al. 2007) led to the formation of steeply-dipping shear zones within the Archean Basement of the Athabasca Basin. In between the Archean Mudjatik and Paleoproterozoic Wollaston domains lies a NE-SW trending structural corridor characterised by a highly strained zone presenting steeply dipping anastomosed shear zones that extends over several hundred kilometres along strike (i.e the Wollaston-Mudjatik Transition Zone). This tectonic evolution has been sealed from around 1.75 Ga with the deposition of the Athabasca Basin that rest unconformably over these two deep eroded domains. Recent geochemical analysis along the structural corridor established that uranium mineralisation was coeval with the reactivation of those fore-mentioned structures (e.g. Mercadier et al. 2013) and is later confirmed in recent numerical experiments (e.g. Li et al. 2018). This event occurred 150 Ma after the deposition of the Athabasca Basin (e.g. Jefferson et al. 2007). Additionally, there was a period of 190 to 240 Ma of tectonic silence between peak-metamorphic THO and the deposition of the Athabasca Basin.

With such long durations between significant tectonic events, any potential fluid-flow activity will eventually reach steady-state conditions. Using a pre-generated tectonic model in relation to the basement of the Athabasca Basin, three types of fluid-thermal modelling scenarios leading up to the deposition of the Athabasca Basin are then constructed to determine hydrodynamic behaviour and ascertain the role of these deep-seated structures in multiple permeability configurations. The implications to how the geological environment prepares for mineralisation is discussed.

2 Modelling Approach

2.1 MDoodz and FLAC3D - Adding fluid-thermal processes to regional lithospheric settings

The experiments were conducted using a numerical code that solves Darcy's law equation to compute the fluid flow rate anytime in a solid matrix controlled by its given permeability (e.g. a tectonic structure prior to tectonic reactivation). The initial geological and structural geometry input (MGeol in Fig. 1) was the outputs taken from a 2D thermo-mechanical study made to understand Precambrian orogenic processes under hot lithospheric conditions (Poh et al. in prep). The
reference model was chosen from the parametric study according to its agreement with the available geological and metamorphic observations of the Trans-Hudson Orogeny, West Canadian Shield. The fluid-thermal code used here is the Fast Lagrangian Analysis of Continua in 3 Dimensions (FLAC3D, Itasca 2012) that has been widely applied to low-temperature geothermal and mineral system simulations (e.g. Li et al. 2018).

2.2 Model setup and boundary conditions

The vertical structures marking the Wollaston-Mudjatik Transition Zone correlates to large shear zones that could predetermine the locations for mineral deposits (e.g. Jefferson et al. 2007). The selected geological and associated geometry is used as inputs and permeability values are assigned to the different rock units (Fig. 1). All models M1 to M4 Topo have the rocks assigned with constant permeability values. The meta-sediments are assigned as permeable ($k = 1.e-14$ m$^2$) whereas the basement is assigned as impermeable ($k = 1.e-18$ m$^2$). Models M2 and M3 employ a simplified depth-dependent permeability in the basement and in the meta-sediments. Models M4 and M4 Topo introduce the deformed rocks (deformed basement at $k = 1.e-16$ m$^2$ and deformed meta-sediments at $k = 2.e-14$ m$^2$) as regions of slightly higher permeability. M4 Topo has the same permeability configuration as M4 but also takes into account the effect of topography. The third scenario, M5 (not shown here due to lack of space), consider the tectonic events leading to the deposition of the Athabasca Basin and the model design is inspired from Li et al. (2018). The geometry for the deformed zones were taken from the accumulated strain profile in the thermo-mechanical study. These strains were recorded in the preceding period of orogenic build up.

For all the experiments, the horizontal and vertical boundary conditions were set to no fluid flow across the boundary. The entire model box is initially saturated in fluids. The initial thermal profile is made in two parts depending on depth. The surface temperature is set at 20°C and is then computed as a linear geothermal gradient of 30°C/km until 600°C (i.e. $z \sim 20$ km depth). Below, the thermal gradient is such as it reaches 1300°C at the bottom boundary. This thermal profile hence corresponds to a standard geothermal gradient for Precambrian craton.

The estimation of rock permeability, $k$ (m$^2$), in any geologic model is a requirement for any fluid flow processes. Assigning permeability values to rocks is a challenge considering its wide range and sensitive to physical processes to either enhance or degrade its value (Rutqvist and Stephansson 2003). Here we use an initial background permeability field in which rock permeability is assumed to be homogenous and it undergoes an exponential decay according to depth, expressed as: $\log k = -14 - 3.2 \log z$, where $z$ corresponds to depth in km (Manning and Ingebritsen 1999).

The width for the deformed zones (seen in Fig. 1) is perhaps the most controversial. Previous fluid-thermal modelling simulations on the Ashanti belt had the dimensions of 10 km ($x$) by 15 km ($z$) with an assigned constant permeability of 1.e-15 to 1.e-14 m$^2$ (Harcouët-Menou et al. 2009). The dimensions for the deformed zones in our models have 5 km as maximum width (M4 and M4 Topo in Fig. 1) and 3 km width for the deep-rooted structures (M1 and M2 in Fig. 1). The assigned permeability values are similar with what Harcouët-Menou et al. (2009) used and is considered as conservative.

3 Results

3.1 Fluid-thermal reference models (M1 – M3)

![Figure 1. Geological model (MGeo) and the permeability fields for models M1 - M4 Topo of increasing levels of complexity. See text for description](image)

![Figure 2. Fluid flow results are shown as fluid velocity magnitude and their corresponding vectors at steady state for M1 models with their variations in A, B, and C. White lines represent isotherms. Red and blue arrows correspond to the vertical direction of fluid vectors. A pair of blue and red arrows indicate fluid-thermal convection occurrence.](image)
The reference model (M1 in Fig 2) shows thermal anomaly outputs (up to 800 °C) and fluid velocities up to 2 orders of magnitude within the tectonic structures when compared to the rest of the model. Occurrence for convection currents is represented by the cycle shape of the 200 °C isotherms within the meta-sediments and vector outputs (illustrated by red and blue arrows in Fig. 2). The results in the model variations of M1 (Fig. 2A, B and C) reinforce the fact that deep-seated structures operate as fluid-thermal conduits in all model variations (i.e. high thermal upwelling anomaly and fluid velocities). When the permeability in meta-sediments was changed, two notable changes ensured; 1) fluid-thermal convections did not occur and 2) the change of the permeability reflects the corresponding increase (Fig. 2A) and decrease (Fig. 2B) in fluid velocity by an order of magnitude. The thermal anomaly distribution in Fig. 2B is more gentle compared to Fig. 2A. An additional scenario was conducted by making the basement more permeable (Fig. 2C). The results for the fluid patterns are comparable with M1 except for the fluid velocity within the basement increased by an order of magnitude.

Depth-dependent permeability fields were applied within the basement for M2 (Fig. 3) and the meta-sediments in M3 (Fig. 4). The permeability for the basement in M3 is set to impermeable (1.e-18 m²). In M2, the fluid-thermal patterns are similar to the results in M1 but with increasing in the number of fluid-thermal convection cells. Fluid velocities near the contact between the basement and the meta-sediments at 10 km depth are increased by an order of magnitude. The simplified depth-permeability of the basement gave additional ‘space’ for the fluid-thermal convections to occur. When the permeability of the meta-sediments changed (Fig. 3A and B), the corresponding changes to the fluid velocities are observed. However, in in both permeability cases, occurrence for convection currents did not occur. Instead, a secondary build-up of temperature within thermal anomaly (black arrow in Fig. 3A). Additionally, the chaotic thermal anomaly did not occur under when the meta-sediments are less permeable by an order of magnitude (Fig. 3B).

The power-law permeability-decay function was applied within the meta-sediments while maintaining an impermeable basin in M3 (Fig. 4). Overall fluid velocity was significantly reduced within the vertical structures. However, the 200 °C isotherm’s cyclical behaviour suggest micro-circulation of fluids closer to the surface, which can be viewed by plotting a line plot of the horizontal component of the fluid velocity. The model variation to a more permeable basement (Fig. 4A), the thermal profile became more homogeneous without any fluid convections. Implementing a less permeable basement resulted in a periodic 200 °C isotherm with the observable instance of circulation of fluids (Fig. 4B).

3.2 M4 and M4 Topo: retrograde metamorphic THO tectonic setting

The results obtained for M4 and M4 Topo are consistent with previous scenarios, by displaying high fluid-thermal anomalies as a result of large permeable zones (Fig. 3). Fluid velocities within the pre-deformed meta-sediments and basement were observed to have half
and 2 times order of magnitude greater than their parent rocks respectively.

Under this permeability setting, fluid-thermal convection did not occur in these scenarios. When the geometries of the deformed zones were included, this not only increases the overall area of more permeable zones, but the rate of fluid-thermal advection is increased as well. The numerical simulation became more unstable as simulation progressed. The difference between the upper thermal boundary (20 °C) and the thermal-fluid anomaly (~800 °C at \( u > 1.\times10^{-7} \) m.s\(^{-1}\)) resulted from a chaotic distribution of thermal advection close to the surface. An additional test was conducted at reduced permeability for the meta-sediments and deformed counterparts, chaotic thermal anomalies did not occur.

M4 Topo included the topography seen in the MGeol (Fig. 1) in which to simulate the effects of topography (max topography ~1 km). Previous fluid-thermal results indicate topography enhances the lateral distribution of the fluids (Hayba and Ingebritsen 1987). However, we did not observe the enhancement of lateral distribution due to the high fluid-thermal advection at depth.

3.3 M5: initial Athabasca basin formation prior to tectonic reactivation setting

The fluid-thermal results for M5 (not shown here) continue to be consistent with the previous scenarios that the deep-seated structures operate as fluid-thermal conduits. Above each aperture of the permeable deep-seated structures, the assigned permeability was conducive for fluids to undergo free convection. The main convection cells found within the basin and permeable deep-seated structures has a wavelength of 5 km, accompanied with fluid velocities of \( 10^{-7} \) m.s\(^{-1}\). Elevated thermals were also observed at the contact between the permeable deep-seated structures and basin reaching at least 250 °C at 6 km depth (~41.67 °C.km\(^{-1}\)).

4 Discussion

In every tested scenario, these deep-seated structures provides the necessary infrastructure to transport fluids and heat to the surface through the form of elevated thermals and faster fluid velocities. The elevated temperatures at the permeable deep-seated structures in M5 correlates well to the fluid inclusion data for uranium mineralisation (e.g. Mercadier et al. 2013) as well as meeting the thermal requirements for the chloritisation of biotite during retrograde metamorphic THO. This particular alteration pattern is essential for the precipitation of graphite, a key chemical reductant for precipitating uranium. Together with the physical conditions required for convection currents is essential for the mixing of basinal and basement fluids, will increase fluid-rock interactions.

5 Conclusion

The fluid-thermal results from the experimentation of different permeability configurations of increasing complexity generate two main conclusions: 1) the deep-seated inherited structures (up to 30 km depth) function as fluid-thermal conduits, bringing fluid and heat towards the upper portions of the crust, and 2) convection cells appearing laterally away from the structures under favourable permeability configurations. The presence for these permeable deep-seated structures are hence instrumental in providing the necessary physical conditions as well as the structural infrastructure to enhance fluid-rock interaction and form regions of key chemical reductants essential for uranium mineralisation.

Acknowledgments

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The uranium metallogeny in the South Armorican detachment zones, Variscan belt, France: geology, tracing (in space and time), numerical modelling

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Abstract. Uranium mineralization is common in geological environments where oxidized uranium-bearing fluids interact with reduced lithologies. This was the case for Variscan detachments in the South Armorican Massif, France. Numerous syntectonic peraluminous granites were emplaced in the footwall of detachments during the Carboniferous. Surface-derived fluids infiltrated the detachment planes and leached out the uranium from the magmatic uraninite that crystallized in these granites at the end of magmatic differentiation. On their way back to the surface, these fluids interacted with reducing black schists, which triggered precipitation of hydrothermal uraninite. This conceptual model serves as a basis for thermal-hydraulic-mechanical modeling.

Introduction

Detachments are syn- to post-orogenic, crustal-scale extensional shear zones. The lower crust is exhumed at their footwall, and the upper crust is stretched at their hangingwall. Numerous fluid circulations are documented in these detachments, originating from deep crustal levels up to the Earth surface. Detachments also control the emplacement of syntectonic granites and the geometry of sedimentary basins. Most of these syntectonic granites form from partial melting of crustal sources, and, as such, are enriched in Large Ion Lithophile and High Field Strength elements, among which uranium. Where magmatic differentiation was sufficiently advanced in peraluminous granitic liquids, uranium may have reached contents large enough to crystallize uraninite. Detachments zones are thus the place where reduced uranium in crystallizing granite may interact with oxygenated aqueous fluids derived from the surface.

This situation occurred at the end of the Variscan orogeny in the south Armorican Massif, western France. In this contribution, we present a general model of uranium mobilization from fertile granites by surface-derived fluids followed by uranium precipitation where these fluids interacted with reducing lithologies. The conceptual model presented here serves as a basis for a thermal-hydraulic-mechanical numerical modeling.

2 Regional geology

The Armorican Massif is divided in three domains separated by two dextral crustal-scale shear zones, the North (NASZ) and South (SASZ) Armorican Shear Zones that were active during the Carboniferous (Gumiaux et al. 2004). The Central Armorican Domain is mostly made of weakly deformed and low-grade sediments of Neoproterozoic to Carboniferous ages. The south Armorican Domain is made of high grade metamorphic rocks, including migmatites, and crustal-derived peraluminous granites. Migmatites have been exhumed due to vertical displacements along the detachment zones from ca. 310 to 310 Ma while the South Armorican Shear zone was also active (Tartèse et al. 2011, 2012, 2013; Ballouard et al., 2015; Gapais et al. 2015). Numerous syntectonic highlyperaluminous two-mica leucogranites were emplaced within the SASZ and detachments. Several metal deposits, mainly Sn and U mineralization (Chauris 1977), are spatially associated with the peraluminous leucogranites. Uranium represents the most important resource in the region and has been mined within the three uraniferous districts of Pontivy, Mortagne and Guérande (Ballouard et al. 2017, 2018; Cathelineau et al. 1990; Cuney et al. 1990).
Field observations

The most interesting outcrops showing the syn-tectonic granites emplaced in detachment zones are located along the coastline, near Quiberon and Guérande (Fig. 1).

Both the Guérande and Quiberon granites display a strain gradient with deformation increasing toward the top of the detachment zone footwall.

In the Quiberon granite, the width of the deformed zone reaches tens of meters. The strain pattern is rather heterogeneous, with deformation being localized in syn-tectonic pegmatites transposed into the foliation (Gapais and Laouan Brem Boundi 2015), leaving volumes of granites much less deformed. Where granite is more homogeneous, typical C/S structure developed.

In the Guérande granite (Fig. 3), a kilometic scale strain gradient is visible towards the detachment zone. Decametric normal faults cut the ductile fabric; this is clearly visible between the cities of Piriac and La Turballe (Fig. 3). The resulting graben-like structure exposes country rocks, comprised of metavolcanic rocks of Ordovician age and black schists.

4 Magmatic differentiation vs. hydrothermal alteration

In the Guérande leucogranite (Ballouard et al. 2015, 2017), magmatic and magmatic-hydrothermal differentiation progressed toward the apical zone of the intrusion, namely toward the detachment. There, tourmaline-bearing highly peraluminous granites reach extremely high content in highly incompatible hygromagmaphile elements such as Sn, Cs and Rb but are paradoxically depleted in U compared to the biotite-bearing samples from the deeper levels of the intrusion. Also, the oxygen isotope composition of the apical samples is lowered by several per mil compared to unaltered samples (Ballouard et al. 2017). This peculiar signature is interpreted to reflect an influx of meteoric water as also supported by low hydrogen isotope ratios of syntectonic muscovite in the upper part of detachment footwalls (Dusséaux et al. in press).

The petrographic characterization of the Quiberon granite is currently in process. First results show that the granite close to the detachment is more evolved than the deeper levels. Interestingly, the hydrothermal alteration seems well recorded by apatite grains (Fig. 5).
Figure 5. Chondrite-normalized REE patterns of apatite grains from the Quiberon granite. To the left, the sample is deformed; to the right, the sample is undeformed. The uranium content is lower in the deformed, and altered, sample. Note also that the U-Pb age of the deformed facies is 10 Ma younger than the undeformed one.

As a summary, the petrological and geochemical characteristics of syn-tectonic granites emplaced in the footwall of detachment are as follows: the most evolved facies and the most altered facies are those emplaced in the higher structural levels of intrusions, close to detachments. Hydrothermal alteration thus affected the most differentiated granitic rocks.

5 Uranium mineralization

The Guérande granite is the only hosts of uranium mineralization. The main mineralization occurs in a fault zone of the graben affecting the apical zone of the granite. There, quartz-uranium oxide bearing veins crosscut the foliation of metavolcanics rocks and are blocked at the contact with black shales (Cathelineau 1981). The age of mineralization is somewhat variable, and comprised between the age of the last magmatic events (around 300 Ma) and Permian times (around 270 Ma; Ballouard et al. 2017).

Figure 6. Chronological sequence comparing the timing of U mineralization in the Variscan belt and the emplacement ages of the associated granites.

It is thus clear that uranium mineralization immediately follows magmatic activity; this relationship is also visible for several other magmatic systems in the Variscan belt (Fig. 6).

From all these observations, a conceptual model of uranium mineralization has been derived (Fig. 7; Ballouard et al. 2017). Fertile granites emplaced below detachment zones. Magmatic differentiation promoted magmatic uraninite crystallization in the apical zone of the granites. The flow of surface-derived fluids induced leaching of uranium from magmatic uraninite. On their way back to the surface along permeable pathways, such as steeply dipping normal faults that control the geometry of the graben in the Guérande granite, these fluids interacted with reducing lithologies (black schists), which triggered precipitation of hydrothermal uraninite.

Figure 7. Conceptual model of uranium mineralization associated with granitic magmatism at the footwall of Variscan detachment zones (Ballouard et al. 2017).

6 Numerical modeling

Such a heuristic conceptual model can be tested through hydro-thermal simulations accounting for darcyan flow. Preliminary simulations have been realized in order to test and combine the effect of different driving forces for fluid flow (e.g. thermal convection, topographic gradient). The permeability of the detachment is assumed to be temperature-dependent. This relationship was designed by analogy with ductile rheology, which is at first order controlled by the temperature. The first results indicate that (i) pluton emplacement and cooling are unfavorable periods for infiltration of surface-derived fluids along detachment. Topographic gradients have to develop in order to create strong pressure gradients that can counterbalance thermal convection triggered by magmas; (ii) after cooling of the pluton, uplift and erosion, the pluton apical zone (source of U, Fig. 7) is in the brittle field strain which implies higher permeabilities along the neighbouring detachment segment. Here, in this internal zone of the Variscan belt, topographic gradients were large enough to promote downward flow circulation of fluids that could be responsible for supplementary cooling (Fig. 8). A next step in the modeling will consist in integrating solute transfer equation for U flux and mass balance calculation. In addition, future models will account for the role of solid rock deformation on the patterns of fluid circulation. Brittle and ductile deformations have different impacts.
on the distribution of permeability. Detachments thus appear as ideal geological objects to study the role of hydro-thermo-mechanical processes on the genesis of mineralizations.

**Figure 8.** Snapshot of a detachment model with thermal convection and topography as driving forces. Advection downward flow of surface-derived fluids is efficient to cool down deeper parts of the detachment.

7 Conclusion

In the southern part of the Armorican Massif, Variscan Belt (France), detachment zones worked during the late Carboniferous. In this context, lower crustal units were exhumed, syn-tectonic peraluminous granites emplaced in the footwall of these structures and downward infiltration of meteoric fluids occurred. Magmatic differentiation of the peraluminous granites led to the crystallization of magmatic uraninite. This crystal was leached through the interaction with oxidized surface-derived fluids. These fluids were then focused on high-permeability zones, like the steeply dipping normal faults associated with the regional extension. Where the faults crosscut black schists in the hangingwall of the detachment, uranium precipitation occurred as hydrothermal uranitite. This conceptual model allows building the set up for a dedicated thermo-hydro-mechanical numerical modeling.

Acknowledgements

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Cyclical development of roll front-type uranium deposits

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**Abstract.** In roll front (RF) deposits across the world, complex ore-stage pyrite textures associated with extreme changes in isotopic and trace element compositions reflect the dynamic internal evolution of the biogeochemical processes responsible for sulfate reduction, thus demonstrating the cyclical development of roll front systems. Upon percolation of oxidizing fluids into the reduced sandstones, RF systems become self-sufficient, with a systematic repetition of their activity cycle. Reducing-dominant conditions at the redox interface favor the formation of biogenic framboidal pyrite by bacterial iron and sulfate reduction ($\delta^{34}$S from -30.5 to -12.5‰) and the genesis of the uranium mineralization. When the redox interface becomes oxidizing-dominant, RF systems enter in a translation stage characterized by the re-oxidation of reduced sulfur minerals inducing an increased supply of sulfate and metals in solution to the bacterial sulfate reduction (BSR) zone. Hence, this stage is marked by increased rates of the BSR associated with the crystallization of variably As-Co-Ni-Mo-enriched concentric pyrite with moderately negative $\delta^{34}$S values. A final stage of pyrite cement with low trace element contents and heavier $\delta^{34}$S signatures marks the end of the RF activity cycle and the transition from open to closed system behavior.

1 Introduction and geological setting

Sandstone-hosted RF type uranium deposits represent the most cost-effective type of uranium resource (30% of the world annual production; OECD-NEA-IAEA 2016), as they are amenable to in-situ recovery. Studies on roll front deposits from the U districts of Wyoming and South Texas, U.S.A; the Central Asia Uraniferous Province (CAUP) extending from Kazakhstan to North China; and Lake Frome Embayment, South Australia, show evidence for biogenic mechanisms for both sulfate reduction and uranium mineralization that were mediated by sulfate-reducing bacteria (SRB) (Fig. 1; Reynolds and Goldhaber 1982, 1983; Min et al. 2005; Cai et al. 2007; Ingham et al. 2014; Bonnetti et al. 2015a, 2015b, 2017, 2018; Lach et al. 2015). They also revealed that RF deposit ore-stage pyrites share remarkably similar evolution of their textures (i.e., early framboidal, followed by concentric overgrowth, and finally idiomorphic cement), with extreme variations in trace element and $\delta^{34}$S signatures (i.e., from -72.0 to +32.4‰), up to the maximum theoretical value of sulfur isotope fractionation for microbial sulfate reduction (i.e., about -70‰; Brunner and Bernasconi 2005). To date, these features have been interpreted as reflecting protracted geological histories and multiple sources of S (e.g., Ingham et al. 2014). Strongly negative $\delta^{34}$S values recorded in pyrite are an unambiguous indicator of bacterial sulfate reduction (BSR) producing reduced sulfur species (H2S, HS-; Machel 2001) that are strongly enriched in $^{34}$S (i.e., isotopically light) compared to the initial sulfate (Habicht and Canfield 1997; Brunner and Bernasconi 2005). Pyrite also incorporates a number of trace elements; uptake is controlled by a combination of equilibrium (P, T, solubility composition) and kinetic processes (Large et al. 2009; Morin et al. 2017). Recent experimental and numerical modeling studies (e.g., Druhan et al. 2014) have demonstrated that large variations in $\delta^{34}$S values (-4 to +12‰ in experiments; up to +30‰ in the model) of bisulfide formed via BSR occur during steady injection of nutrient- and sulfate-bearing water through a meter-long sediment column over 43 days. Such a steady flow of oxidized waters defines an open system that closely matches the well-accepted model for roll front deposit formation.

Here, we demonstrate that a dynamic BSR-driven model explains the distribution of S isotopes and trace elements in RF system ore-stage pyrites. We show for the first time that the observed complexity of pyrite signatures reflects the successive stages characterizing the activity cycle of uranium RF systems and their biogeochemical internal dynamic setting, rather than external forcing and multiple element sources. The variations in the signatures of ore-stage pyrites, interpreted as a continuum reflecting the evolution of the processes responsible for RF ore genesis, were examined based on the study of ore-stage pyrites from the Bayinwula deposit, a typical RF uranium deposit located in the southeastern part of the CAUP (Bonnetti et al. 2015b, 2017).

The Mesozoic sedimentary basins of northeast China and southeast Mongolia (e.g., the Ordos, Erlian, Songliao and East Gobi basins) host numerous RF deposits (Cai et al. 2007; Bonnetti et al. 2015b, 2017). RF deposits in the Erlian Basin are mostly hosted by confined reduced braided river sandstones (Bonnetti et al. 2015b). The Bayinwula deposit, located in the north of the Basin, is characterized by disseminated P-rich coffinite, ningyoite and pitchblende in association with
ore-stage pyrite, inherited organic matter (OM) and altered Fe-Ti oxide.

Figure 1. Model section with geochemical and mineralogical zoning of the Bayinwula deposit (modified from Devoto 1978; Bonnetti et al. 2015b). The yellow diamonds indicate the location of the two representative samples used for the study. BSR = bacterial sulfate reduction; Sst = sandstone; Approx. = approximate; U min. = uranium mineralization; Pitch. = pitchblende; Molyb. = molybdenite; Alt. = altered.

Table 1. Geochemical / mineralogical zoning

<table>
<thead>
<tr>
<th>Hematite core</th>
<th>Altered envelop</th>
<th>Ore stage pyrite</th>
<th>Ore stage pyrite</th>
<th>Reduced Sst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>Goethite</td>
<td>Pyrite</td>
<td>Pyrite</td>
<td>Siderite</td>
</tr>
<tr>
<td>Magnetite</td>
<td>P-coffinite</td>
<td>Molyb.</td>
<td>Calcite</td>
<td>Ni</td>
</tr>
<tr>
<td>Ferrosilite</td>
<td>Pyrite</td>
<td>Calcite</td>
<td>Fe-Ti oxide</td>
<td>Mo</td>
</tr>
<tr>
<td>Selenium</td>
<td>Pyrite</td>
<td>Alt. OM</td>
<td>Alt. Fe-Ti oxide</td>
<td></td>
</tr>
</tbody>
</table>

2 Material and methods

As the signature evolution of ore-stage pyrites that defines the model presented in this study occurs at the mineral scale, we selected two samples for detailed characterization. These samples were selected based on the detailed geochemical and mineralogical study conducted by Bonnetti et al. (2015b) on the Bayinwula deposit from an extensive sample set comprising sixty-three samples collected on several drill holes distributed along a profile oriented perpendicular to the main geochemical/mineralogical zoning of the deposit. These two samples represent the wing and nose of the deposit (Fig. 1); they are representative of the signatures observed throughout the deposit and display the most complete paragenetic relationships of ore-stage pyrite populations.

Ore-stage pyrite populations from the Bayinwula deposit were characterized by: (i) petrographic observations using a reflected-light optical microscope and a Scanning Electron Microscope (SEM), (ii) in situ mineral analysis using an Electron Microprobe Micro-Analyzer (EPMA) to determine their major and minor elements chemical composition and high-resolution trace element mapping by Laser Ablation Inductively-Coupled-Plasma Mass-Spectrometry (LA-ICP-MS), and (iii) in situ measurements of sulfur isotopes by Secondary Ion Mass Spectrometry (SIMS).

3 Results

3.1 Morphology and texture

Ore-stage pyrites were formed in the pyrite zone (Fig. 1), identified as the BSR zone by Bonnetti et al. (2015b), either located at the nose or at the wings of the RF. Ore-stage pyrite morphologies display the following sequence of crystallization: (i) framboidal, (ii) concentric overgrowth and (iii) sub-idiomorphic to idiomorphic cement (Fig. 2a-a). Clusters of authigenic framboidal pyrite, predominantly replacing OM fragments and Fe-Ti oxides, are the most widespread type of pyrite observed in the BSR zone. The concentric pyrite forms overgrowth rims around the framboids in either colloform or idiomorphic textures. The framboids and the concentric overgrowth were both cemented by a final stage of sub-idiomorphic to idiomorphic pyrite. These three generations of pyrite were then partly to totally replaced by uranium minerals that occur in the ore zone (Fig. 1) during the downward translation of the RF (Bonnetti et al. 2015b). In the oxidized sandstone, ore-stage pyrites were re-oxidized into hematite or limonite by fresh batches of oxygenated groundwater.

3.2 Trace element distribution in pyrite

LA-ICP-MS trace element maps of As, Ni, Co and Mo revealed highly contrasted compositions of ore-stage pyrites (Fig. 2). As a general trend, the trace element contents of pyrite located at the nose of the RF are one order of magnitude higher than pyrite from the wings. At the wings, the framboids have low to high concentrations of As, Ni and Co (10's to 1000's of ppm) but relatively low Mo content (< 100 ppm; Figs. 2c-c to f). The first rim(s) of concentric pyrite has almost systematically higher Ni, Co, Mo and in particular As contents (10's to 1000's of ppm) relative to the framboids (Fig. 2c-a). Moving outwards, the concentric pyrite shows variable and rim-dependent As, Ni, Co and Mo contents, but generally the most abundant for the first rim (Fig. 2c-a). The final stage of pyrite cement is low in As, Ni and Co (several ppm to 100's of ppm) but can contain moderate Mo concentrations (up to 500 ppm) locally. At the nose of the RF, the variations of trace element concentrations in the three populations of pyrite are similar to pyrites at the wings. However, here the framboids and the concentric pyrite have moderate to very high concentrations of Ni, Co and Mo (100's to 10,000's of ppm), and especially high As contents (to 50,000 ppm). The higher trace element concentrations in pyrite from the nose compared with pyrite from the wings is mainly related to higher permeability of the host sediment at the nose (Fig. 1), hence more fluid-mobile trace metals transported by the fluid will be concentrated at the nose.
Figure 2. Petrographic, chemical and isotopic signatures of ore-stage pyrites characterizing the activity cycle of the Bayinwula roll front deposit. (a) Development of roll front deposits. (a) Back-scattered electron (BSE) image of the three ore-stage pyrite populations in the Bayinwula deposit (sample 1). (i) = framboidal, (ii) = concentric, (iii) = cement. (b) The main stages of the roll front activity cycle. BSR = bacterial sulfate reduction; SRB = sulfate-reducing bacteria. (b) Sulfur isotopes signature of ore-stage pyrites (modified from Bonnettic et al., 2015). (c) Trace element concentrations in ore-stage pyrites. (a) LA-ICP-MS profile (AB-CD) showing the evolution of concentrations in As, Ni and Co from framboidal to cement pyrite; (b) BSE image of the mapped pyrite zone from sample 1. Annotated values correspond to $\delta^{34}$S in ‰; (c-f) LA-ICP-MS semi-quantitative element maps showing the distribution of trace element concentrations (As, Co, Ni, Mo) in ore-stage pyrites; (g) LA-ICP-MS semi-quantitative element map showing the distribution of uranium concentration/mineralization associated with ore-stage pyrites.
3.3 Sulfur isotopes signatures

The δ34S signatures for the three ore-stage pyrites measured from samples throughout the deposit range from -30.5 to +18.8 ‰ (Fig. 2B): (i) the frambooids have a very light signature ranging from -30.5 to -12.5 ‰ (mean -18.4 ‰), (ii) the concentric overgrowth presents moderately negative values ranging from -13.7 to -7.5 ‰ (mean -9.6 ‰), and (iii) the late stage of pyrite cement has a heavier signature from -6.9 to +18.8 ‰ (mean +4.0 ‰).

4 Discussion and conclusions

The well-accepted model for RF deposits involves formation of a translating redox interface under the influence of oxidizing groundwater flow within a confined, reduced aquifer. Based on ore-stage pyrite signatures from the Bayinwula deposit, we propose for the first time that the complex textural, chemical, and isotopic signatures observed in ore-stage pyrite from RF deposits are a directed result of the dynamic, continuous and cyclical nature of these systems, which generally form from a single fluid. The biogenically driven evolution of sulfate reduction at the redox interface defines their activity cycle, which can be subdivided into four main stages (Fig. 6a-b): (0) the initiation stage, (1) the mineralization stage, (2) the translation stage and (3) the end stage. Upon percolation of oxidizing meteoric water, RF systems become self-sufficient in their development with a repetition of the sequence Stage (1) to (3) for each new influx of oxidizing groundwater, until the reservoir is completely oxidized, or major tectonic uplifts disrupt the system. The cyclical development of roll front deposits is characterized by alternating reducing and oxidizing conditions at the redox interface and transitional open to closed system behavior. In this context, ore-stage pyrite signatures in RF systems reflect the internal dynamic evolution of the biogeochemical processes responsible for sulfate reduction with sulfur derived from a single source, rather than externally driven changes in fluid or sulfur sources through time. The remarkable wide range of their chemical and isotopic signatures recorded during roll front activity cycles originated from BSR-mediated extreme S isotopes and trace elements fractionation.

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Advances in Understanding Hydrothermal Processes 51
Methaniferous active faults and seismic cycle in the
genesis of the Athabasca giant U deposits: conceptual
and numerical investigation

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Abstract. The reduction process of uranyles and the
graphitic faults dynamics are still unconstrained in the
formation of giant unconformity-related uranium deposit
of Athabasca. Previous and new data on graphitic faults
and mineralization are suggestive of paleo-seismicity,
possibly during the mineralizing event. Highlighted by
data from current active methaniferous fault, we
proposed a new model based on seismic cycle for that
mineralization, implying seismic pumping, methane
production and discharge. Numerical modeling shows
that consequences are of first order on paleo-
hydrodynamics.

1 Introduction

The Athabasca Paleo- to Mesoproterozoic basin in
northern Saskatchewan hosts the largest reserves of
high-grade unconformity-related uranium deposits in the
world. The major U deposits from the eastern part of the
basin (e.g. Mc Arthur, Cigare Lake) are located at the
intersection between graphitic shear zones and faults
(GSZF) within the basement and the basal unconformity,
frequently in the apical zone of basement structural highs. The GSZF are inherited from the Trans-
Hudsonian orogen (ca. 1800-1720 Ma) and are localized
where Paleoproterozoic carbonaceous sediments have
been buried, deformed and metamorphosed between
orthogneisses slices during thickening and tectonic
escape at crustal scale (Jeanneret et al., 2016)

Updated metallogenic models postulate that (Fig. 1):
(i) concerning U source-extraction, the mineralizing
fluids were brines, derived from primary brines issued
from seawater evaporation. These brines percolated in
the Trans-Hudsonian basement and leached U from U-
bearing bearing minerals like monazite. The infiltration
of brines was favored by an high-permeability paleo-
weathering horizon at the top of the basement; (ii)
concerning U trap-deposit, driven by free convection
within the basin/basement interface, reduction of
uranyles-bearing brines and precipitation of UO₂
occurred in spatial relation with GSZF. Mineralization
occurred at 120-200°C and under fluid pressure close to
hydrostatic regime below a maximum basin thickness of
about 5-6 km (Pagel, 1975; Hoeve and Sibbald, 1978;
Richard et al., 2013). Duration of a single mineralizing
event is about 0.1-1 Myrs (Richard et al., 2012); (iii)

primary mineralization events were post Athabasca
sedimentation and spanned at least the 1600-1300 Ma
period during uplift, tilting and unroofing of the basin
(Jefferson et al., 2007)

At least two major points still deserve better
understanding: (i) The reducing agent and process for
uranyles is not clearly identified. In fluid inclusions,
traces of methane have been measured (Derome et al.,
2003); methane has been therefore proposed as a
possible reducing agent. Also, whether the reducing
agent, like methane, was derived from “internal”
sources, through the reaction between the infiltrated
brines and a local reducing lithology (graphite precursor,
sulfides... Derome et al., 2005; Fig. 1a) or corresponded
to the upward flow of a deeply-originated “external”
reducing fluid, (Dargent et al., 2015, Fig. 1b), is a matter
of debate (Fig. 1); (ii) Although recognized as a major
exploration guide (e.g. conductors), little is known about
the mechanical behavior and fluid flow dynamics of
GSZF within the basement, particularly during the
mineralizing events.

Here, we address these two points. We compile and
present recent data allowing discussing the dynamics of
the GSZF to better understand their role in the
metallogeny of uranium. In the light of the studies
dedicated to methaniferous active faults, we propose a new conceptual model for the Athabasca-like giant U deposits involving a seismic cycle for the GSZF and the influx of externally-derived methane. Thereafter, we develop numerical hydro-thermal simulations to test this mechanism and discuss the implications on paleohydrodynamics of the mineralizing system.

2 Dynamics of graphitic shear zones and faults (GSZF)

2.1 Overview through geological times

The graphitic shear zones and faults (GSZF) are distributed following an anastomosing pattern of steeply dipping structures within the basement (Jeanneret et al., 2016). Since the Trans-Hudsonian ductile shearing HT metamorphic conditions, the GSZF have had a long-lasting history as they record multiple brittle reactivations (Jefferson et al., 2007; Martz, 2017): (i) during the late Trans-Hudsonian orogen exhumation and uplift. Graphite enrichment of the faults is supposed to have occurred at this stage through precipitation of hydrothermal graphite; (ii) during the Athabasca basin deposition and subsidence (not well documented); (iii) during the basin border “inversion” uplift and unroofing through reverse faulting, a period corresponding to the main mineralization stage (between ca. 1600 and 1300, Alexandre et al., 2007); (iv) during multiple post-Athabasca reactivation increments depicted through late U mineralization and remobilization events (up to 200 Ma at Cigar Lake; Martz, 2017). The successive reactivations of the GSZF resulted in basement highs associated with reverse offsets (Fig. 2a) as frequently observed for major U deposits (e.g. McArthur). Therefore, the GSZF represent weak inherited crustal structures which have been reactivated several times during late and Post Trans-Hudsonian events.

2.2 Structural and textural fingerprint, links with the mineralization

From damage zone to fault core, fault-rocks present nearly all the textural facies produced by cataclastic flow (Fig. 2b). In the graphite-fault core foliated ultracataclasites display rounded clasts in a gouge matrix composed of fine-grained white micas, crushed carbonaceous material, pyrite and quartz (Fig. 2c, d). Timing of that cataclastic flow is attributed to late Trans-Hudsonian brittle reactivation and exhumation near 450°C coeval with hydrothermal graphite precipitation (Martz et al., 2017).

Some GSZF are mineralized, some are not. In a fertile GSZF with various aligned branches, the ore bodies are restricted to few segments. Ore is basically massive and/or disseminated but is also present in veins (Khairallah, 2017) in fault damage zone. Primary ore is abundantly reworked, fractured, and brecciated by sulfides and secondary U deposition.

During the mineralization stage at Cigar Lake, Martz et al. (2018) demonstrate that mineralizing brines percolated within the GSZF by re-opening of previous cracks during a bulk brittle reactivation of the faults. They suggest that during this reactivation, methane traces detected in mineralizing brines fluid inclusions were issued from the release of former Late Trans-Hudsonian volatile-rich fluids responsible for hydrothermal graphite precipitation (from re-opened fluid inclusions or from desorption from minerals surfaces like chlorite). To summarize, GSZF were active during mineralization and part of the cataclastic flow observed (Fig. 2) is coeval with mineralizing brines circulation and methane mobility.

Figure 2. Cross section (A) and fault rocks textures of the Cigar North conductor (Cigar Lake trend, from Khairallah, 2017). Between fractured damage zones, the GSZF core present ultracataclasites (B) and foliated gouges (C) in a white micas matrix (W.m) supporting rounded clasts (D). Former hydrothermal graphite is reworked, crushed and brecciated in faults rocks.

The fact that GSZF were active does not imply that these structures were seismogenic during the mineralization history. Rowe and Griffith (2015) performed a detailed review of fault textures diagnostic of different slip rates over the course of the seismic cycle. Even though no pseudotachylite has been unequivocally identified in drill cores crossing GSZF, the zonation of fault-rocks types, the rounded clasts within a fined-grained matrix, the degree of tectonic comminution in foliated gouge (Fig. 2) are significant of high
(ultracataclasites) and low (protocataclasites) slip rates along active faults. Therefore, activity of GSZF during mineralization might record seismic cycles.

3 Lessons from current seismogenic methane seepage

Fluid venting, gas and specially methane cold seeps in seawater or sediments above active fault systems are known for a long time and currently receive much attention for seismic hazard monitoring/forecasting. Submarine dives and acoustic techniques indicate that seismogenic fault segments release more gas than non-seismic ones (Géli et al., 2008). Moreover, Gasperini et al. (2012) demonstrate that methane seepages are persistent (up to tens of years) after the seismic event. In those studies dealing with the Marmara Sea the methane is microbial in origin and derives from young sediments lying close to the seafloor. However, deeper methane reservoirs participating to seismic methane venting have also been identified (Geersen et al., 2016). In spite of those assessments, the dynamics of methane seeps and generally the fluid venting above active fault still remain unclear relatively to the seismic cycle itself.

4 A new conceptual model

The GSZF in the Athabasca systems were active, likely seismogenic, and in the meantime the locus of methane influx. We thus propose that U deposits of Athabasca may results from fossils seismogenic methane-rich flows along GSZF (Fig. 3).

Actually, the distribution of mineralized bodies itself, restricted to peculiar segments of the GSZF also argues for seismicity. Indeed, if hydrodynamics of the mineralizing brines was likely controlled by large convections cells (Li et al., 2016), this 3D mineralized pattern implies channeling of flow within reactivated high-permeable segments of GSZF. Among other explanations, the seismic failure of loaded segments of an active fault and its associated fluid discharge is a good candidate.

Two main sources of methane can be envisaged: (i) the thick GSZF are vertical fractured structures that can be viewed as reservoirs at depth with residual methane trapped in microcracks and/or adsorbed on phyllicit minerals. In the case permeability increased through seismogenic reactivation of GSZF would be quite similar to the effects of hydraulic fracturing used in gas shale recovery exploitation. Nevertheless, the probability to trap methane from Trans-Hudsonian HT metamorphism to basement uplift and erosion is low, and this scenario may not be favored; (ii) methane may have been produced at depth by downward flows of diagenetic aqueous fluids (not necessary the mineralizing brines themselves even if they represent a good candidate) which reacted with graphite. Production of such reducing agent through consumption of graphite by water has been extensively invoked in metallogenic models. One could argue that textural evidence of graphite consumption are very scarce within and around the U deposits (Martz et al., 2018). Note then that in the present scenario methane generation occurred in the basement much deeper than the actual sites of mineralization. Abrupt permeability increase of GSZF during seismogenic reactivation may have induced seismic pumping of basinal aqueous fluids and subsequent methane production at depth (Fig. 3). This downward flow was possibly favored by pre-existent high-permeability funnels or corridors around GSZF issued from the weathering of the basement before the deposition of the Athabasca sediments.

No structural and textural evidence of fluid overpressure regime has been reported during the U mineralizing stage. Therefore, GSZF might not behave as “classical” seismic valve implying a permeability barrier. Fault-induced pressure gradients (compaction, dilatancy) have been addressed for the U deposits through numerical modeling (Li et al., 2017). Such compaction might induce successive methane pulse during inter-seismic reloading of active segment (Fig. 3).

5 Numerical modeling

We performed transient numerical simulations in order to investigate impacts of such conceptual model on bulk hydrodynamics and thermal pattern. At this stage, the models were not designed to simulate brines penetration within the basement. We used a darcyan hydro-thermal coupling accounting for topography and buoyancy (temperature dependent fluid density) as fluid driving forces. The fault domains are vertical and extend through all the basement thickness. Seism’s along faults and subsequent methane-rich fluid discharges have been simulated through successive and abrupt fluid pressure variations of low amplitude at the basal limit of faults domains. Such single set up allows to roughly...
reproduce successive seismic cycle and to explore how hydrodynamics are modified near the unconformity (Fig. 4). Benchmarks have been run based on the works of Li et al. (2016).

We found that for the cases in which topographic gradient controls the fluid flow in the basin, abrupt methane discharge from faults triggers thermal convection cells which tend to regulate the thermal and fluid flow regime. This result has important implication on brines availability and the extraction of U(VI) from basement through hydrothermal alteration. Indeed, convection cells likely increased the time integrated water/rock ratio and thus increased the mass transfer between fluids and rocks.

Figure 4. 2D Hydro-thermal modeling simulating seismogenic methane discharge near the basin/basement unconformity. Black arrows: fluid velocity (normalized), red lines are streamlines.

References


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Multi-scale advanced argillic footprints on emergent volcanoes: Milos island, Greece

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Abstract. The shallow submarine environment is known to be prospective for precious- and base-metal mineralization (e.g. Eskay Creek). Recently emerged volcanic-hydrothermal systems provide an ideal location to understand the influence of emergence on submarine systems. This study integrates hyperspectral airborne and handheld shortwave infrared (SWIR) spectroscopic techniques, with geological observations and mineralogy (XRD). Mineral mapping on Milos reveals a previously unrecognized alunite-kaolinite topographically controlled steam-heated horizon. We suggest hydrothermal activity was contemporaneous with emergence, and can potentially be used to track the paleo-shoreline. Downhole SWIR data from the shallow submarine Profitis Ilias low-sulfidation Au-Ag deposit displays pervasive alunite-kaolinite overprinting on the original argillic assemblage. Preliminary ratios between the brightness of the ~1.48 µm feature and ~1.76 µm in the SWIR may infer crystallographic order with increasing temperature. We conclude that the shallow submarine environment can be deleterious to ore preservation.

1 Emergent volcanoes

Recently emerged volcanic-hydrothermal systems provide a geologically young and accessible laboratory to study the interaction between the discharge of thermal fluids and landscape evolution as volcanism transitions from submarine to subaerial. Ore forming in the shallow (<1500 m) submarine environment can contain significant Au, Ag, Pb, Zn and Cu (e.g. Eskay Creek). Emergent volcanic islands such as those found in the Aegean and Aeolian arcs, are limited to <500 m and <1000 m water depths respectively. The overlying water column modifies the depth-to-boiling of thermal fluids (e.g. Sherlock et al. 1999), which are subjected to dynamic processes in the steep submarine landscape (Smith et al. 2018).

Remote sensing imagery (SWIR; 1.00-2.43 µm) has demonstrated its effectiveness in the discovery of ore deposits at a range of scales (e.g. Kruse et al. 2012). Distinctive wavelength profiles and major absorption features assist in differentiating groups significant to exploration including clays, sulfates and micas at 2.2-2.3 µm associated with Al-OH, Mg-OH and Fe-OH bonding. Alteration zoning within volcanic-hydrothermal and geothermal systems can infer conduits for thermal fluid flow (e.g. Simpson and Rae 2018) and level of erosion (e.g. Márton et al. 2010).

This study evaluates the use of spectroscopy at different scales (airborne survey, drill core and hand samples) to understand landscape evolution using the advanced argillic footprint on the emerged volcanic edifice of Milos island, Greece.

2 Milos island, Greece

The island of Milos has on-land exposures of young calc-alkaline volcanic activity (3.5 – 0.1 Ma; Fytikas et al. 1986; Stewart & McPhie 2006) associated with a range of mineralization styles and alteration products. It is centrally located within the South Aegean Volcanic Arc (SAVA; Fig. 1) and transitioned to subaerial eruptive activity 2.18 – 1.44 Ma (Fytikas et al. 1986; Stewart & McPhie 2006). The SAVA formed from back-arc extension initiating 35 – 30 Ma (Walcott and White 1998; Jolivet and Faccenna 2000), after the convergence of the African plate beneath the Aegean microplate.

Basement exposures of Cyclades metamorphic core complex is widely overlain by Miocene and Lower Pliocene sediments and late Pliocene volcanism in the form of lava domes, pumice breccia, tuff and dacitic cryptodomes (Fytikas et al. 1986). Intensely altered volcanics result in abundant non-metaliferous deposits on the island including bentonite (Christidis 1995), and kaolinite (Fig. 1).
Pb-(Ag) deposits at Triades-Galana (Marschik et al. 2010). The metallogenic evolution of these varied minerals deposits is summarized in Alfieris et al (2013). Eastern Milos has an active geothermal system with expressions in the shallow submarine and terrestrial environments (Valsami-Jones et al. 2005), where active venting, fumaroles, steam caves and thermal springs are within close vicinity to paleosurfaces.

3 Methods

This study utilizes a high-resolution airborne survey (Specim AISA Eagle/Hawk 970-2450 nm scanner) flown by NERC Airborne Research & Survey Facility (ARSF) in 2012 over the island of Milos (project EM10/02) to map hydrothermally altered rocks by their spectral signature, through measuring the reflected electromagnetic radiation in the short-wave infrared (SWIR) region (1.60-2.43 µm). The dataset is integrated with an airborne LiDAR (Light Detection and Ranging) digital elevation model (DEM) providing a high spatial resolution (2 m) topographic dataset of Milos. Abundant rock exposure combined with the dry summer climate makes Milos an ideal location to mineral map with ENVI’s Spectral Angle Mapper (SAM) tool. The dataset was groundtruthed by field observations, laboratory spectroscopy measurements (ASD) and bulk mineralogy conducted at the British Geological Survey (X-ray diffraction; XRD). Selected samples were further scanned using Corescanner’s in-house Hyperspectral Core Imager II (HCl-2) in Perth, WA.

4 Spectroscopic mapping: alunite-kaolinite

Alunite [KAl₃(SO₄)₂(OH)₆], a sulfate mineral in the advanced argillic assemblage, is found in both volcanic-hydrothermal and geothermal systems (Hedenquist et al. 2000). It forms in a range of environments (Deyell and Dipple 2005) including supergene settings (~30°C) to epithermal conditions: steaming ground (~110-140°C), magmatic steam (200-300°C) and magmatic-hydrothermal fluids (~200-340°C). Alunite has diagnostic absorption features at ~1.76 µm, ~2.16-2.17 µm and a doublet at ~1.44-1.36 µm and ~1.47-1.48 µm in the SWIR part of the electromagnetic spectrum (Kokaly et al. 2017). Wavelength shifts at ~1.76 µm reflect cation substitution between potassium, sodium and calcium (Bishop and Murad 2005).

4.1 Island scale

Combining mineralogy (ASD and XRD), field observations and reflectance from hyperspectral airborne imagery, mineral mapping reveals a widespread alunite-kaolinite alteration on western Milos. The assemblage typically contains heterogeneous amounts of alunite (30-70%), kaolinite (<10%) and silica (30-70%), likely a function of permeability of the volcanic host. The alteration is near-white, fine-grained (<50 µm), friable and pervasively overprints original volcanic fabrics. The horizon varies in thickness (< 10 m), with the base not often observed unless actively quarried. It is often capped by frequently massive but locally laminated silicified volcanics (amorphous silica, opal-C or opal-CT: XRD). When integrating the sample locations with the DEM (Fig. 2), the alunite-kaolinite assemblage is situated ~130-170 meters above current-day sea level (asl).

4.2 Deposit scale

The Profitis Ilias Au-Ag deposit is located on the western peak of Milos island, topographically much higher than the island-wide alunite-kaolinite horizon observed on western Milos (Fig. 2). Crustiform-banded quartz-adularia veins host pyrite, galena, chalcopryite, electrum and native gold, within sericitied rhyolitic lapilli-tuffs and ignimbrites (Kilias et al. 2005). Limited alteration exposures between Profitis Ilias and Chondro Vouno consists of quartz, Na- and K-feldspar, mica and minor kaolinite (XRD). Downhole SWIR data from PD007 located near the peak of Profitis Ilias displays alunite (both K- and Na-) from surface with mica, to depths beyond 70 m (Fig. 3).

4.3 Sample scale

Crystallographic order usually reflects relatively high formation temperature (e.g. Oluwadebi 2015). Selected alunite-bearing samples (Fig. 2) were scanned to determine the ratio between the absorption features at ~1.48 µm and ~1.76 µm. Control samples of known origin (hypogene and supergene) were also scanned using Corescan’s HCl-2 to compare to the blind Milos alunite samples. The depth of ~1.48 µm absorption feature (OH and water) increases with the depth of ~1.76 µm (OH) feature (Fig. 4), which may reflect increased crystallinity with increased absorption. Hypogene control samples exhibit the deepest absorption features, reflecting relatively higher formation temperatures. One sample from Milos lies between the hypogene cluster and the lower temperature samples, identified by ENVI mineral mapping and confirmed by ASD and XRD measurements.
Figure 3. Downhole data for PD007 drillcore (location Fig. 2) from Profitis Ilias Au-Ag deposit on western Milos. Minor alunite Al-OH absorption features observed in the Spectral Geologist. Lithology adapted from Alfieris (2006).

suggesting that this sample may have been closer to an upflow zone or has a magmatic steam origin. Mineral mixing affects the amount of free or bonded water, the width and depth of diagnostic absorption features, resulting in highly variable wavelength profiles.

Figure 4. Linear relationship between the absorption features at ~1.48 and ~1.76 µm. Control samples displayed for comparison to unknown samples from Milos Island. Drainback sample identified from field observations after steaming ground waned.

5 Landscape evolution

Integrating the spectroscopic datasets with XRD, the western alunite-kaolinite horizon (130-170 m asl) is topographically controlled, likely the product of a single hydrothermal event. Alunite infers oxidizing conditions (Marumo and Hattori 1999) indicating formation likely took place from subaerial hydrothermal activity, at or after island emergence, possibly reflecting a paleo-shoreline. Such a horizon overprints the Cuprite low-sulfidation system in Nevada (Swayze et al. 2014) and is indicative of steaming-ground conditions within the vadose zone. The silicified cap located directly above is likely a paleo-piezometric surface, such as the paleowater table. At areas of discharge, the silica displays laminations and evidence of fluid upflow. The relative inversion of the preserved paleowater table above the paleo-vadose zone indicates a preservation bias. The inversion is often explained by burial or significant landscape incision causing the water table to descend, subjecting the rocks above the original water table to steam-heated conditions (Sillitoe 2015). Neither hypotheses are observed on Milos island.

Downhole SWIR data from the Profitis Ilias Au-Ag deposit displays veining pervasively overprinted by a relatively acidic advanced argillic assemblage. Steaming-ground conditions during emergence agree with fluid inclusion data that suggests mineralisation occurred in the shallow submarine environment (Naden et al. 2005). Abundant K-feldspar remaining may indicate the short longevity of the hydrothermal activity, resulting in minimal dissolution of K-feldspar by the acidic steam, or rapid uplift of the mineralised block, from either faulting or magmatism. Depth-to-boiling curves suggest the paleosurface at Profitis Ilias was 200 m above the present summit (Killas et al. 2001). Since the alunite-kaolinite and silica horizons are usually the uppermost unit exposed on western Milos bar magmatic centres, this may suggest 200 m of erosion occurred prior to emergence in the shallow submarine environment. Moreover, the alunite-kaolinite assemblage at Profitis Ilias could be a different steaming-ground event entirely, due to the presence of Na-alunite, assuming no recent tectonic movements. The sodic exchange may indicate higher temperatures (Deyell and Dipple 2005) or cation exchange with seawater, as observed at the Taupo volcanic zone.

Results of the reflectance ratio of the ~1.48 µm and ~1.76 µm features may infer crystallographic order with increasing temperature. Steam-heated alunite-kaolinite horizons form at much lower temperatures (~110-140°C) than the hypogene (~200-340°C) control samples (Fig. 4). Drainback alunite displays the same signature as the original steam-heated counterparts, suggesting alunite is not mobilized in solution, rather transported already once crystallized when hydrothermal activity wanes. The supergene control samples cluster around the steam-heated samples of Milos. This may suggest that the vibrational bonds <140°C and subsequent crystallinity below this temperature are similar and data cannot be further deconvolved.

5.1 Implications of emergence

The steep submarine environment is deleterious to ore preservation as suggested by high erosion observed at Profitis Ilias prior to emergence and overprinting steaming-ground activity. Relative inversion of a widespread alunite-kaolinite horizon suggests exhumation rates of <10 m post-emergence (1.4my). Submarine erosion through mass wasting and collapse of volcanic edifices can be an order of magnitude larger than subaerial volcanic edifices. Hydrothermal activity (i.e. steaming-ground) during or after emergence...
overprints submarine systems, further complicating exploration if remote sensing is used alone.

6 Conclusions

Emergent volcanic-hydrothermal systems display pervasive advanced argillic alteration from steaming-ground activity, related to or directly after emergence and can help to deduce landscape evolution. Shallow submarine ore deposits can be overprinted by steaming-ground activity, such as at the low-sulfidation Au-Ag Profitis Ilias deposit on western Milos. Remote sensing techniques should be integrated with geological observations to put mineralization and alteration into the correct context. Ratios of the reflectance wavelengths of ~1.48 µm and ~1.76 µm in the SWIR may infer crystallographic order with increasing temperature and could offer a faster and cheaper alternative to stable isotopes to decipher the origin of alunite. The shallow submarine environment is deleterious to ore preservation with erosion significant prior to emergence.

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Advances in Understanding Hydrothermal Processes
What does resemble the root zones of serpentinite-hosted black-smokers: insights from an Alpine analogue

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Abstract.
Hydrothermal processes are important processes at Mid-Oceanic Ridges (MOR). However, limited exposure on the seafloor often restricts complete understanding of these complex systems at depth. Fossil hydrothermal systems, such as the Marmorera/Cotschen system preserved in the Platta nappe, SE Swiss Alps, offer insights to decipher the hydrothermal architecture and processes. The serpentinite-hosted Cu-Fe-Ni-Co-Zn mineralization at Marmorera/Cotschen (MCHS) displays a close association with mafic intrusions. Mineralogical and geochemical investigation allowed to highlight an evolution from the fresh serpentinite to Fe-Ca-rich silicates to semi-massive sulphides and then to Cu-rich massive sulphide. Even if the geometry, mineralogy and sulphide geochemistry of the MCHS are close to those of ultramafic-hosted black-smokers (e.g., Rainbow) at the MOR, the lack of chimneys and the systematic association between mineralization and mafic dykes suggests that the MCHS likely corresponds to the root zone of an ultramafic-hosted black-smoker system.

1 Introduction

Extensional ridge settings are an ideal setting for the element mobility related to elevated fluid-rock ratios. Fluid circulation during on-going deformation, leaching of metals from rocks and subsequent deposition from the hydrothermal fluid (source-transport-deposition) lead to numerous reactions such as: i) the serpentinization of the peridotite mantle at (ultra)slow-spreading ridges, ii) the formation of hydrothermal mineralized systems (black and white smokers), and iii) the carbonation of the mantle seafloor (ophi-calcitization). Active hydrothermal vent systems and associated seafloor massive sulphides have been recognized in oceanic settings, worldwide. At the Mid-Atlantic Ridge, these hydrothermal systems have been extensively studied through mineralogical (Hannington et al., 1995; Marques et al., 2006), geochemical (Herzig et al., 1998; Douville et al., 2002) and tectonic studies (McCaig et al., 2007; McCaig et al., 2010). Unfortunately, the remote nature of seafloor deposits often limits understanding of the internal hydrothermal architecture and characterization of the hydrothermal system involved in the metal deposition.

Magma-poor Ocean-Continental Transitions (OCTs) show numerous similarities with slow spreading MOR realms; coupled mantle exhumation along detachment faults, instauration of mafic magmatism and a high geothermal gradient can trigger the development of hydrothermal systems. Hence, magma-poor rifted margins presently outcropping on land are favorable targets for the study of oceanic hydrothermal processes. Here we present geometric, petrological and geochemical information on a fossil serpentinite-hosted hydrothermal system preserved in a fossil hyper-extended Tethys margin preserved in the Platta nappe, Eastern Switzerland. Our first results indicate that it closely resembles the oceanic hydrothermal systems hosted in ultramafic-rock at slow-spreading MOR, with the noticeable advantage to expose the roots of the hydrothermal system.

2 Geological context

The Platta nappe is located in the southeastern part of the Swiss Alps (figure 1). It represents the OCT of the Adriatic margin. During the E-W oriented opening of the Alpine Tethys Ocean during the Jurassic, crustal breakup triggered exhumation of the sub-continental mantle. Mantle exhumation occurred along detachment faults rooting towards the west underneath the European plate (Froitzheim and Manatschal, 1996). Contemporaneous mafic magmatism is related to emplacement of gabbroic bodies and the extrusion of basalt flows and pillow lavas onto the exhumed mantle (Desmurs et al., 2002). U-Pb zircon ages from the gabbros yield 161±1 Ma (Schaltegger et al., 2002). The deposition of the Radiolarian Chert Formation has been
dated between 161 and 147 Ma (Bill et al., 2001) assumed to be the end of the rifting phase. During the Late Cretaceous tectonic inversion, the subduction of the European plate beneath the Adriatic plate induced the closure of the Alpine Tethys Ocean. As a result of its paleogeographic position, the Platta Nappe escaped strong Alpine deformation and metamorphic overprinting. The host rock represents fresh serpentinite, which contains small disseminated euhedral grains (<50 µm) of magnetite and pentlandite. Magnetite grains are generally located at the grain boundaries of the serpentinite, whereas pentlandite grains may occur within these limits (figure 2E). Textural relationships indicate that this mineralization was formed prior to the Cu-rich hydrothermal event, likely during the serpentinization of mantle rocks.

Close to mafic dykes, in the centre of the mineralization, serpentinite is extensively replaced by Cu-rich massive sulphides (Cu-rich MS). This facies has only been encountered at Marmorera but evident mining activity at higher elevations suggests it occurred there as well. Cu-rich sulphides are coarse grained (up to 2 cm) and represent approximately 50% of the total rock volume. The mineralized assemblage comprises chalcopyrite, magnetite, pyrrhotite, isocubanite, pentlandite, and minor sphalerite (figure 2C). Chalcopyrite is the main phase and exhibits typical isocubanite exsolutions. Coarse pentlandite grains display irregular shapes and are commonly surrounded by pyrrhotite. Chalcopyrite and pyrrhotite are often found as inclusions in euhedral magnetite grains suggesting a contemporaneous crystallization of these phases from the same mineralizing fluid. Diopside crystals are abundant within the sulphide mineralization and display equilibrium textures with the surrounding chalcopyrite suggesting that they crystallized contemporaneously.

Cu-rich MS are accompanied by a halo of semi-massive sulphide mineralization (SMS) in the serpentinite, which systematically decreases away from the proximal mineralization. The copper content is lower in this transitional zone, where mineralization is comprised of pyrrhotite, magnetite, pentlandite, and minor chalcopyrite (figure 2D). There, the mineralization forms veins replacing the serpentinite. The relative proportion of pyrrhotite and magnetite inside the veins is highly variable. Chalcopyrite is commonly oxidized and in places a supergene assemblage of bornite and covellite replaces chalcopyrite.

Away from the mafic dykes, a network of veins crosscut the serpentinites. They define a typical stockwork structure composed of ilvaite, andradite and diopside (Fe-Ca-rich stockwork). The proportion of minerals composing the stockwork is variable. Locally the silicates almost completely replace the former serpentinite and the proportion of ilvaite increases. These silicates can either surround blebs of sulphides and magnetite or can be crosscut by sulphide veins suggesting they precipitated synchronously from the same hydrothermal event. On the vertical scale, the size of the Fe-Ca-silicates stockwork becomes more important at Cotschen. Locally, the serpentinite along some mafic intrusions are barren and develop a whitish alteration due to actinolite enrichment.

At Snake Pit (upper part of the MCHS), the metallogenic sequence appears different. Disseminated

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Image 1. (A) Simplified geological map of western Alps and Apennines (B) Geological map of the Platta nappe (Coltat et al., 2019, modified after Desmurs et al., 2002)
euhedral pyrite rimmed by pyrrhotite, pentlandite, chalcopyrite and sphalerite is crosscut by late calcite veins. Some pyrite grains appear zoned.

3.3 Trace element signatures of the mineralized phases

Electron microprobe analyses have been carried out on both representative sulphides (chalcopyrite, pyrrhotite, pentlandite) and oxides (magnetite) sampled at different elevations throughout the mineralized profile. Pentlandite grains from the various mineralized units at Marmorera (Cu-rich MS, SMS and disseminated sulphides in the fresh serpentinite) display specific Ni and Co contents (figure 3A). Early pentlandite from the fresh serpentinite displays the highest Ni and the lowest Co contents (36.1% and 1.7% respectively) giving an average Co/Ni ratio of 0.05. In the semi-massive sulphides, pentlandite displays an enrichment in Co up to 3.6% and a decrease in the Ni content with mean concentration about 22.5% giving a Co/Ni ratio about 0.15. These Ni contents are low for pentlandite grains and cannot be explained only by lattice substitution of Ni by Co. However, these pentlandite show typical oxidation features resulting in their transformation into violarite and Fe oxi-hydroxides (figure 2D). In the Cu-rich MS replacing serpentinates, pentlandite displays the highest Co concentrations (up to 15.3%) and homogenous Ni contents at approximately 25.5%. The average Co/Ni ratio for these pentlandite grains is 0.58.

Magnetite grains also display a specific distribution of Si and Mg from the Cu-rich MS to the disseminated mineralization in the fresh serpentinite. Indeed, in the disseminated mineralization, Si+Mg contents range from 0.7 to 1.8% whereas they range from 0.07 to 0.5% and from 0.2 to 0.4% in the semi-massive sulphides and Cu-rich MS respectively.

Pyrite grains have Ni and Co concentrations ranging from 1164 to 2678 ppm and from 1227 to 2947 ppm respectively. Although most of the grains have concentrations below the detection limits, these concentrations seem similar to those described in ultramafic-hosted hydrothermal systems at the Mid-Atlantic Ridge (figure 3B, Marques et al., 2006).

4 Conclusions

In the Platta nappe, Swiss Alps, a fossil hydrothermal system hosted in serpentines has been characterized. Mineralogically, it resembles those associated with slow-spreading MORs, notably the Rainbow site along the
The overall geometry of the Marmorera-Cotschen hydrothermal system and the differences observed between the MCHS and present-day systems (dykes, lack of chimneys, lower size of the mineralization) suggests that the MCHS likely corresponds to the feeding zone of present-day systems.

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References


Constraints on sub-seafloor hydrothermal mineralising processes and metal fluxes using deep sulphide-rich scales from the Reykjanes geothermal system, Iceland

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Abstract. Sulphide-rich scales precipitated in wells of the seawater-dominated Reykjanes geothermal system on the Mid-Atlantic Ridge (MAR), Iceland are directly comparable to mineralisation in active seafloor hydrothermal systems. Geochemical profiles from 2.7 km depth to low-temperature silica-rich surface discharge show consistent temperature-dependent enrichment and depletion trends under well-constrained conditions. Copper, Zn, Cd, Co, Te, Ni, Mo, Sn, Fe and S are enriched at higher pressures and temperatures in the deepest scales, and Zn, Bi, Cu, Pb, Ag, As, Sb, Ga, Hg, and Tl are enriched at lower temperature and pressures near surface. Cobalt, Se, Cd, Zn, Cu, and Au have bimodal distributions and are hosted by different mineralogical assemblages at higher- and lower-temperature and pressures. Boiling and destabilisation of metal-bearing aqueous complexes are the dominant controls on sub-seafloor deposition of most metals (particularly Au), although some (e.g., Cu and Se) may be transported in the vapour phase. At least three quarters of the total Reykjanes metal budget is precipitated downhole and indicates a significant proportion of metals will be precipitated in the sub-seafloor of other boiling systems in the oceans. Extreme enrichment of Au, Ag and Pb further highlights potential metal accumulation and enrichment in the deep geothermal reservoirs.

1 Introduction

Knowledge of the behaviour of trace metals in submarine hydrothermal systems is limited by the difficulties of directly sampling the high-temperature upflow. Compositions of venting fluids have been extensively studied (e.g., Von Damm 1990), but little is known about metal behaviour in the deepest part of systems at >2 km where metals and reduced sulphur concentrations in end-member high-temperature (~400°C) hydrothermal fluids are highest (Hannington et al. 2016). Except in a few cases where underlying stockwork zones have been drilled, in-situ subseafloor geochemical profiles of actively-forming massive sulphide deposits have not been possible. Questions remain about metal contents in deeper parts of hydrothermal systems, and how much of the metal load may be deposited at depth or in upflow zones before ever reaching the seafloor.

2 Geology

2.1 Reykjanes geothermal system

The high-temperature Reykjanes geothermal field is located on the subaerial continuation of the slow-spreading MAR on the southwestern tip of Iceland and is the only seawater-dominated, basalt-hosted energy production site globally (Fig. 1). At least 37 wells have been drilled to a maximum depth of 3028 m drawing on a high-temperature reservoir fluid of modified seawater directly analogous to vent fluids in modern black smoker systems (Hardardóttir et al. 2009).

At the time of sampling, the reservoir fluid was boiling in every well from the surface to depths of ~1500 m, below which the system is liquid-dominated (one-phase) and temperatures of 280°C to 380°C to a minimum depth of 2.5 km (Sigurdsson 2012). Wells are classified according to the fluid pressure (P) at the wellhead: high pressure (HP; 32-50 bar), medium pressure (MP; 28-32 bar), and low pressure (LP; 25-28 bar). Supercritical fluids have recently been measured in permeable layers below the current production zone (426°C and 340 bar; Fridleifsson et al. 2017). Metal-rich sulphide scales precipitate in closed production pipes as a response to temperature and pressure changes during artificial well management (Fig. 1).

2.2 Mineralogy

Down-hole and surface scales were sampled from five different zones, each with well-defined conditions: I) below the boiling zone in wells RN-10, RN-22, and RN-; II) within the deep part of the boiling zone, from 1504 m to 1085 m in RN-10 and 1064 m to 1088 m in RN-22; III) in the central part of the boiling zone from 904 m to the wellhead in RN-10, from 669 m to 141 m in RN-22, and then from the wellhead to the first orifice plate where
Figure 1. Schematic profile of sulphide scaling across the high-pressure well RN-10 in the Reykjanes geothermal field from 1.8 km depth to the Grey Lagoon (not to scale). Circles indicate two-phase fluid. Minerals: grey = sphalerite, yellow = chalcopyrite, pink = bornite. FFCV = fluid flow control valve. All photomicrographs contain numerous <5 µm electrum (el) inclusions similar to Figure 2. Roman numerals indicate scale group locations (see text).

pressure drops to ~22 bar; IV) in the surface boiling zone from the first OP and FFCV to ~40 m downstream; V) in distal surface pipes from the separation station to the Grey Lagoon.

The most common sulphides in Group I below the boiling zone are dark brown to black sphalerite and wurtzite. Zn-sulphides exhibit a variety of textures, most commonly as lath-shaped crystals up to 3 mm in size and as fine-grained dendrites, often with a preferred alignment or growth direction. Chalcopyrite is also associated with bornite and/ or covellite and complexly intergrown with the host Zn-sulphide at a micron scale, giving the sphalerite and wurtzite a mottled appearance (Fig. 1). Trace galena, pyrrhotite, pyrite, and magnetite are also present. Numerous inclusions of electrum occur associated with sphalerite and chalcopyrite. Above the onset of boiling, Group II scales are dominated by massive, dendritic and skeletal Zn-sulphides.

Chalcopyrite abundance increases upwell and bornite and digenite are the most abundant Cu-sulphides between ~1130 to 1085 m depth (well RN-10), coinciding with abundant magnetite and electrum (Fig. 2). Sphalerite is the dominant sulphide in Group III scales with similar textures to Groups I and II. All sulphides become distinctly finer-grained towards the surface OP (Fig. 1). Minor wurtzite, bornite and rare pyrite and pyrrhotite are present in some wells. Abundant electrum is associated with chalcopyrite and discrete <5µm clusters of silver are intergrown with sphalerite and bornite at shallow downhole depths (RN-22; Hardardóttir et al. 2010).

Figure 2. Gold-rich electrum associated with chalcopyrite and sphalerite at 1098 m below surface in well RN-10 (location shown in Fig. 1). Bulk assays comprise 72.5 ppm Au and 85.0 ppm Ag.

Group IV scales are dominated by sphalerite and minor wurtzite intergrown with digenite and bornite within fine-grained silica. Zn sulphides textures are similar to Group I, II, and III scales but much finer-grained. Chalcopyrite is much less abundant, and bornite and digenite are the most common Cu-sulphides, particularly on the OP and FFCV. In MP and LP wells, fine-grained galena is intergrown with Cu-(Zn)-sulphides on OPs and FFCVs. Discrete grains of electrum (<1-2 µm) occur with trace chalcopyrite where Au concentrations exceed ~250 ppm; concentrations reach a maximum of 948 ppm on the FFCV cone in HP wells. Late covellite coats scales immediately after the OP in some MP wells. Downstream of the OP, sulphide abundance relative to silica decreases in all wells, however scales in HP wells ~32 m downstream still contain significant sphalerite. Silica-rich Group V precipitates beyond the separator station contain sphalerite as trace disseminations or as discrete layers.

3 Hydrothermal mineralisation

3.1 Controls on ore mineral distributions

The Reykjanes system can be viewed as mostly a closed system (particularly in surface pipes) as there is limited or no influx of cold seawater reacting with hot
hydrothermal fluid. Scaling is mainly caused by pressure (and temperature) decrease due to boiling during power production. Precipitation in the surface pipes is also caused by large pressure changes across the OP and, to a much lesser extent, by conductive cooling of hydrothermal fluids. The main ore minerals (sphalerite and wurtzite, chalcopyrite and bornite, galena, native silver and electrum) are precipitated due to abrupt changes in temperature and pH during phase separation. High degrees of supersaturation are indicated by mineral textures such as hopper crystals and dendrites and shows that precipitation conditions are far from equilibrium.

There is a strong temperature-dependent zonation of the major ore minerals in the Reykjanes system. Zinc is precipitated as the hexagonal polymorph wurtzite at higher temperatures and mainly as the cubic polymorph sphalerite at and below ~250°C. Abundant Zn-sulphides are deposited at the onset of boiling in the Reykjanes system. Chalcopyrite precipitation occurs mainly at temperatures between 280° to 320°C, coincident with the onset of boiling, and boiling cause further temperature decrease and precipitation. In the HP wells, more of the Cu remains in solution up to the FFCVs where the largest pressure and temperature decrease in the boiling zone occurs, and the temperature drop results in scales with the highest Cu concentrations (mainly as Cu-sulphides; Group IV). In many wells, unordered intermediate Cu-Fe-S solid solutions are produced as a result of rapid quenching during well management (Hardardóttir et al. 2010). Because the Au is likely transported as aqueous sulphur complexes, any processes that cause a loss of reduced sulphur, such as sulphide precipitation, boiling, or fluid mixing will destabilize the Au complexes (Seward et al. 2014). Boiling is the dominant mechanism, and the abundance of Au (i.e., electrum) in the wells increases dramatically with the onset of boiling. Whereas Ag-chloride complexes predominate at aquifer temperatures, at boiling temperatures, Ag may also be partly transported as aqueous sulphur complexes, like Au (e.g., AgHS₂⁻).

3.2 Controls on trace element distributions

The compositions of the scales can be divided into two main groups: those enriched in elements deposited at high pressures and temperatures at depth in the wells (Fe, Mn, Zn, Cd, Cu, Co, Ni, Sn, Se, Te, V, Ni, Mo, W), and those enriched in elements deposited at lower temperatures and pressures in the surface pipes (Pb, Ag, Sb, Bi, As, Hg, Ga). Consistent enrichments and depletions of the trace elements, according to temperature-dependent solubilities, are similar to those observed in seafloor chimneys and in ancient volcanogenic massive sulphide (VMS) deposits. Scales formed at the highest temperatures below the boiling zone are particularly enriched in Fe, Mn, Co, and Ni, as well as Zn, Cd, and Sn and represent mineral scales that precipitated directly from unboiled fluids. The latter are also highly enriched in scales throughout the boiling zone and on the FFCV and OP. Copper, Se, and Te are mostly enriched in scales from the lower (higher-temperature) part of the boiling zone, but also where flashing has been induced in the surface pipes at the FFCV. Lead, Ag, Sb, (±Bi) are most enriched in the upper (lower-temperature) part of the boiling zone and immediately downstream of the FFCV. Arsenic and Hg are enriched in scales even farther downstream. Other trace elements, such as Mo, Ga, V, and Cr are enriched in the deepest scales and also in silica-rich precipitates in the surface pipes, but are not present in abundance in the boiling zone. This behaviour reflects different aqueous complexing at different temperatures and precipitation in different mineral phases in different parts of the system (e.g., sulphides and oxides at depth; clays and other silicates in the downstream precipitates). Importantly, some trace elements, such as Se and Cu, are enriched in both the deep, high-temperature scales and in some distal scales downstream of the boiling. This may be attributed to a combination of transport in either the liquid of the vapour phase and can produce unexpectedly high, distal concentrations of trace elements normally considered to be of a high temperature affinity.

4 Quantification of Reykjanes metal fluxes

The documented major and trace element associations in the Reykjanes system are directly comparable to trace element distributions in modern sub-seafloor seafloor massive sulphide (SMS) mineralisation, as

![Comparison of selected elements using the average bulk geochemistry for all Reykjanes scale samples (n = 129) versus average bulk geochemical data for high-temperature sulphide (black smoker) samples from analogous basalt-hosted MAR deposits (n = 103; GEOMAR unpublished database). Elements plotting above the 1:1 line are enriched in Reykjanes scales, and elements plotting below the 1:1 line are enriched in MAR samples. The darker the marker symbol is the higher the relative enrichment. Au, Ag, and Pb are significantly enriched in Reykjanes scales. Ba is significantly enriched in MAR samples due to seawater mixing.](image-url)
observed in the large, actively-forming TAG deposit (e.g., Grant et al. 2018).

Flashing of the high-pressure fluids also promotes deposition of some elements in the scales that otherwise might have been expected to remain in solution as aqueous complexes stable at lower temperatures (e.g., Zn, Cd, Au), particularly at the OP where massive changes in concentrations of Ag, As, Sb, and Hg illustrate the efficiency of deposition by flash boiling. Similar enhanced deposition of metals has been noted in boiling seafloor hydrothermal vents (e.g., Gartman et al. 2018).

A calculated estimated sulphide mass accumulation rate of ~91 t/yr for the Reykjanes geothermal system is comparable to large basalt-hosted seafloor hydrothermal systems elsewhere on the MAR, and corresponds to metal flux rates of 27 t/yr Zn, 9 t/yr Cu, 3 t/yr Pb, 0.4 t/yr Ag, and 16 kg/yr Au. The majority of siderophile elements (e.g., Mn, Cd, Ni, Zn) are enriched in the Reykjanes system compared to black smokers, in part because of dilution by silica and sulphate in the seafloor vents, however, Fe, Co, Ga, Ge, In, and Mo are relatively depleted, implying a significant difference in fluid or source-rock concentrations. Very large enrichments of Au, Ag and Pb in the scales (e.g., 948 ppm Au, 23,200 ppm Ag, and 18.8 wt.% Pb) versus average concentrations in black smoker chimneys (Fig. 3) show that some elements are preferentially deposited in boiling systems.

The major differences in the trace metal concentrations between the Reykjanes scales and black smokers reflect the important role of boiling as a depositional mechanism; however, this cannot account for some of the high metal concentrations, as previously observed by Hardardóttir et al. (2009). Hannington et al. (2016) recently suggested that some metal enrichment may be due to accumulation of the metals in the deep geothermal reservoir prior to discharge into the hydrothermal system – a process that has not yet been observed in active seafloor hydrothermal systems. This is supported by the significant enrichment of Au, Ag and Pb in Reykjanes scales versus MAR black smokers (Fig. 3), analogous modern mafic-dominated SMS deposits, and ancient mafic-dominated VMS deposits.

At least three quarters of the Reykjanes metal budget may be deposited at depth or in the upflow zones of the boiling system. Discovery of a supercritical fluid reservoir at 4.5 km depth at Reykjanes (Fridleifsson et al. 2017), and the accumulation of Au and potentially Ag and Pb in deep reservoirs (Hannington et al. 2016, and this study) further highlights the potential for metal enrichment and accumulation in the deep parts of the geothermal system.

The results of this study are among the first to document sub-seafloor mineralisation directly associated with boiling of end-member, primary metal-rich hydrothermal fluids in an active hydrothermal system and provides an important baseline against which similar conditions of primary mineralisation trends can be recognised in modern and ancient seafloor hydrothermal systems.

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References


Diagenesis of clastic sulfide sediments from the Semenov-3 hydrothermal field, mid-Atlantic ridge

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Abstract. The sulfide breccias from the Semenov-3 hydrothermal field (Mid-Atlantic Ridge) are composed of marcasite–pyrite clasts enclosed in barite–sulfide–quartz matrix. Pyrite, marcasite, and quartz are accompanied by barite, chalcopyrite, hematite, jarosite, bornite, sphalerite, pyrrhotite, covellite, HgS, rutile, chlorite and plagioclase. The mineralization is of hydrothermal and diageneric origin. The colloform and fine-crystalline pyrite–marcasite clasts are hydrothermal. The coarse-crystalline pyrite and marcasite, as well as pyrite framboids, ovoids and nodules, are authigenic. Hydrothermal chalcopyrite occurs as (i) subhedral crystals in the matrix and volcanic clasts, (ii) intergrowths with sphalerite and bornite and (iii) anhedral inclusions in marcasite–pyrite clasts. Authigenic chalcopyrite occurs (i) in authigenic pyrite together with pyrrhotite and sphalerite and as (ii) anhedral aggregates in the matrix and (iii) reniform aggregates after marcasite.

1 Introduction

Most studies of oceanic hydrothermal fields concern the sulfides from smoker chimneys, diffusers, massive or colloform ores, which are the result of medium- to high-temperature hydrothermal processes. Little attention has been paid to the products of erosion of massive sulfide (MS) bodies (clastic sulfide sediments), although some MS bodies host significant amounts of clastic sulfides, e.g., Bent Hill, Middle Valley of the North Juan de Fuca Ridge (Goodfellow et al. 1993). Fossil MS deposits may be completely composed of clastic layers produced by vigorous erosion of massive sulfide mounds (Ohmoto 1996; Prokin and Buslaev 1998; Maslennikov 2012; Tornos et al. 2015). Here, we investigate the formation of authigenic minerals in pyrite-rich sulfide breccias from the Semenov-3 hydrothermal field (Mid-Atlantic Ridge) and illustrate the differences between primary hydrothermal and authigenic minerals.

2 Geological background

The Semenov-3 hydrothermal sulfide field is part of a giant eponymous hydrothermal sulfide cluster located at 13°30’ N on the Mid-Atlantic Ridge (Beltenev et al. 2007). The cluster consists of four inactive (1, 3, 4 and 5) and one active (2) hydrothermal fields (Fig. 1). The Semenov-3 field (13° 30.70’ N, 44° 55.00’ W) is located on the northeastern slope of the seamount at depths of 2400–2600 m and is associated with altered basalts (Fig. 1). Sulfide breccias were recovered using dredge station 30L284 (Beltenev et al. 2007). They were studied macroscopically on-board and by reflected light at the Institute of Mineralogy (IMin UB RAS), Miass (Russia).

3 Results

Sulfide breccias are composed of angular clasts of marcasite–pyrite aggregates up to 10 cm across and rare angular fragments of strongly altered volcanic rocks ~1 cm in size (Fig. 2a). The breccia matrix mostly consists of quartz accompanied by small (<1 cm) sulfide aggregates similar to large clasts and newly formed sulfides. The major minerals are pyrite, marcasite, and quartz, which are accompanied by barite and rare chalcopyrite, hematite, jarosite, bornite, sphalerite, pyrrhotite, covellite, HgS, rutile, chlorite and plagioclase. Marcasite–pyrite clasts exhibit colloiform, concentric-zonal, massive, radial and porous structures (Fig. 2b). Colloform and concentric-zonal clasts consist of aggregates of dendritic, fine-grained and fine-crystalline pyrite and marcasite. Locally, the clasts contain small inclusions of chalcopyrite, sphalerite and barite. In the breccia matrix, pyrite and marcasite occur as small clasts or as individual crystals and their aggregates; pyrite also forms framboids, ovoids and nodules (Fig. 2c, 2d). Pyrite framboids or their coalesced aggregates are locally overgrown by crystalline pyrite.

Lens-like, ovoid or round porous fine-crystalline pyrite aggregates are composed of small (1 to 3 µm) cubic crystals, often with round areas interpreted as former pyrite framboids (Fig. 2c). Rare nodular pyrite aggregates are composed of two domains: a strongly porous central inclusion of barite and quartz and a more compact exterior, which is made up of small crystals of pyrite and less abundant marcasite, with fine (<5 µm) inclusions of sphalerite, chalcopyrite, and pyrrhotite. Coarse-crystalline pyrite is observed as euhedral to subhedral crystals and their aggregates in both the breccia matrix and within the pores of fine-grained clasts. Coarse-crystalline pyrite replaces clasts of fine-grained pyrite and is host to inclusions of pyrrhotite, chalcopyrite, sphalerite, and quartz. Some pyrite crystals contain “shadows” of earlier barite crystals.

Chalcopyrite in sulfide breccias occurs as (i) small subhedral to euhedral crystals and their aggregates in the breccia matrix and altered volcanic clasts, (ii) individual acicular crystals and their radial aggregates in the breccia matrix (Fig. 3a); (iii) zonal crystalline intergrowths with sphalerite in quartz; (iv) small round grains and their aggregates in the breccia matrix, which...
Figure 1. Geological scheme of the Semenov hydrothermal cluster in the Central Atlantic (a), simplified after unpublished PMGE open-file reports.

Figure 2. Sulfide breccias from the Semenov-3 hydrothermal field: a. combination of clasts of various textures and structures (on-board photograph); b. fragment of colloform marcasite-pyrite aggregate and authigenic pyrite crystals; c. ovoid (former frambooidal) pyrite aggregate; d. pyrite nodule with porous center and crystalline exterior with inclusions of other sulfides and barite (indicated by arrows). Photo b–d, reflected light; pya, clastic pyrite; mc, clastic marcasite; pya, authigenic pyrite; mc, authigenic marcasite; qtz, quartz.
Figure 3. Morphological varieties of accessory minerals in sulfide breccias from the Semenov-3 hydrothermal field: a. radial aggregate of acicular chalcopyrite crystals in quartz; b. small bornite grain with chalcopyrite rim in quartz; c. pyrrhotite-chalcopyrite-sphalerite assemblage in crystalline pyrite; d. reniform chalcopyrite after radial marcasite aggregate (etched by vapors of a HNO₃ + HCl mixture; black dots are areas of LA ICP MS analysis). Reflected light: ccp, chalcopyrite; bn, bornite; sp, sphalerite; po, pyrrhotite.

replace and overgrow bornite from the rims, and rims around bornite and lamella inside it (Fig. 3b); (v) rare inclusions in marcasite-pyrite clasts; (vi) intergrowths with pyrrhotite and sphalerite inside crystalline pyrite crystals (Fig. 3c); (vii) relatively large anhedral aggregates in the breccia matrix; and (viii) single reniform aggregates, which show radial structure after etching indicating possible replacement of radial marcasite aggregates abundant in sulfide breccias (Fig. 3d).

Bornite occurs as small (~10 μm) isometric grains in the breccia cement and quartz rims around pyrite crystals and is associated with chalcopyrite. Covellite replaces chalcopyrite and bornite. Pyrrhotite is observed as small (<10 μm) anhedral grains or intergrowths with chalcopyrite and sphalerite, which fill the pores inside crystalline pyrite, and as rare inclusions in crystalline chalcopyrite. Sphalerite forms crystalline aggregates in assemblages with crystalline chalcopyrite (see above) or subhedral grains up to 10 μm in crystalline pyrite.

Hematite is found as globules ~20 μm in size in the quartz rims around pyrite clasts or as specular crystals up to 70 μm long and ~5 μm wide in the breccia cement. A mineral with approximate composition HgS was found as tiny (~1 μm in size) round grains in chalcopyrite and pyrite crystals.

Quartz composes most of the breccia matrix also overgrowing the pyrite clasts and the barite crystals. Tabular barite crystals up to 1 mm in size fill fractures in the sulfide clasts, are present in the breccia matrix and form druses up to 0.5 cm thick. Jarosite replaces the marcasite-pyrite clasts. Rutile, chlorite and plagioclase were found as inclusions (~20 μm in size) in the coarser-crystalline pyrite.

4 Discussion

In the Semenov-3 sulfide breccias, the sulfide clasts have only occasional contacts, lack any sorting or bedding and show a variety of textures typical of primary hydrothermal ores. According to the morphological analysis of the massive sulfide bodies developed for the Uralian MS deposits (Maslennikov 2012), these features are characteristic of proximal sulfide breccias, which have been transported for some distance from the place of erosion. In well-preserved sulfide mounds from the Urals (e.g., Yaman-Kasy, Safyanovskoe, Dergamish deposits), these breccias occur at a distance of at least ~25 m from the center of the interpreted sulfide mounds.

Pyrite and marcasite in the sulfide breccias represent a variety of morphological aggregates. Their clastic nature is mainly indicated by cutting-off of their textural
pattern and zoning, as well as by the similarity of their internal structure with that of larger sulfide clasts.

The sulfide breccias underwent a series of lithification processes (Fairbridge 1967). The presence of some indicative morphological varieties of pyrite is evidence for their diagenetic origin, e.g., framboidal pyrite (Love 1967). The next stage of the diagenetic process, when framboïds coalesce and are recrystallized, is most likely marked by the formation of ovoid fine-crystalline (former framboïdal) pyrite aggregates and by the replacement of framboïds by crystalline pyrite. Nodular pyrite, which is characterized by a porous core and a polycrystalline exterior, and subhedral to euhedral coarse-crystalline pyrite were formed during late diagenesis.

The diverse morphology and mineral assemblages of accessory minerals are also indicative of their clastic and authigenic origin. Subhedral to euhedral isometric chalcopyrite crystals in the breccia matrix and altered volcanic clasts could represent the fragments of Cu-rich stringer–disseminated mineralization from high-temperature feeder zones of the sulfide mound (cf., Fouquet et al. 1993). Chalcopyrite inclusions in pyrite–marcasite clasts are most likely of primary hydrothermal origin. The acicular chalcopyrite crystals and zoned crystalline intergrowths with sphalerite and bornite resemble the fragments of black smoker chimneys (Maslennikov et al. 2017). In contrast to primary hydrothermal chalcopyrite, the authigenic phase is observed as inclusions in authigenic coarse-crystalline pyrite,anhedral aggregates in the breccia matrix, and pseudomorphic reniform aggregates after radial marcasite.

Sphalerite and pyrrhotite associated with hydrothermal chalcopyrite are hydrothermal in origin, whereas those found in authigenic coarse-crystalline pyrite, are authigenic. The euhedral morphology of the hematite crystals, its presence in the breccia cement and assemblage with quartz most likely indicate its authigenic origin. The fact that crystalline hematite is never in contact with authigenic chalcopyrite, bornite, pyrrhotite and sphalerite indicates its probable crystallization during late diagenesis.

Barite, which is associated with pyrite–marcasite clasts, is most likely hydrothermal in origin. The well-formed barite laths in the breccia matrix likely formed during early diagenesis were further replaced by late diagenetic coarse-crystalline pyrite.

5 Conclusions

Diagenetic transformation of hydrothermal sulfide clasts into a lithified rock has resulted in the formation of various authigenic mineral assemblages: framboïidal pyrite, ovoid fine-crystalline (former framboïdal), nodular and coarse-crystalline pyrite; zoned bornite–chalcopyrite grains; pyrrhotite–sphalerite–chalcopyrite inclusions in coarse-crystalline pyrite; specular and globular hematite, and HgS in authigenic chalcopyrite and pyrite.

Recognition of clastic Cu- and Zn-rich mineral assemblages in sulfide breccias indicates the erosion of primary Cu–Zn sulfides within the Semenov-3 hydrothermal field, including a black smoker complex, which have not yet been discovered.

Morphological similarities between pyrite nodules of sulfide breccias from the Semenov-3 hydrothermal field and fossil MS deposits point to a common diagenetic process, which occur in sediments composed of clasts of variable size, from coarse-clastic breccias to fine-clastic sediments (cf., Maslennikov et al. 2019).

The discovery of an authigenic HgS phase in sulfide breccias indicates possible environmental hazards of seafloor sulfide sediments similar to eroded pyrite-rich ores and primary massive sulfides.

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References


4D history of the Nimbus VHMS ore deposit in the Yilgarn Craton, Western Australia: a multi-disciplinary approach.

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Abstract. The Nimbus Ag-Zn-(Au) deposit is located in the Kalgoorlie Terrane of the Yilgarn Craton and has been recently presented as the first reported case of an older episode of VHMS mineralisation associated with c. 2705 Ma plume magmatism in the Eastern Goldfields Superterrane. However, the absence of typical indicators of syn-volcanism prevents Nimbus from being unambiguously classified as VHMS-replacement type. A more detailed understanding of the timing of mineralisation could test and improve exploration models for this type of deposit in the Kalgoorlie Terrane.

We present a detailed multi-disciplinary study to constrain the processes involved in the evolution of Nimbus and generate a 4D evolutionary model of the Nimbus VHMS system. Re-Os ages for the first sulphide phase provides a maximum age for the ore formation. Alteration is constrained by Ar-Ar dating of altered plagioclase and U-Pb SHRIMP dating of hydrothermal monazites. Pb-isotopes in galena track chemical variations in the sulphides over time and help support the observed ages. The result is the detection of a strong late hydrothermal alteration event at c. 2640 Ma, which indicates that the mineralisation at Nimbus could be significantly younger than the formation of the host sequence.

1 Introduction

Volcanic-hosted massive sulphide (VHMS) ores are relatively common in a wide variety of extensional environments ranging in age from 3.55 Ga to modern deposits and are exceptional sources of Cu, Zn, Pb, Au and Ag. The Nimbus Ag-Zn-(Au) deposit is located near the margin between the Kalgoorlie and Kurnalpi Terranes in the Eastern Goldfields Superterrane (EGS) in the Yilgarn craton, Western Australia (Fig. 1). This deposit was formed through the replacement of the host stratigraphy associated with c. 2705 Ma plume magmatism of the Kambalda Sequence (Hollis et al. 2017).

The establishment of the 2.7 Ga plume stratigraphy in the EGS as a prospective target for comparable VHMS deposits (Hollis et al. 2017) would open up new areas for VHMS exploration in the EGS. For that reason, it is important to comprehend the timing of mineralisation in the Nimbus deposit for the future of VHMS exploration in Western Australia.

The age of the mineralisation at Nimbus is still unclear due to the lack of strong textural and stratigraphical evidence of syn-volcanism.

Figure 1. Location of the Nimbus deposit. Also indicated are the low-Ca Four Mile Hill granite (magmatic age from Nelson 1997) and Golden Mile gold mine (lamprophyre age from McNaughton et al. 2005).

We use here comprehensive studies of multiple isotope systems such as Re-Os dating of massive sulphides, Ar-Ar dating of altered plagioclase, U-Pb dating of hydrothermal monazites and Pb-Pb isotopes in galena to develop a 4D model of the Nimbus deposit with time constraints for mineralisation and alteration in
addition to the previously established age of volcanism. Our findings have a direct and significant impact on assessing the prospectivity of the ~2.7 Ga plume sequence in the EGS.

2 Geological context

The Nimbus deposit lies in the Kalgoorlie Terrane, in the footwall of the Mt. Monger Fault, part of the Ockerburry Fault System that separates the Kalgoorlie and Kurnalpi Terranes (Fig. 1). The host stratigraphy at the Nimbus deposit consists of stacked dacitic rocks with hyaloclastite-rich margins, intruded by mafic sills that were interpreted as broadly coeval (Hollis et al. 2017). Both lithologies exhibit peperitic relationships with less common carbonaceous mudstones. These rocks are geographically superimposed by a sedimentary sequence of polymict conglomerates with carbonaceous matrix interpreted to represent pulsing debris flow units from a subaerial shoreline into a deeper anoxic basin (Hildrew 2015; Hollis et al. 2017).

Two dacite samples from Nimbus were dated at 2703 ± 5 and 2702 ± 4 Ma, indicating that the volcanism is part of the Kambalda Sequence of the Kalgoorlie Terrane, which is further supported by a predominant mantle oxygen isotope signature of zircon from this unit ($\delta^{18}$O = +6.03 ± 0.23%) (Hollis et al. 2017).

The Kambalda Sequence is contemporaneous to localized high-T metamorphism in the eastern Yilgarn. This high-T phase is followed by a regional metamorphism stage, with temperatures ranging between 300 and 550 °C. The main regional metamorphism is locally overprinted by localized hydrothermal events (M3b) associated with the emplacement of significant volumes of low-Ca granites in the Kalgoorlie Terrane (Czarnota et al. 2010). Multiple Au-mineralisation events are recorded during the late M3b metamorphic stage, including evidences of gold mineralisation associated with lamprophyre emplacement at the world-renowned Giant Golden Mile Deposit, Kalgoorlie, approximately 10 km west of the Nimbus deposit (McNaughton et al. 2005).

3 Results

3.1 Re-Os in pyrite

In the Nimbus deposit, primary Ag-Zn mineralisation occurs as a series of stacked, steeply plunging and subparallel lenses (Hollis et al. 2017).

Caruso et al. (2018) classified the sulphide occurrences at Nimbus according to mineral association, texture and host lithology. The sulphides were subdivided into 7 main occurrences from older to younger: colloform pyrite, barren pyrite, polymetallic ore, arsenopyrite-rich veins, stringer sulphides, disseminated sulphides and siltstone-hosted pyrite.

Six samples of colloform pyrite from a single 15cm interval (NBDH035 136.10m to 136.25m) yield an isochron with a Model 1 age of 2719 ± 45 Ma and MSWD of 0.55. Re and Os concentrations range from 5.8 to 8.0 ppb and 0.2 to 0.3 ppb, respectively. All samples have highly radiogenic Os contents (>29), which diminishes the precision of the isochrons and initial $^{187}$Os/$^{188}$Os.

3.2 Pb-isotopes in galena

Two types of galenas were analysed for Pb isotopic composition including galenas from the polymetallic ore phase, proximal to the mineralisation (ore galenas), and galenas from disseminated or stringer phases (late galenas).

Ore galenas form a cluster with an average value of 13.5291 ± 0.0007 for $^{206}$Pb/$^{204}$Pb, 14.7168 ± 0.0007 for $^{207}$Pb/$^{204}$Pb and 33.3433 ± 0.0021 for $^{208}$Pb/$^{204}$Pb. A Pb evolution curve from a single source was determined considering the average value calculated from the cluster of ore galenas as the initial Pb. Evolution from this composition is modelled using $\mu$ = 7.19 (Stacey and Kramers 1975) and is shown from 2.7 to 2.6 Ga in figure 2. Late galenas have more radiogenic Pb when compared to ore galenas and show both a slight $^{207}$Pb/$^{204}$Pb enrichment and depletion relative to the calculated growth curve. These reflect: (a) galena formation at a later time, (b) Pb-sources from an older component, most probably the host sediment, and in-situ U-decay.

Figure 2. Pb modelling of double-spike galenas analyses from Nimbus. Stacey and Kramers (1975) growth curve with initial Pb-Pb at the ore cluster at 2.7 Ga. U-decay in closed system represents the 2.7 Ga isochron with initial Pb-Pb value at the ore cluster.

3.3 $^{40}$Ar/$^{39}$Ar geochronology

Alteration ages were obtained by $^{40}$Ar/$^{39}$Ar dating of different types of dacites, both proximal and distal to the mineralisation that contained plagioclase crystals with 30% or more of its structure replaced by sericite.

The best quality analyses yielded plateau ages of 2659 ± 22 and Ma 2630 ± 10 Ma. Other significant results include a plateau age of 2606 ± 5 Ma with approximately 70% of $^{39}$Ar released included in the calculation and a mini-plateau age at 2626 ± 8 Ma.
3.4 U-Pb of hydrothermal monazites

A number of monazite crystals of size ranging from approximately 20 to 60 µm were observed in thin section from the polymict (meta) conglomerate with carbonaceous matrix from the sedimentary sequence of rocks that overlie the mineralized dacites. Monazites in such rocks are in most cases either detrital of igneous origins or post-depositional hydrothermal/metamorphic. The monazites crystals appear to be syn- to late-foliation, therefore their crystallization age is inferred to be coeval to the main deformation/metamorphic event that affected these sedimentary rocks. Concordant measurements produced a concordia age of 2627±16 with MSWD = 0.73 and probability = 0.67.

4 Discussion

Considering that the colloform pyrite exhibit textures which indicate insignificant modification by later hydrothermal or metamorphic overprint, the age obtained for these pyrites of 2719 ± 45 Ma indicates the time of precipitation of these sulphides. The colloform pyrites show textural and chemical evidence of syn-volcanic/syn-sedimentary precipitation which is further demonstrated by the similarity between the age obtained in this study and the reported age of volcanism (Hollis et al. 2017 c. 2700 Ma). The precipitation of the colloform pyrites can be interpreted as a maximum age for the mineralisation emplacement, as they represent the earliest form of sulphide and have been interpreted to act as a seal to the hydrothermal system (Caruso et al. 2018).

The existence of multiple sources of lead in late galenas, specially the involvement of a younger source of more radiogenic lead, suggests remobilization of metals and potentially a second mineralisation episode related to a late alteration event.

Alteration ages obtained by ⁴⁰Ar/³⁹Ar dating of sericite or sericitized plagioclase are commonly slightly younger than the mineralisation ages in VHMS systems, when the alteration is the product of the same process that results in the mineralisation (e.g., Tessalina et al. 2017; Barrote et al. in prep). However, in the case of the Nimbus deposit the alteration ages obtained are much younger than the magmatic age of the dacites and are unlikely to be related to the volcanism of the host rocks.

The U-Pb age of hydrothermal/metamorphic monazites from the polymict conglomerates of the sedimentary sequence that overlie the mineralized rocks further supports the existence of a significant alteration event much younger to the volcanic system. This age also suggests that the peak alteration/metamorphism is at ~2630 Ma. This age is broadly coeval with the emplacement of low-Ca granites (Fig. 3).

The classification of the Nimbus deposit as a replacement type VHMS is dependent on identifying features that demonstrate the temporal link between volcanic activity and mineralisation.

Previous models have questioned the classification of Nimbus as a VHMS deposit (Henderson et al. 2012), suggesting a structural control to the mineralisation at Nimbus, hosted within faults and shear zones. Although the model proposed by these authors is not the most accepted for the Nimbus deposit, the observation of a younger alteration event associated with the main foliation could be linked to a potential late structural control to the mineralisation in this deposit.

Therefore, in light of our discoveries there are two possible evolutionary models for Nimbus: (1) Nimbus is a replacement-type VHMS deposit formed in a mantle plume context, the age of the main mineralisation is close to 2700 Ma, slightly younger than the dacites, but resulting from the same magmatic activity. The late alteration simply modifies the pre-existent ore and overprints the previous VHMS-related alteration. (2) The mineralisation at Nimbus postdates the dacitic volcanism and colloform pyrite precipitation, is fault-hosted and is associated with metamorphic and hydrothermal fluids (~2660-2620 Ma), broadly coeval with the main metamorphic and Au-mineralisation events in the Yilgarn Craton (Czarnota et al. 2010).
and metallogenic history of the Nimbus deposit. The younger alteration may account for the absence of alteration fronts in this deposit. The recognition of post-volcanic processes in the early stages of exploration planning may avoid incorrect geological interpretations, not only at Nimbus, but in other unusual VHMS deposits worldwide.

5 Conclusions

A multi-disciplinary approach to understanding ore deposits allows for better constraints on the timing and processes involved in VHMS mineral systems. That is especially true when dealing with the less conventional VHMS-replacement type deposits, where the syn-volcanic nature of ore formation is not always clear.

Our observations regarding the Nimbus deposit evolutionary model indicate a strong late alteration overprint. This alteration is possibly linked to the mineralisation itself, in which case the search for similar deposits to Nimbus should focus on areas of intense hydrothermal alteration of similar age.

Alternatively, the ore formation could be linked to volcanism and the late alteration is only responsible for remobilizing metals. In this case there is potential for sub-mineralisation to be found at Nimbus by understanding the effect of the younger fluid to the main ore.

Direct Re-Os dating of sulphide phases does not offer enough age precision to resolve the mineralisation timing issues. However, further multi-disciplinary studies could be applied to better constrain the relative age of the polymetallic ore phases, including trace element determinations on different sulphides and the expansion of high-resolution Pb-isotope studies to incorporate other Pb-bearing minerals, among others.

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References


Identifying deep hydrothermal fluids that leach metals from the oceanic crust and generate seafloor VMS deposits

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Abstract. Metasomatic alteration of the deep oceanic crust by heated seawater produces a variety of hydrothermal–metamorphic mineral assemblages including spilites and epidotes. Epidotes have been proposed as markers of deep upflow in hydrothermal convection cells and as source rocks for the metals in seafloor VMS deposits. Whereas spilitization is attributed to fluid of seawater salinity, the salinity of epidotizing fluids is debated. In addition, the metal contents of the fluids have been constrained by experiments and observations of vent fluids, but no direct analyses are available.

We have analyzed primary fluid inclusions in spilites and epidotes in the Semail ophiolite (Oman). The results confirm that both fluids have salinity close to that of seawater (2.6–4.1 wt.% dissolved solids). The fluid inclusion data reveal that the alteration occurred over a range of P–T conditions: 170–430 °C for spilitization and 235–400 °C for epidotization, all at hydrostatic pressures of 27–50 MPa. Laser-ablation-ICP-MS analyses show that the spilitizing fluid is enriched in Fe, Cu and Zn, whereas the epidotizing fluid is metal-depleted. Therefore, we view the spilitizing fluid rather than the epidotizing fluid as the major carrier of metals to black-smoker sulfide deposits on the seafloor.

1 Introduction

Seafloor massive sulfide (VMS) deposits in basaltic lavas are widely considered to be products of metal-leaching from the oceanic crust by circulating hot seawater. Metasomatic alteration of the basaltas at greenschist-facies P–T conditions produces spilites (rocks consisting of chlorite + albite + quartz ± actinolite ± epidote) at low to moderate water/rock ratios, and locally epidotes (rocks consisting of epidote + quartz + titanite + Fe-oxides) at very high water/rock ratios (Weber and Diamond 2019). Richardson et al. (1987) proposed that epidotes mark deep upflow zones in the hydrothermal convection cells and that they are the source rocks for metals in VMS deposits. However, Jowitt et al. (2012) showed that spilites may be just as depleted in metals as the epidotes. Constraints on the metal contents of sub-seafloor fluids are available from experimental studies and observations of seafloor vents (e.g. Seyfried and Ding 1995), but no metal analyses of deep spilitizing or epidotizing fluids have been available so far to test the plausibility of the source-rock proposal. Another point of contention is whether the fluid that produces epidotes has seawater salinity or if it is a hypersaline brine, as argued from fluid inclusion studies in plagiogranites (Juteau et al. 2000).

To clarify these issues we have investigated fluid inclusions in hydrothermally altered basaltic dikes and lavas as well as plagiogranites in the Semail ophiolite, Oman. The salinity of the inclusions was determined by microthermometry and the major- and trace-element compositions were analyzed by laser-ablation-ICP-MS analyses. By comparing the results to hydrothermal vent fluids at mid-oceanic ridges we are able to identify which of the hydrothermal fluids likely feed the black smokers and generates seafloor VMS deposits.

2 Geological setting

The oceanic crust that is observable today in the Semail ophiolite formed above a nascent subduction zone in the Mid-Cretaceous southeastern Tethys Ocean (Belgrano and Diamond 2019, and references therein). The upper crustal sequence of the ophiolite consists of a basaltic sheeted dike complex covered by axial (spreading ridge) and off-axial basaltic volcanic units which host late off-axial gabbros, diorites and plagiogranites. Numerous VMS deposits occur at various stratigraphic levels in the volcanic sequence (Gilgen et al. 2014), and spilitite and epidosite alteration can be found in all stratigraphic positions of the Semail crust, from the basal gabbros through the overlying sheeted dikes to the upper pillow lavas (Gilgen et al. 2016).

3 Results of fluid inclusion analyses

3.1 Fluid inclusion petrography

The analyzed samples from plagiogranites contain three stages of fluid-inclusion-bearing quartz: (1) magmatic-hydrothermal quartz in miarolitic cavities which is locally overgrown by (2) hydrothermal quartz belonging to a spilitite alteration assemblage (accompanied by albite, actinolite and chlorite), which is in turn occasionally overgrown by (3) hydrothermal quartz belonging to an epidosite assemblage. Cathodoluminescence (CL) in the quartz crystals helps discriminate between light-grey magmatic and magmatic–hydrothermal-stage quartz, medium-grey spilitite-stage quartz and dark-grey to almost black epidosite-stage quartz (Fig. 1b).

Early crystal growth zones in magmatic quartz hosts devitrified melt inclusions consisting of several solid phases + aqueous liquid + vapor. Later overgrowths of magmatic–hydrothermal quartz contain aqueous liquid +
vapor + halite (LVH) inclusions with coexisting vapor-rich inclusions. The variation of phase proportions between inclusions in coeval assemblages shows that these hypersaline brine + vapor inclusions were trapped heterogeneously, i.e. from a two-phase fluid.

Figure 1. a. Field, b. CL and c. transmitted light microphotographs of hydrothermal quartz in plagiogranite. d. Magmatic quartz hosts liquid–vapor–halite fluid inclusions. e. Later hydrothermal spilite with primary aqueous liquid-vapor inclusions. f. Latest epidote in an epidosite assemblage consisting of epidote + hydrothermal quartz hosting primary aqueous liquid–vapor inclusions.

The fluid that precipitated the spilitic mineral assemblage is trapped as inclusions in the second-stage hydrothermal quartz within plagiogranites, and also within quartz in amygdales of pillow lavas (Fig. 1b and e). The inclusions consist of liquid (L) and vapor (V) with uniform phase proportions in individual inclusion assemblages, implying entrapment from a homogeneous (one-phase) fluid.

The epidotizing fluid, which is trapped as fluid inclusions in epidote + quartz, has salinities from 2.4–4.0 wt.% NaCl$_{eq}$ as calculated from $T_m$(Ice) values of -1.4 to -2.4 °C. Homogenization (LV→L) temperatures vary from 130–140 and 160–180 °C in quartz within amygdales and cavity fillings in pillow lavas, and from 380–390 °C in spilitic-altered plagiogranites.

3.2 Fluid inclusion microthermometry

Upon heating, the LVH inclusions in the magmatic-hydrothermal quartz homogenize either by (a) vapor disappearance after halite melting ($T_h$ (LV→L)) or (b) by halite dissolution after vapor disappearance ($T_h$ = $T_m$(H)). In case (a) halite melts in the range of 210–285 °C, implying salinities from 32–38 wt.% NaCl$_{eq}$, and the vapor phase disappears from 400–410 °C in individual fluid inclusion assemblages. In case (b), in contrast, $T_h$(LVH→LH) = 231–273 °C and $T_m$(H) = 355–445 °C, which implies fluid salinities from 44–52 wt.% NaCl$_{eq}$. In both cases, V-rich inclusions homogenize to the V phase. Freezing of the V-rich inclusions shows final ice melting temperatures ($T_m$(Ice)) from -2.2 to -1.4 °C, equivalent to 2.4–3.7 wt.% NaCl$_{eq}$.

Fluid inclusions trapped in spilite quartz show $T_m$(Ice) over small ranges within individual fluid inclusion assemblages, varying from -1.4 to -2.4 °C and corresponding to 2.4–4.0 wt.% NaCl$_{eq}$. Homogenization (LV→L) temperatures vary from 130–140 and 160–180 °C in quartz within amygdales and cavity fillings in pillow lavas, and from 380–390 °C in spilitic-altered plagiogranites.

The epidotizing fluid, which is trapped as fluid inclusions in epidote + quartz, has salinities from 2.4–4.0 wt.% NaCl$_{eq}$ as calculated from $T_m$(Ice) values of -1.4 to -2.4 °C. Homogenization temperatures are tightly clustered within fluid inclusion assemblages, with values of 220–315 °C in epidotized sheeted dikes and pillow lavas, and 365–370 °C in epidotized plagiogranites.

3.3 Fluid inclusion analysis by laser-ablation-ICP-MS

Element concentration ratios were determined by laser-ablation-ICP-MS analysis of individual fluid inclusions (method of Pettke et al. 2012) in petrographically well-defined inclusion assemblages in spilitic-stage, epidotite-stage and magmatic-hydrothermal-stage quartz. The detected elements are displayed in figure 2 in units of molality, calculated from the known fluid salinities. To facilitate comparison with the various fluids shown in figure 2, the extremely high concentrations of elements in the hypersaline brines have been normalized to seawater chlorinity (0.57 mol/kg$_{H_2O}$). The metals Fe, Cu and Zn were below detection in the epidotite fluid and so their analytical limits of detection (LOD) are shown in figure 2 to provide maximum possible concentrations.

3.4 P-T conditions of hydrothermal alteration

Since the splittizing and epidotizing fluids were originally trapped as homogeneous liquids in the fluid inclusions, their homogenization temperatures set minimum limits on trapping temperatures ($T_{trap}$). Estimates of the true trapping temperatures were obtained by reconstructing the fluid pressure at the time of fluid entrapment, based on a pressure–temperature ($P$–$T$) plot of the fluid isochores. Fluid pressure is assumed to have been
hydrostatic, as the overlying rocks are porous and permeable. The values of fluid pressure were calculated from the sub-seafloor depth of the rocks during alteration (0.9–1.8 km; Table 3 in Gilgen et al. 2016) and from the assumed thickness of overlying seawater (2000–2500 m, as typical of modern oceanic ridges). Owing mostly to the wide $T_1$ ranges of the fluid inclusions from different localities, the resulting trapping conditions of the spilitic fluid spread from 140–430 °C and 27–50 MPa. Similarly, the epidotisitic fluid is estimated to have been trapped at 235–400 °C and 27–50 MPa.

4 Discussion

4.1 Fluid origins

In all the samples we studied the hypersaline brine is petrographically of magmatic-hydrothermal origin. This fluid is thus interpreted to represent saline magmatic water exsolved from the crystallizing plagiogranites at pressures low enough (27–50 MPa) to induce unmixing into hypersaline brine + vapor. The inferred magmatic origin of the brine is consistent with the ratios of its non-volatile elements (especially K, Mn, Zn, Rb and Sr with respect to Na; grey curve in figure 2), which are notably higher than those of the spiliting or epidotizing fluids. The hypersaline brine is therefore not the product of boiling of chemically modified seawater near the cooling plagiogranites.

In contrast, the spilites and epidotisites evidently formed from homogeneous aqueous liquids with salinities (2.4–4.0 wt.% NaCl eq) in the range of modern seawater (3.1–3.8 wt.% total dissolved solids, cf. Levitus et al. 1994). They thus represent modified seawater that maintained its chlorinity while changing its cation ratios during circulation through the basaltic crust.

4.2 Chemical evolution from seawater to vent fluid

The multi-element plot in figure 2 demonstrates that recharging seawater (light blue curve) decreases its Mg concentration by more than two orders of magnitude and increases its Ca content by one order of magnitude as it converts its basaltic wall rocks to chlorite- and albite-bearing spilites (dark blue curve). Also Mn, Fe, Cu and Zn become significantly enriched along the path from seawater to spilitic fluid. The epidotisitic fluid shows an even lower Mg concentration and a higher Ca/Mg ratio (green curve), consistent with its replacement of the spilitic assemblage by epidote and quartz.

In the epidotisitic fluid, the concentration of VMS-type ore metals Fe, Cu and Zn and also Mn (often deposited distally to VMS mounds) are all at least an order of magnitude lower than in the spilitic fluid. This is because the epidotisites form by metasomatic replacement of spilites that have already been depleted in metals. For this reason we view the spilitic fluid, rather than the epidotisitic fluid, as the essential carrier of metals to form seafloor vents VMS deposits. The vent fluids themselves (red curve) have very low Fe, Cu and Zn contents, because they are sampled above the black smokers following loss of their metals as sulfide precipitates at and below the seafloor.

5 Conclusions

We conclude that any genetic model of VMS deposits in basalt-dominated systems should consider the spilitic fluid, which is formed by interaction of basalt with seawater under greenschist-facies conditions, as the ore-bearing fluid. Although epidotisites may indeed represent focused upflow zones in hydrothermal circulation cells, the fluid from which they form appears to be too poor in metals to form massive sulfide deposits upon venting at the seafloor.

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Same, same, but different: recent advances in our understanding of modern seafloor hydrothermal systems

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Abstract. Seafloor massive sulfides (SMS) have become a target of increased global exploration activity due to their presumed resource potential. Recent investigations have shown that these occurrences are more variable than previously thought and that this variability is not necessarily reflected in analogous volcanic massive sulfide deposits preserved in the ancient rock record. The geological differences strongly affect the fluid composition, mineralogy as well as the major and trace element geochemistry of the deposits. New technologies are helping us to define their third dimension and to understand the subseafloor processes taking place, but also shed light on their fate after hydrothermal activity ceases and seafloor weathering and oxidation take over.

1 Introduction

Seafloor massive sulfides (SMS) are occurrences of metal-bearing minerals that form on and below the seabed from the interaction of heated seawater, magmatic volatiles and a large variety of source rocks. These SMS deposits have become a target of increased global exploration activity (seven exploration licenses granted by the International Seabed Authority by the end of 2018) due to their presumed resource potential. We know that SMS deposits form as a consequence of seawater circulating through hot oceanic crust deep beneath the seabed with possible contributions from magmatic volatiles and metals. This usually occurs at volcanically active tectonic plate margins including mid-ocean ridges, back-arc spreading centres, and volcanic arcs (Hannington et al. 2005). Over the past few years scientific research and state-funded exploration activities have identified significant variations in the simple convection cell deposit model.

2 Geological setting

By early 2019, about 400 sulfide-bearing or high-temperature hydrothermal sites have been found throughout the modern global ocean, indicating the widespread occurrence of this type of seafloor mineralization. Deposits are commonly basalt-hosted at typical Mid-Ocean Ridges (Fig. 1), but over one third is related to subduction zones, where they are associated with back-arc spreading centres (in either continental or oceanic crust), arc volcanoes or rifted arc. The majority of the occurrences (73%) are active black-smoker type high-temperature vent fields with only about one quarter being inactive. This is still a reflection of the exploration methods that are being used and does not represent the true distribution at the seafloor that is expected to contain far more inactive occurrences than active ones. This has been confirmed in recent years as more inactive sites have been found due to a slow change in methodology used for exploration.

Figure 1. Variability of the tectonic setting of SMS occurrences on the modern seafloor (N=400; GEOMAR). BA = back-arc; MOR = Mid-Ocean Ridge; UM = ultramafic-hosted.

Until 1984, it was widely accepted that hydrothermal activity on slow-spreading ridges would be rare because of the limited input of near sea-floor magmatic heat. However, since the discovery of the TAG hydrothermal...
field on the Mid-Atlantic Ridge, it became apparent that the slow-spreading ridges may host some of the largest hydrothermal systems (Hannington et al. 2011). Recent increased exploration activities along those slow- to ultraslow-spreading ridges, commonly by state parties, result in a growing number of known SMS occurrences (Fig. 2). Within this setting, hydrothermal fluid flow is strongly controlled by tectonic processes and especially deeply-penetrating faults that favor circulation of seawater to considerable depths and, in some cases, to some distance off-axis. This concept is supported by recent discoveries in the Indian and the Atlantic Ocean, where many of the sites are unusually large and enriched in metals (German et al. 2016).

The diversity of the regional and local geological settings in which SMS occurrences are found also has increased. Detailed investigations of areas with exposure of mantle rocks (oceanic core complexes), for instance, have shown that hydrothermal activity is widespread on these core complexes. They largely form along slow- and ultra-slow spreading mid-ocean ridges, but are also observed in back-arc basins (Anderson et al. 2017). This is an important addition to geological models for the formation of seafloor massive sulfide occurrences. It also indicates that off-axis magmatism in areas of presumably low-magma budget is still capable of forming seafloor massive sulfide deposits. Recent investigations along slow- to intermediate-spreading ridges have shown important occurrences of active venting over 14 kilometers away from the neo-volcanic zone. This has important implications, not only for our understanding of hydrothermal processes at spreading centers, but also for the exploration of seafloor massive sulfide occurrences, the global distribution of associated chemosynthetic faunal communities and how they colonize new areas. It is now clear that research programs and exploration must consider larger areas of the modern seafloor than previously thought.

SMS deposits are 3-dimensional bodies and drilling is still rarely conducted on the modern seafloor. Over the past few years, a number of drilling and coring campaigns have investigated the interior of various occurrences (Petersen et al. 2014, Murton et al. 2019. Additionally, new geophysical methodologies and tools, including seismic and electromagnetic systems, are currently being developed and used to image the subseafloor of SMS occurrences. It is clear that subseafloor processes such as replacement and the formation of siliceous cap rocks within the overlying sediments are important processes for the preservation potential of SMS deposit as observed in ancient VMS deposits in the geological record.

3 Mapping the Seafloor

Another recent advance in the understanding of SMS deposits comes from new efforts to truly map the geology of the modern seafloor. Such geological maps are fundamental for systematic exploration because the depicted features (lithology, composition, structural relations, age) correspond to diagnostic elements in genetic models of the mineral deposit types (e.g., metal sources, transport pathways, and depositional traps). Regional geological maps of the oceans are rudimentary and to a large part limited to the sedimentary cover and the ages of the oceanic crust as defined by paleomagnetic studies. A step change is further required in the density of sampling for regional groundtruthing. Spatial and temporal variability in the composition of the crust, especially in the geologically more complex and metal endowed arc/back arc regions such as the SW Pacific, is significant, yet samples that are needed to identify rock types are often collected 10s or even 100s of kilometres apart or only along the recent spreading centres, neglecting the majority of the crust surface.

4 Hydrothermal processes

Advances in analytics such as laser-ablation ICP-MS and unconventional metal isotopes have a resulted in a multitude of papers describing the trace element composition of the major sulfide minerals, the distribution of trace metals within deposits, and the variable influence of magmatic contributions and their impact on metal endowment. Further to the overall regional geological control on metal endowment, a strong influence of even the local geological settings (here proximity to the arc) has been shown in studies of the vent fluid and sulfide composition of several closely spaced vent fields in the Lau Basin (Evans et al. 2017) Sampling of deep, boiling and precious-metal-rich hydrothermal fluids at the Reykjanes peninsula, Iceland (Hannington et al. 2016) and of gold nanoparticles in boiling vents in the West Pacific (Gartman et al. 2018) have shown that precious metals are likely enriched in the deeper part of the hydrothermal convection cells and that transport of colloidal particles could be important in hydrothermal systems. This has clearly changed our understanding of SMS formation.

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Epidosite alteration of oceanic crust: quantifying water–rock ratios with reactive-transport modeling

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Abstract. Epidosites (basalts altered to epidote + quartz with minor titanite and Fe-oxide) have been proposed to form along the deep segments of hydrothermal upwelling zones in oceanic crust, possibly leading up to VMS deposits at the seafloor. During epidosite alteration of the precursor rock, Na and Mg are leached completely and Ca is added. This metasomatic exchange requires substantial fluid flux but the exact amount is unclear. We use reactive-transport modeling to calculate the mass of fluid per mass of rock (water–rock ratio) needed to form complete epidosites. Our simulated mineralogical changes during epidosite alteration closely match changes measured in samples from the Oman ophiolite, supporting the validity of our approach. Calculated water–rock ratios for epidosite alteration range from 1200 up to as high as 80,000, strongly depending on the reactant rock composition. Such high water–rock ratios support the proposal that epidosites form along focused flow paths of discharging hydrothermal fluid.

1 Introduction

It is well known that seawater infiltrates the basaltic oceanic crust in response to thermal gradients above shallow intrusions in extensional tectonic environments (e.g. Alt 1995; Fig. 1). The circulating seawater reacts with its wall rocks, leading to substantial chemical changes in the crustal rocks as well as to the formation of volcanogenic massive sulfide (VMS) deposits at seafloor vents. Understanding the formation of VMS deposits is therefore intimately linked to understanding the processes of hydrothermal alteration below the seafloor (e.g. Alabaster and Pearce 1985).

Two main types of hydrothermal alteration are recognized in seafloor and ophiolite studies. First, regionally distributed “spilite” alteration pervasively overprints most of the upper crust, due to recharge of seawater, which leaches Ca from the rocks and enriches them in Na and Mg. Greenschist-facies spilites are thus characterized by albite and chlorite with minor Fe-oxides, titanite, epidote, quartz and actinolite. Relict magmatic augite is common. The second, less abundant alteration type is “epidosite”, consisting of epidote and quartz with minor titanite and Fe-oxides. These rocks have been found in modern oceanic crust, albeit rarely, in both MOR (Quon and Ehlers 1963) and forearc settings (Banerjee et al. 2000). Epidosites are also commonly exposed over large areas in ophiolites, e.g. in the sheeted dyke complex of the Troodos ophiolite in Cyprus (Schiffman et al. 1987) and in the extrusive sequence in the Semail ophiolite in Oman (Gilgen et al. 2016). To form epidosites from spilites, Na and Mg need to be entirely leached and Ca needs to be added to the rock, i.e. the spilitization reaction is reversed. Epidosites have therefore been assumed to be the fossil upflow zones of hydrothermal convection cells (Richardson et al. 1987). The low concentrations of base metals such as Cu and Zn led to the conclusion that epidosites could be the source rocks for metals deposited in VMS deposits (Richardson et al. 1987). This would imply that the presence of deep-seated epidosites in ophiolite terranes may be an indicator of the presence of overlying VMS deposits. On the other hand, Jowitt et al. (2012) showed that spilites may be depleted in Cu and Zn too, thus the significance of epidosites for VMS formation remains enigmatic.

One of the parameters required to test the source-rock model is the amount of water that is required to create epidosites. The mass of fluid per mass of rock (water–rock or W/R ratio) has been estimated by different methods. Kawahata et al. (2001) calculated a W/R ratio of 22 based on the change in Sr isotopes during alteration. Seyfried et al. (1988) calculated a much higher W/R ratio of 1040, based on the experimentally determined Mg-leaching capacity of hot, seawater-derived fluids. Bettison-Varga et al. (1995) calculated a similar W/R ratio of up to 1250 with batch-reaction thermodynamic modeling.

Our goal was to calculate the W/R ratio needed to form an epidosite by using reactive-transport modeling based on the thermodynamic properties of minerals and aqueous solutes. We assess the effect that different precursor rock compositions have on the product epidosite and on the W/R ratio. We verify our predicted precursor-to-epidosite reaction paths by comparing them to the mineralogy of reaction fronts in real epidosites from the Semail Ophiolite.

2 Samples and element maps

Samples were collected in the volcanic sequence of the Semail ophiolite. Each consists of an alteration halo around an epidosite nodule, which contains both spilite (reactant) and epidosite (product) zones. Thin-sections were cut perpendicular to reaction fronts to analyze mineralogical changes during epidosite alteration. Element concentration maps of thin-sections were acquired by electron-microprobe and minerals were assigned to each measured spot using XMapTools (Lanari et al. 2018).
3 Reactive-transport modeling

3.1 Model setup

We used the fully coupled reactive-transport code Flotran (Lichtner 2007) to perform numerical simulations based on the thermodynamic database supctr92 (Johnson et al. 1992). The epidote zone was simplified as a 1D flow-through domain composed of 10 sequential cells of 1 cm length each, somewhat larger than the width of observed reaction zones (e.g. Fig. 2). The cells were initially assigned the composition and mineralogy of a porous spilite rock and saturated with an aqueous solution in equilibrium with the spilite. The simulations were run at constant temperature (350 °C) and pressure (50 MPa), corresponding to representative formation conditions of the epidote mineral assemblage determined from fluid inclusion analysis (Richter and Diamond 2019). A fluid pre-equilibrated with the epidote mineral assemblage enters the model at a constant flow rate from one side and exits on the other side, thereby continuously replacing spent fluid with fresh fluid. Flow is held at a very low rate to assure local equilibrium is reached at the scale of individual cells within the model domain. The W/R ratio is calculated as the time-integrated mass of fluid that passed through the model at the time of complete epidote formation divided by the initial mass of spilite. Unfortunately, we cannot model the presence of titanite in our simulations due to the absence of thermodynamic data in the supctr92 database.

3.2 Composition of the epidotizing fluid

We used three different sources to estimate the chemical properties of the fluid in equilibrium with epidote. Firstly, total chloride concentration and the Na/Ca molal ratio were obtained from analyses of fluid inclusions in epidotes (Richter and Diamond 2019). Secondly, the pH of the fluid was constrained to be around 5, due to the narrow stability range of the epidote mineral assemblage. Thirdly, knowing the above parameters allows us to calculate total aqueous Al, Fe and Si concentrations from mutual equilibrium with quartz, epidote and hematite.

3.3 Composition of the reactant rock

Most spilites from the extrusive sequence in the Semail ophiolite can be classified in two mineralogical groups. One is composed of hydrothermal albite, chlorite, titanite, hematite and variable amounts of quartz and epidote. The other additionally contains relict magmatic augite. We discuss only two examples here, but the relative mineral abundances vary within each group.

4 Results

The mineral map of an epidote reaction front is shown in Fig. 2a. The epidote assemblage replaces a spilite composed of albite, augite, quartz, chlorite, epidote, hematite and titanite. Calcite is interpreted to have precipitated during or after ophiolite obduction and is therefore ignored in the modeling. Albite is clearly consumed first, followed by chlorite and later augite. The reactive-transport simulation with a comparable spilite reactant assemblage is shown in Fig. 2b. Complete epidote alteration would only be achieved at a W/R ratio of about 80,000, although complete alteration is clearly not reached in the real sample, as abundant relict augite is still present in the epidote zone.

We also show the results of a simulation with an augite-free spilite assemblage in Fig. 2c. The sequence of alteration is comparable to the spilite in Fig. 2b. Albite is consumed first, followed by chlorite. The calculated W/R ratio at complete epidote alteration is only about 1200 for this example, much lower than the sample shown in Fig. 2b.

5 Discussion

Our calculated W/R ratio needed to form complete epidotes can be as high as 80,000. This extreme W/R ratio, calculated for augite-rich samples is almost two orders of magnitude higher than previously assumed in the literature. However, for augite-free samples W/R ratios can be as low as 1200, which are comparable to the ratios calculated by Seyfried et al. (1988) and Bettison-Varga et al. (1995).
Figure 2. (a) Mineral map of epidosite reaction front in thin-section. Epidosite replaces augite-bearing spilite from right to left. (b) Mineral evolution with increasing W/R ratio during epidosite alteration calculated in reactive-transport simulation. (c) Calculated mineral evolution during epidosite alteration of augite-free spilite.
The close match between observed intermediate reaction products in thin-section and reactive-transport simulations (Fig. 2a & 2b) supports the validity of our reactive-transport simulations. Albite is replaced readily during epidote alteration, whereas the W/R ratio required to completely destroy chlorite is much higher. The reason is the low Mg concentration in the epidote-equilibrated fluid, which has only seawater chlorinity for complexing. If augite is present, a much higher W/R ratio is required to achieve complete epidote alteration. The fact that augite solubility is very low at epidote-forming conditions is confirmed by the reaction front in the thin-section in Fig. 2a. While albite and chlorite are leached readily, augite is mostly untouched by alteration, showing only minimal dissolution features towards the epidote zone of the thin-section. This indicates that the mineralogical composition of the spilite has a larger impact on the W/R ratio required for complete epidote alteration than the bulk elemental composition of the spilite.

Our reactive-transport simulations predict approx. 10 vol.% increase in porosity, which fits that measured by Brett et al. (2017). This further validates our simulations. The very high calculated W/R ratios confirm that enormous amounts of water have to flow through discrete zones of the upper oceanic crust to form end-member epidotes. While it is clear that epidotes are deep markers of hydrothermal discharge paths, future simulations will show if these W/R ratios coupled with the metal contents of the epidotizing fluid recently indicated by fluid inclusion analyses (Richter and Diamond 2019) can account for the base-metal leaching observed in epidotes.

Acknowledgements

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Subseafloor alteration of the mafic volcaniclastic-hosted Tinakula SMS deposit, Jean Charcot Troughs, SW Pacific

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Abstract. Tinakula is the first massive sulfide deposit described in the Solomon Islands, located in the Jean Charcot Troughs at ~1100 mbsl. It is the first modern analog of a mafic volcaniclastic-hosted massive sulfide deposit. Barite- and sulfide-rich chimneys and mounds cover an area of ~77,000 m² along a submarine scoria cone row. The shallow footwall consists of intensely-altered volcaniclastic breccias variably cemented by anhydrite, and cross-cut by sulfate-sulfide veins. Stratiform alteration assemblages show progressive changes in clay mineralogy with depth, from smectite to mixed-layer illite/smectite, to chamosite and corrensite. δ¹⁸O and δD values of clays confirm increasing temperature with depth from 124–256°C, associated with seawater-dominated hydrothermal fluids at high water:rock ratios. This study shows how hydrothermal fluids can become focused in permeable rocks by progressive low-temperature fluid circulation, leading to a large area of alteration with reduced permeability close to the seafloor. Over-pressureing and fracturing of the sulfate-cemented volcaniclastic rocks produced the pathways for higher-temperature fluids to reach the seafloor, present now as sulfate-sulfide veins in the footwall. This reveals the important role of anhydrite in fluid focusing, which is usually not preserved in the geologic record.

1 Introduction

Studies of ancient volcanogenic massive sulfide (VMS) deposits have revealed that the nature of the substrate (coherent vs. clastic) plays a first-order control on the sizes and shapes of VMS deposits, the flow of hydrothermal fluids, and the nature of the footwall alteration zones (e.g., Franklin et al. 2005; Hannington et al. 2005). In successions that are dominated by coherent lavas, hydrothermal fluids tend to be focused along faults with minimal influx of cold seawater, forming discordant pipe-like alteration zones (cf. Franklin et al. 2005). In contrast, successions that dominated by volcaniclastic strata have high permeabilities that promote lateral fluid flow, widespread seawater mixing, and stratiform alteration zones (cf. Franklin et al., 2005).

A lack of drilling of modern seafloor massive sulfide (SMS) deposits has resulted in relatively little information about the third dimension of actively-forming deposits. Commercial drilling at the Tinakula SMS deposit in the Jean Charcot Troughs (Solomon Islands) provides a rare view into subseafloor alteration processes of a modern mafic volcaniclastic-hosted deposit. We investigate how this substrate has influenced fluid flow and fluid mixing at Tinakula in order to understand how high-temperature fluids can become focused to the seafloor in permeable successions.

2 Tectonic setting

The Jean Charcot Troughs comprise one of the youngest back-arcs in the world, forming ~4 m.y. ago in response to eastward subduction and rollback of the Indo-Australian plate beneath the Pacific plate (Monjaret et al. 1991; Pelletier et al. 1998). The back-arc consists of a series of complex horst and graben structures over ~120 km from the arc (Fig. 1) that have variable orientations. The seafloor depths range from ~800–3600 mbsl, and individual grabens are 20–65 km in length and 5–15 km in width.

Figure 1. Satellite altimetry from Sandwell et al. (2014) showing the back-arc Jean Charcot Troughs (grey hatched pattern) and the location of the Tinakula deposit (yellow star).
In the central part of the JCT, there is a notable bathymetric high that bisects the trough morphology (Fig. 1). We interpret this to be a recent volcanic complex related to basement structures that extend from the North Fiji Basin into the JCT along a paleo-spreading center (the Tikopia fracture zone). Here, the seafloor is dominated by N-S trending structures that are exploited by magmas, producing linear volcanic ridges and volcanic cones aligned along fissures. The Tinakula deposit occurs along one scoria cone row associated with this area of enhanced magmatism.

3 Methods

3.1 X-Ray diffraction

Bulk samples of crushed altered material were separated into clay-sized fractions (<2 μm) by settling in cylinders of standing water, following Moore and Reynolds (1997). The mineralogy of the clay fraction from 58 samples was determined using a Philips X-ray diffractometer PW 1710, equipped with a Co-tube and an automatic divergence slit and monochromator, located at GEOMAR. Operating conditions were 40 kV and 35 mA. Oriented mounts were prepared by wet suspension followed by air-drying, and were measured with a 2-theta scanning angle of 3–40°, at a scan rate of 1 second per 0.01° step. Samples were then saturated with ethylene glycol following a standard vaporization technique and re-analyzed. MacDiff v.4.2.6 software was used for mineral identification and display of XRD data.

3.2 Whole-rock geochemistry

Whole-rock geochemistry was determined on 47 clay-altered volcanoclastic samples (<63 μm) at Activation Laboratories. A lithium metaborate/tetraborate fusion was used; the major elements were analyzed by ICP-OES, and the trace elements (Ba, Be, Bi, Co, Cs, Ga, Ge, Hf, In, Mo, Nb, Rb, Sr, Ta, Th, Ti, U, V, W, Y, Zr, REEs) were analyzed by ICP-MS, with additional elements (Ag, Cd, Cu, Ni, Pb, and Zn) analyzed by ICP-OES following a total acid digestion technique. Cold vapor AAS was used to determine Hg and infrared detection (IR) was used to determine total S. INAA was used to determine Au, As, Br, Cr, Ir, Sc, Se, and Sb. Duplicates and standard reference materials were analyzed after every 10–15 samples and indicated a precision of better than 10% and accuracy of better than 5% for most elements.

3.3 O-H isotopes

Oxygen and hydrogen isotope analyses were performed at the Queen’s Facility for Isotope Research, Canada on monomineralic clays (<2 μm), including nontronite (n = 2), chamosite (n = 9), corrensite (n = 2), and rectorite (n = 1) from depths of 2.8–22.5 mbsf. Oxygen was extracted from 5 mg samples at 550–600°C using the BrF5 technique of Clayton and Mayeda (1963). Samples were analyzed via dual inlet on a Thermo-Finnigan DeltaPlus XP IRMS. For hydrogen isotope measurements, samples were weighed into silver capsules, degassed for one hour at 100°C, and then crushed and loaded into a zero-blank auto sampler. Hydrogen isotopic compositions were measured using a Finnigan thermos-combustion elemental analyzer coupled to a Thermo-Finnigan DeltaPlus XP continuous-flow IRMS. All values are expressed in δ-notation as per mil (%) deviation from V-SMOW, with analytical precision and accuracy for δ18O values of 0.1 ‰ and for δD of 3 ‰ and 1.5 ‰, respectively.

4 Deposit geology

The volcanoes in the Tinakula area are composed of basaltic-andesite and dacite (Anderson 2018). They include composite cones, cinder cones, and craters without cones. The volcanic cones are aligned along a large (~1.6 km-long) N-S-trending fissure (Fig. 2). The southern part of the fissure is dominated by a large composite cone with bimodal lava flows. This is followed northwards by the 900 m-long row of basaltic-andesitic cinder cones on which the deposit is centered.

Sulfide chimneys and mounds are distributed over a strike length of ~1050 m along this fissure (Fig. 2). They occur on the tops and along the flanks of the cinder cones, as well as inside the summit craters. West of the row of cinder cones, over a strike length of ~400 m, the chimneys and mounds are not associated with observable volcanic features at the seafloor but instead appear to occur along two NE-SW and NW-SE structures. The chimneys are characterized by irregular bulbous ‘beehive’ morphologies that lack central orifices. The chimneys are commonly surrounded by sulfide talus and form hydrothermal mounds that rise ~2–3 m from

Figure 2. High-resolution (0.2 m) multibeam bathymetry (RESON SeaBat 7125-ROV2 400 kHz) showing a series of volcanic cones along a fissure, and the distribution of chimneys and mounds.
the seafloor. The extent of these mounds is largely unknown due to burial by late volcaniclastic sediments. Where exposed, the mound material is distinctly laminated with layers of barite and sulfide minerals up to 0.5 m thick with unexpectedly smooth surfaces. The layered barite-sulfide mounds are most similar to features described by Hein et al. (2014) from the East Diamante caldera in the Mariana arc. The surface expression of hydrothermal precipitates covers ~77,000 m², including ~13,800 m² of active chimneys and mounds, 51,800 m² of inactive chimneys and mounds, and 9,300 m² of partially-buried chimneys and mounds.

The subseafloor consists of variably-altered basaltic-andesitic volcaniclastic material, with vertical and lateral facies variations over several meters, including changes in clast size, shape, composition, and degree of sorting. The volcaniclastic facies are dominated by massive to crudely-bedded lapillistone with clasts containing up to 20% vesicles, interpreted to be phreatomagmatic breccias. Minor hyaloclastite breccia and proximal resedimented breccias were also identified. Alteration and late infill by patchy sulfate cement obscures many of the primary volcanic textures.

5 Alteration mineralogy and geochemistry

The volcaniclastics breccias in the footwall of the Tinakula deposit have been intensely hydrothermally-altered, with clay minerals occurring as replacement of volcanic material and pore-space infill. Alteration minerals identified by XRD include: diocathedral smectite (montmorillonite and nontronite), chlorite (mainly chamosite, with minor clinoclore), minor chloritoid, illite, and mixed layer clays: illite/smectite, muscovite/illite (rectorite), and chlorite/smectite (corrensite). Mixed-layer illite/smectite (I/S) ranges from 50% illite to ~91% illite. These minerals comprise five alteration facies associated with increasing depths: (1) montmorillonite/nontronite; (2) nontronite + corrensite; (3) I/S + pyrite; (4) I/S + chamosite; and (5) chamosite + corrensite.

Compared to the least-altered rocks (basaltic-andesite, described by Anderson 2018), the whole-rock geochemistry of the altered samples reveals variations in the concentrations of Ba, Si, Al, Fe, S, Mg, Ca, Na and K, consistent with their mobility during hydrothermal alteration. High Ba, Ca and S or T reflect the abundance of barite and anhydrite/gypsum in the samples. High Fe, O or T and S or T are related to pyrite. Illite-smectite alteration is characterized by relative enrichments in K2O compared to the least-altered basaltic andesite; whereas the chamosite + corrensite alteration is dominated by MgO addition.

Mass balances were calculated for all alteration assemblages following the single precursor method of Barrett and MacLean (1994a, 1994b, 1999), using immobile Zr to calculate the enrichment factor. The main difference between the low-temperature alteration stage and the higher-temperature alteration stage is the mass change of MgO (higher in chamosite) and K2O (higher in I/S).

6 O-H isotopes

Values of δ18Ovs/mow range from +12.3 to +12.5 ‰ for nontronite, +2.2 to +8.3 ‰ for chamosite, +9.6 to +11.1 ‰ for corrensite, and +5.9 ‰ in rectorite. The large range and high δ18O values reflect substantial shifts relative to hydrothermal seawater. Values were calculated following Savin and Lee (1988) assuming a δ18O of the hydrothermal fluid close to that of typical MOR hydrothermal vent fluids (δ18O = +1.3‰; Shanks et al. 1995). The calculated temperatures show a systematic increase from nontronite (136–138°C), to chamosite (124–205°C), corrensite (207–227°C), and rectorite (256°C). The δ18O of the hydrothermal fluid in equilibrium with the analyzed clay minerals could have been closer to +5.0 ‰, if we assume a temperature of formation of 240°C, following Sheppard and Gilg (1996). The large range of calculated δ18O values at the inferred temperatures of alteration is consistent with boiling of the hydrothermal fluids. Values of δ18Ovs/mow range from -92 to -86 ‰ for nontronite, -85 to -52 ‰ for chamosite, -85 to -80 ‰ for corrensite, and -69 ‰ in the single sample of rectorite. There is a general increase in δ18Ovs/mow with depth.

7 Discussion and conclusions

Drilling of the Tinakula deposit has revealed widespread hydrothermal alteration within ~10 m of the seafloor in the highly permeable volcaniclastic substrate. The alteration assemblages are consistent with a near-neutral or mildly acidic pH. The calculated temperatures of clay formation (124–256°C) are lower than the predicted temperatures of formation for anhydrite and sphalerite, indicating that the late sulfate-sulfide veins were likely transporting hotter fluids. Several lines of evidence indicate increasing temperature with depth: (1) the transition from barite near the surface to anhydrite at depth; (2) the transition from smectite to mixed-layer I/S (with increasing proportions of illite) to corrensite to
chamosite; and (3) decreasing δ¹⁸O and increasing δD of clay minerals.

The main difference between the low-temperature alteration stage (dominated by I/S + pyrite) and the higher-temperature alteration stage (dominated by chamosite + corrensite) is the mass change of MgO (higher in chamosite) and K₂O (higher in I/S), typical of VMS-style alteration in permeable volcaniclastic rocks (e.g., Franklin et al. 2005). Therefore, ratios of these elements may be the most useful for land-based exploration in mafic terranes.

High δ¹⁸Owater values have been reported for Kuroko-type hydrothermal fluids (up to 10.8 ‰; Ohmoto 1996), and δ¹⁸Owater shifted to lower values at higher temperatures are typical of the stringer zones of ancient VMS deposits (e.g., Cathles 1993). We interpret the combination of higher δ¹⁸Owater and lower δDwater at Tinakula to be a result of subsea-floor boiling, which is likely because of the shallow water depths. The lack of low-pH mineral assemblages suggest that there was no or limited direct magmatic contribution to the hydrothermal fluids.

In permeable volcaniclastic rocks, an important question is how the permeability becomes sealed enough to allow focusing of the hydrothermal fluids to the seafloor. Here, we propose that the pervasive alteration of the volcaniclastic units close to the seafloor coincided with a progressive increase in subsea-floor temperatures parallel to the seabed, from initial low temperatures during precipitation of nontronite (136–138°C), increasing to chamosite (124–205°C), corrensite (207–227°C) and eventually rectorite (256°C). At 250°C, the temperatures were high enough to form anhydrite at depths of only a few meters below seabed (>2 mbsf), sealing some of the permeability and focusing fluids into channelized pathways to the seafloor. Continued hydrothermal circulation resulted in over-pressuring and fracturing of this relatively impermeable horizon, precipitating late sulfate-sulfide veins. In ancient deposits, the anhydrite is rarely preserved because of its retrograde solubility; the only evidence remaining of an “anhydrite seal” would be the presence of alteration minerals formed at temperatures that would have caused anhydrite deposition.

The style of hydrothermal upflow also plays an important role in the nature of the seafloor deposition. Diffuse venting is likely responsible for the formation of porous beehive-like structures and unusual bulbous chimneys observed at Tinakula (Anderson 2018). This style of venting may therefore be common in volcaniclastic-dominated environments.

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References

Origins of Si-Fe cap rocks at extinct seafloor massive sulphide (eSMS) deposits from the TAG Hydrothermal Field (26°N), Mid-Atlantic Ridge

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Abstract. Extinct seafloor massive sulphide (eSMS) deposits represent an understudied phenomena of modern seafloor hydrothermalism, and are thought to be a potential resource for base and precious metals if exploitation of seafloor mineral resources becomes economically viable in the future. The transition from active to inactive mounds poses important, but as of yet, unanswered questions about their preservation after hydrothermal venting ceases and oxygenated seawater circulates. This has the potential to destroy the metal tenor in SMS deposits, unless they are somehow protected. Here, we show the common occurrence of a silica-rich ‘jasper’ layer that forms the interface between unaltered sulphide below and oxidized metal-rich sediments above. The jasper layer is up to several m-thick and was encountered, in some form, at each of three extinct SMS deposits drilled in the TAG are of the Mid-Atlantic Ridge. The silification events which have created these capping materials result in the decrease in permeability and is likely a common process during the waning stages of a hydrothermal cycle. As such, the Si-Fe cap could be a common product at eSMS deposits, and potentially provide an auto-preservation mechanism, restricting oxygenated seawater ingress and halmyrolysis of eSMS deposits.

1 Introduction

It is widely thought that seafloor massive sulphide (SMS) deposits, the modern analogue of volcanogenic massive sulphide (VMS) deposits, present a potential global resource for base (Cu, Zn) and precious metals (Au, Ag). In addition, SMS deposits can be enriched in ‘critical metals’ including Se, Te, Tl (Monecke et al. 2016), which are essential for use in the construction of modern and green low-carbon technologies. Globally, over 340 high temperature hydrothermal sites have been identified at a range of ocean spreading centres (Petersen et al. 2016), significant massive sulphide deposit formation has been recorded at 165 of these sites (Hannington et al. 2011).

13 SMS deposits have undergone intrusive investigation (drilling or coring) and of these, only 6 sites have published tonnage estimates (Petersen et al. 2016). While almost all research and drilling of SMS deposits has been focused on active systems, the investigation of the morphology, subsurface structure and mineralogy of eSMS deposits is almost non-existent. As such, little is known about the mechanisms that operate post-SMS formation and which have an impact on the preservation and hence resource value of SMS. Identifying these generic processes and mechanisms, and the extent to which they impact the resource grade, is critical in evaluating the global potential of SMS.

This research forms part of a holistic study of eSMS deposits in the TAG hydrothermal field (26° North, Mid-Atlantic Ridge - MAR) and identifies surface and near-sub-surface features that indicate if and how such deposits are preserved. Two research cruises (M127 and JC138) were undertaken during the summer of 2016 as part of the EU-funded Blue Mining programme. These obtained new geological and geophysical data that enables characterisation of eSMS deposits in three dimensions including: high resolution bathymetry (obtained by Autonomous Underwater Vehicle - AUV), seismic reflection and refraction, 3D controlled source electromagnetics, Robotic Underwater Vehicle (RUV) surveys and samples, sediment cores, and rock-drill core, obtained using the British Geological Survey’s robotic seafloor drilling rig (RD2). This contribution focuses on near-sub-surface coring, and highlights a Si-Fe rich capping lithology which has the potential to act as an auto-preservation mechanism that we suggest reflects a generic global process during the waning stages of hydrothermal fluid flow.
2 Geological setting and near surface geology

The TAG Hydrothermal field is located at 26°N on the slow spreading, Mid-Atlantic Ridge, and is host to the TAG active Mound, along with multiple areas of inactive hydrothermal mounds, the MIR zone, and the ALVIN zone. High resolution bathymetry and high definition video footage obtained during the Blue Mining cruises in 2016 provided new data to enable surface mapping three inactive hydrothermal mounds in the TAG Hydrothermal field: Southern Mound, and Rona Mound in the ALVIN Zone, and the MIR Zone (Fig. 1).

Following mapping of the three sites, drilling was undertaken using the BGS RD2 seafloor drill rig at Southern Mound, Rona Mound, and the MIR zone with maximum depths drilled of ~6.75m, ~12.5m, and ~7.5m respectively below the seafloor.

Si-Fe lithologies, ~2-3 m thick, were recovered from all three hydrothermal mounds drilled, and sub-categorised into three separate units: A, B, and C, based upon textural observations and mineralogy. This work focuses on the transition through the three Si-Fe units in Southern Mound. At Rona Mound Units B and C were recovered, and at MIR Zone, only Unit B was recovered.

3 Mineralogy and textural assessment of the Si-Fe lithologies

3.1 Unit A

Unit A is mineralogically homogenous with near equal concentrations of goethite (~33 wt.%), opal-CT (~30 wt.%) and quartz (~34 wt.%), and minor haematite (up to 4 wt.%), analysed by quantitative X-ray Diffraction (XRD). It is the least 'silicified' of the Si-Fe units with SiO₂ averaging ~65 wt.% (n=4, analysed by X-ray fluorescence, XRF).

Unit A samples are typically clast supported breccias composed of jasperoidal (sub-microscopically bonded iron oxide and silica) clasts ranging from anhedral shapes to angular laminated clasts, with areas of dendritic iron oxide and filamentous iron oxide growth. Occasional jasperoidal fragments display desiccation fractures, some which cross cut laminations. The clasts, filamentous, and dendritic textures observed within Unit A are comparable to unsilicified overlying sediments recovered from Southern Mound.

3.2 Unit B

Three Unit B samples were recovered from Southern Mound, two at ~85 wt.% quartz (XRD, 94 wt.% silica, XRF), and ~7.5 wt.% hematite, with a third showing lower SiO₂ (~72 wt.% XRD, and XRF), and quartz (~56 wt.% XRD), and higher hematite (~32 wt.% XRD, and Fe₂O₃ = ~29 wt.% XRF). The lower silica value was considered to be anomalous in comparison to Unit B material recovered across the 3 mounds investigated (SiO₂ average ~85 wt%, n =14). With the exception of this anomalous sample, Unit B material at Southern Mound has ~20 wt% higher SiO₂ than the average Unit A samples.

Unit B material from Southern Mound comprised of sub angular to angular jasperoidal clasts, cemented by iron oxide free silica. Iron oxide free-silica typically coats jasperoidal clasts and either fully or partially infills void space. Patches of filamentous and strands of hematite (typically ~10 microns diameter) are present within discrete areas and are similarly coated with quartz.

Comparable unsilicified surface sediments from Southern Mound were recovered as fine grained, dark red hematite-rich material, the main significant difference was the presence of crystalline hematite not present within Unit B samples.

3.3 Unit C

Unit C material is broadly mineralogically comparable to Units A and B, and has a slightly higher SiO₂ content (~95 wt%, n=3), but contains disseminated sulphide. The main defining textural difference is the presence of grey-white 'bleached' sulphide rich silica, and the presence of pyrite, chalcopyrite, and sphalerite. Lobes of bleached material at Southern Mound are restricted and consist of iron oxide free silica hosting euhedral to subhedral pyrite grains, with minor sphalerite. Interstitial
sulphides (pyrite, and chalcopyrite) are also present within near vertical, quartz lined, pore spaces within the two deepest Si-Fe samples from Southern Mound.

4 Oxygen isotope data

Powdered whole rock samples underwent a leaching process to remove iron oxides, leaving a silica residue, on which laser fluorination was undertaken to obtain $\delta^{18}O_{\text{VSMOW}}$ values for the silica component of the Si-Fe lithologies. Two groups of values were established: Unit A between 24.1 and 28.0, and Units B and C between 14.8 and 21.5. Using the assumption that the silica formed in equilibrium with either seawater ($\delta^{18}O = 0$, Craig 1961), or TAG hydrothermal fluid ($\delta^{18}O = +1.7$, Shanks et al. 1995) a potential range of formation temperatures were calculated. Samples dominated by quartz used the parameters defined by Sharp et al. (2016), and for Opal-CT dominated samples the parameters defined by Kita et al. (1985) were used.

Formation temperatures for the silica of Unit A average to $\sim 63^\circ \text{C}$ compared to an average of $\sim 115^\circ \text{C}$ for Units B and C.

![Figure 2. Summary of $\delta^{18}O_{\text{VSMOW}}$ values from Units A-C, inclusive of samples obtained from Southern Mound, Rona Mound, and MIR Zone by this study. All temperature values from other samples were recalculated from the original $\delta^{18}O$ using the methodology stated in Section 4 for direct comparison including: silica/jasper samples from the MESO hydrothermal Field (Halbach et al. 1998), amorphous silica and iron oxide chimney from MIR Zone (Petersen 2000, unpublished data), and silica chimneys from the Galapagos spreading centre 86°W (Herzig et al. 1988). Halbach data point represents a ‘calculated’ value for pure silica $\delta^{18}O$ based on an average of 6 whole rock $\delta^{18}O$ values for ‘jasper’ samples.]

5 Discussion of paragenesis

A mechanism of jasper formation is commonly described by the early formation of subsurface or surface amorphous silica gels, as a result of conductive cooling of hydrothermal fluids (Grenne and Slack 2003). Typically, once the amorphous gel has formed it incorporates iron oxides and then the electrostatic charge between iron oxide grains and polarised silica molecules form an even distribution within the gel (Halbach et al. 2002). As this silica gel undergoes maturation, the amorphous silica dewaters to transition through opal-A, to opal-CT, and finally quartz.

5.1 Unit A

Unit A is the shallowest and has undergone the least silification of the three Si-Fe lithologies. It has retained and preserved the iron oxide mineralogy and textures of the goethite rich sediment precursor also observed at Southern Mound. The occurrence of both opal-CT and quartz in Unit A samples could be potentially explained by partial maturation of silica. Alternatively, it could be representative of two independent silica generations at different states of maturity. The absence of silica infilling around jasperoidal clasts, however, and the homogeneity of the oxygen isotope values implies a single-stage silification event.

5.2 Units B and C

The same jasper formation mechanism is valid for Units B and C, with the hematite/goethite distribution likely preserved from the sediment ‘protolith’ during silification. At least two silification events have affected these units, the first potentially similar, if not the same event which silificed the overlying Unit A forming jasperoidal clasts. The second occurring after silica maturation as shown by the infill of early desiccation cracks with a later generation of iron oxide free silica. This process is likely the cause for the increased silica content ($\sim 20–25$ wt.%) of Units B and C compared to Unit A.

5.3 Formation temperatures

Formation temperatures between Unit A, and Units B and C, calculated from $\delta^{18}O_{\text{VSMOW}}$ values of silica, show a difference of around $50^\circ \text{C}$. The $\delta^{18}O$ from Units B and C corresponds to silica precipitated from a higher temperature fluid than the silica in Unit A, supporting the textural evidence of a second silification event limited to Units B and C. Higher temperatures would likely help convert opal-CT to quartz faster by driving off the hydrous group, therefore a second silification event at a higher temperature could potentially explain the lack of opal-CT in Units B or C, compared to Unit A.

$\delta^{18}O$ data from Si-Fe precipitates from active hydrothermal vents MESO hydrothermal (sphalerite bearing jasper breccia), Galapagos silica chimneys, and a relict silica and iron oxide chimney from the MIR zone (Halbach et al. 1998; Herzig et al. 1988; Petersen 2000 unpublished data) show that this data is comparable with recovered hydrothermal silica to date, and it is likely that similar processes which formed these other samples have resulted in the silification observed at Southern Mound. The two different temperature groups ($\sim 50-60^\circ \text{C}$ and $\sim 100-120^\circ \text{C}$) established between Units A, and Units B and C are also seen in the other samples, with the majority falling into the 40-60°C range.
5.4 Implications from the sulphides

The fluid which caused the early stage of silicification of the Si-Fe capping lithologies would not have had the same geochemical properties (i.e. redox) as the fluid which precipitated the sulphides present in Unit C. If that were the case, bleaching and sulphidation of the shallower units would have occurred.

It’s not implausible that the fluid which precipitated the sulphides at depth was also responsible for the secondary silicification of Units B and C, however, several unlikely factors would need to have occurred together. The fluid would have to been limited in sulphur, with sulphur reserves exhausted before the fluid reached Unit B, otherwise sulphidation would have occurred throughout the Si-Fe cap. If this was the case, the fluid would not have reached Unit A, or undergone a significant evolution as to not precipitate a second silica generation within. Consideration should also be given to the temperature of the fluid. It seems unlikely that a fluid which precipitated chalcopyrite would also precipitate silica with a calculated formation temperature of ~110°C. Two silica samples from Galapagos silica chimneys have a similar calculated formation temperature, but associated sulphides of pyrite, sphalerite, and marcasite (Herzig et al. 1988) represent a lower temperature assemblage than one including chalcopyrite.

Another potential explanation is that the sulphidation occurred after silicification events, by a third, higher temperature and reduced fluid. The early silicification events would have decreased the porosity and permeability of the Si-Fe materials, limiting the fluid pathways through the Si-Fe lithologies, spatially constraining the fluid. Additionally, the silica coating, or ‘armourment’ of the iron oxides would decrease the amount, and surface area, of iron oxide available to interact with the fluids, also explaining the restrictive relationship between bleaching and sulphidation. This relationship can be observed in thin section where individual filaments are composed of oxidised iron outside the bleached zone, and of reduced iron sulphide within the bleached zone. The extent of existing silicification would control the amount of iron oxide available for this reduction, and can potentially explain the juxtaposition of both reduced and oxidised iron at a micron scale.

6 Conclusion

The interpreted silicification process formation the Si-Fe material would likely have a direct impact on the fluid flow regime of the hydrothermal mound, where the cap is present. Silicification of the material leads to a decrease in porosity and permeability, and thus the formation of a comparatively impermeable layer directly overlying massive sulphide ore. This decrease in permeability would inhibit ingress of seawater into the hydrothermal mound, and would potentially limit the amount of halmyrolysis of the massive sulphide ore. Southern Mound shows evidence of multiple stages of silicification, and similarly potentially shows evidence of limited fluid flow through the Si-Fe cap, proof of the impermeability.

The observation of a Si-Fe ‘cap’ was not limited to Southern Mound, with Si-Fe materials recovered from both Rona Mound and the MIR Zone. This implies that the formation of a Si-Fe cap is not a unique feature of Southern Mound, and is likely a product of common hydrothermal processes during the waning stages of a hydrothermal cycle. It is therefore likely that Si-Fe lithologies are ubiquitous at other eSMS deposits around the world where they have the potential to act as an auto-preservation mechanism of the underlying massive sulphide ore.

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Zinciferous mineralization at the Neves-Corvo deposit, Iberian Pyrite Belt, Portugal: the other end of the spectrum

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Abstract. The Neves-Corvo deposit is widely known as a world-class copper mine, but it constitutes as well one of the world’s largest repositories of zinc, especially in its northernmost orebody – Lombador -, which represents alone 62% of the total zinc reserves of the deposit. The orebody lies on a stratabound stockwork that extends across its entire length. Hydrothermal alteration in the Lombador orebody contrasts with alteration signatures ascribed to the high-temperature parts of the ore-forming system, namely at the Corvo and Graça orebodies. A chloritic core grades outwards into sericitic peripheral zones, but intense carbonatization constitutes a key distinctive feature of the zinc mineralization. The zinc-related mineralization and alteration facies indicate mild temperatures, and formation from reduced, Fe-rich, moderately low pH, CO₂-enriched solutions, and a combination of sub-seafloor replacement and episodic direct exhalation onto the seafloor in closed basins. A magmatic-hydrothermal model emerged from the ore geochemistry, hydrothermal alteration patterns, trace elements, and unique stable and radiogenic isotopic signatures found at the Corvo orebody. Conversely, direct magmatic contributions to the metal budget of the low-temperature end of the Neves-Corvo mineralization spectrum are precluded by the Pb and Nd isotope signatures of the Lombador zinciferous ores, which compare to typical IPB deposits.

1 Introduction

The Iberian Pyrite Belt (IPB) has global resources totaling over 21 Mt Cu, 34 Mt Zn, 12 Mt Pb and 0.8 kt Au, contained in about 2,500 Mt of ores from 88 known deposits (Barriga 1990; Carvalho et al. 1999). The Neves-Corvo (NC) deposit is definitively the jewel of the crown of this outstanding province. The deposit represents the most valuable metal-mining operation in EU. Its ores are anomalously enriched in Cu and Sn, with Cu/Zn ratios significantly higher than the typical IPB range, they contain huge amounts of Zn, and are known to incorporate significant concentrations of Ag, In and Se. These features make the NC deposit unique among known IPB deposits, the host sequence to the deposit being nevertheless similar to that elsewhere in terms of lithology, volcanology and geochemistry (Munhá et al. 1997; Relvas et al. 2002; Rosa et al. 2008; 2010; 2016).

While NC continues on today as a world-class copper mine, zinc production is an important reality since 2006, which justified an on-going, large-scale zinc expansion project. Zinc constitutes the metal resource responsible for extending the lifetime of the mine through the next decade. The underground mining works and surface drill programs have revealed that NC actually represents one of the world’s largest repositories of zinc, with particular emphasis on its northernmost orebody: the Lombador orebody (Fig. 1). The NC total Zn resources include 118.2 Mt of massive sulfides @ 0.30% Cu, 5.94% Zn and 1.27% Pb, at a cut-off grade of 3.0% Zn, and a total resource of 7 Mt of Zn metal (Lundin Mining Technical Report, June 2017).

Figure 1. Zinc grade and contained zinc metal of both the overall NC deposit, and its Lombador orebody, in the general context of VHMS deposits worldwide (USGS database).

Previous research on NC provided many answers to metallogenic questions, such as the sources for tin and copper, the high-temperature and acidic alteration patterns of the Cu-rich feeder zones, or the relevance of sub-seafloor replacement depositional mechanisms in the inner parts of the overall ore-forming system, nicely represented by the Corvo and Graça orebodies (Relvas et al. 2006a; 2006b). A magmatic-hydrothermal genetic model for this ore-forming system is heavily supported.
by its unique ore geochemistry, and its hydrothermal alteration patterns, mineral assemblages, and trace element signatures, coupled with the distinctive stable (O, H, S) and radiogenic (Pb, Os and Nd) isotopic signatures found in the deposit (Relvas 2000; Relvas et al. 2001; 2002; 2006a; 2006b; Munhá et al. 2005; Jorge et al. 2007; Relvas et al. 2009; Huston et al. 2010; Carvalho et al. 2018; Li et al. 2019).

This study focuses on the formation and distribution of the Zn-rich ores at the NC deposit, the low-temperature end of its mineralization spectrum. Understanding the metallogeny of zinc in the context of the unique hydrothermal processes that formed this remarkable deposit represents a major and unsolved scientific challenge, which interest goes far beyond the scale of this particular deposit.

2 The Lombador orebody: ore geochemistry and hydrothermal alteration

The NC deposit comprises seven laterally bonded, lens-shaped orebodies, five of which are in production, which grade downward into stringer ores that cut intensely altered footwall host rocks. Strong metal zoning allowed clear definition of several ore types, which are used, with minor overlapping drawbacks, for geologic modeling of the deposit and sorting of its ore reserves.

Previous study of the volcanic lithofacies of the NC succession provided constraints on the ore-forming environment and timings with respect to volcanic events (Rosa et al. 2008). The geometry, size and distribution of the ore-related feeder systems reflect constraints imposed by primary characteristics of the host sequence such as permeability and structural control. Due to long-lasting hydrothermal reworking and zone-refining effects, zinc mineralization occurs in the most peripheral parts of the camp, especially in the Lombador orebody (Relvas et al. 2006a; Carvalho, 2016).

Lombador is a huge, NW-SE oriented orebody, with a 20º to 40º northward dip. The massive sulfide lens can reach over 100 m thick and includes intersections such as 27 m @ 8.9% Zn, and 22 m @ 8.9% Cu (Pacheco et al. 1999). At Lombador, lenticular to stratabound Zn-rich (MZ), Cu-rich (MC), Pb-rich (MP), Cu-Zn-rich (MCZ), Zn-Pb-rich (MZP) and barren (ME) massive sulphides; as well as Zn-rich (FZ), Cu-rich (FC) ores, and barren (FE) stringer/fissural mineralization have been identified. An allochthonous zinciferous stringer ore (RZ), tectonically emplaced in a hanging wall position, was also defined. The Lombador orebody is the largest and Zn-richer orebody of the NC deposit, representing alone 62% of its total zinc reserves. Lombador comprises over 106.2 Mt of massive sulfides @ 0.78% Cu, 4.42% Zn, 1.16% Pb, 0.04% Sn, and 53 g/ton Ag, of which 70% (73.5 Mt) are Zn resources @ 0.3% Cu, 5.9% Zn, 1.4% Pb, 0.04% Sn, and 56 g/ton Ag (Somincor-Lundin Mining, unpublished report, 2013; in Carvalho, 2016).

A well-developed metal zonation, going from a Cu to Zn–Pb to Fe zone was recognized at Lombador, although significant thrusting processes are common, often forming “secondary” Cu-rich oreshoots superimposed over barren and/or Zn-rich ore domains, due to ductile and/or fluid assisted copper remobilization processes (Carvalho 2016).

The ore sulfides found consist mostly of pyrite, sphalerite, galena, chalcocpyrite, arsenopyrite, and minor tetrahedrite, stannite, bournonite, boulangerite, pyrophyllite, cobaltite, glaucodot, cosalite, bismuth, gold, electrum, and roquesite. EPMA data indicate also the presence of fine-grained complex intergrowths of rare selenium-rich sulfosalts, tentatively classified as junonite, Se-cannizarite and wittite (Pinto et al. 2013; 2014; Carvalho et al. 2013; 2014; Carvalho 2016).

Relvas et al. (2006a) have studied in detail the alteration signatures ascribed to the high-temperature parts of the NC ore-forming system, namely at the Corvo orebody, and have shown that there is compelling textural, mineralogical and isotopic evidence that indicate hotter and unusually acidic ore-forming fluids and, probably, longer than average lifetime of this hydrothermal system relative to typical IPB deposits. To a certain extent, these features contrast with those of the hydrothermally altered facies underlying the zinc mineralization at the Lombador orebody.

This orebody lies on a huge, stratabound stockwork system that extends across its entire length. Although two discharge zones have been found in the orebody’s footwall, the main stockwork system develops in its central-W sector, where the axis of the main feeder system is located. As elsewhere in the IPB, the hydrothermal alteration zonation comprises a chloride-dominated innermost alteration zone (Type I alteration) that grades outwards into K-sericite-dominated peripheral alteration zones (Type IIa alteration). The distal Na-sericite alteration (Type IIb alteration), known from other IPB deposits, was only found in some coherent rhyolite lenses tectonically emplaced in a hanging wall position. Significantly, intense carbonatization, expressed by thick massive siderite levels, occurs associated to both main alteration facies and represents a key distinctive feature of the zinc mineralization (Carvalho et al. 2013; Carvalho, 2016). Also, some massive zinc ores contain abundant carbonate gangue and show finely banded and rhythmic textures, which resemble the “massive carbonate ore” described at the Tharsis deposit, in Spain (e.g. Tornos 1998; 2008; Sáez et al. 1999).

The secondary mineral assemblage related to the Lombador Zn-rich ores is extremely enriched in iron (chlorite, siderite, pyrite, iron-rich sphalerite, arsenopyrite and, to a lesser extent, pyrrhotite), and less aluminous than the one described at the Corvo orebody. Its nature and chemical compositions indicate formation from Fe-rich, moderately low pH, CO2-enriched ore-forming solutions, under fairly reduced conditions, and relatively mild temperatures. Factors such as a porous and chemically reactive footwall host sequence, temperature drop, brusque pH variations, probable boiling, and fluid mixing with unmodified seawater both in the subseafloor, and by direct exhalation onto the seawater column, promoted extensive, stratabound hydrothermal alteration in the footwall succession, and ore deposition by both shallow subseafloor replacement,
Significant thrusting and tectonically-controlled enrichments, which are extremely relevant for the remobilization processes generated secondary copper occurrences in the orebody, whereas Zn-rich ores and barren sulphides occur towards its top and peripheral domains. Significant thrusting and tectonically-controlled remobilization processes generated secondary copper enrichments, which are extremely relevant for the mining operation.

3 The zinc-rich mineralization: discussion

The immediate footwall sequence underlying the Lombador orebody shows marked lateral and vertical lithofacies changes. In a significant part of its extension, the Lombador massive sulphide lens directly overlays the Phyllite-Quartzite Group sequence (PQ group, Oliveira et al. 2004), whereas in other areas the immediate footwall rocks consist of a variably thick volcano-sedimentary complex (VSC, Oliveira et al. 2004) composed of coherent rhyolite facies, especially in the central and south sectors, and a large component of clastic material, either volcanic, or sedimentary in origin, towards the northern sector, where they alternate with thinly laminated, sometimes graded-beded massive sulfide levels. This is thought to reflect a variable paleo-topography of the basin, characteristic of highly compartmented and tectonically instable multi-order basins, where the volcanoclastic and fine-grained detrital sediments variably accumulate, alternating with thinly laminated sulphides deposited from suspension. This geologic setting favored the precipitation of abundant carbonates in response to the right chemical conditions. The discharge of the mineralizing solutions was strongly constrained by tectonics. At the Lombador orebody, textural evidence corroborated by geochemical data, including Sr isotopes, are consistent with a depositional model involving Zn-rich mineralization formed by a combination of sub-seafloor replacement and episodic direct exhalation onto the seafloor in closed basins (brine-pool model). The Cu-rich ores formed in the clear dependence of fault zones and should correspond to late-stage mineralizing pulses in the evolution of the hydrothermal system, which overprinted the previously formed Zn-rich ores. Sub-seafloor replacement phenomena occurred in texturally and compositionally favorable footwall host rock settings, following sustained and long-lasting ore-forming processes. The NC orebodies display different degrees of hydrothermal maturity, similar to what can be observed in present-day submarine hydrothermal systems. The distinct petrographic and geochemical features shown by the various ore types of the Lombador orebody, coupled with its lower copper grades and the predominance of Zn-rich ores, strongly suggest that the Lombador orebody is hydrothermally less mature than the remaining orebodies of the NC camp. In this orebody, most of the hydrothermal activity was characterized by low to moderate temperature (300 ºC) hydrothermal circulation. Moreover, the abundance of carbonate ores speaks for predominantly near neutral to mildly acidic conditions. The local formation of high-temperature, Cu-rich ores should have resulted from focused, short-lived pulses of higher temperature hydrothermal upflows.

In contrast with Lombador, the Corvo and Graça orebodies seem to be the most mature orebodies within the NC hydrothermal field. The occurrence of massive and stringer cassiterite ores is almost restricted to these two orebodies, and, in particular, to the Corvo orebody ("tin corridor", Relvas et al., 2001; 2006a). In addition, these orebodies show the highest copper grades and copper ratios in the deposit, which conforms with a massive influx of high-temperature Cu-rich hydrothermal fluids and a sustained, long-lived hydrothermal activity responsible for extensive zone-refining.

Direct magmatic-hydrothermal contributions to a large proportion of the world’s Sn, W, Cu and Mo resources are reasonably established, whereas magmatic sources for Zn are considered unlikely and extremely difficult to demonstrate. Magmatic metal contributions are commonly excluded from zinc metallogenesis as leaving from the footwall successions usually accounts for the zinc supply of VHMS deposits with no need to invoke external metal contributions. The previously demonstrated multi-sourced nature of the NC ore-forming processes justified, however, a closer look over the isotopic signatures of the Lombador ores.

Relvas et al. (2001; 2006a; 2006b) have shown that, for the Corvo and Graça orebodies, in addition to a major fraction of the metal budget that should be ascribed to typical IPB ore-fluids and sources, the formation of the Cu-rich ores in these orebodies required significant contributions of high-temperature (>350 ºC) Cu-rich hydrothermal fluids, during sustained, long-lived hydrothermal activity. These authors proposed the involvement of metal contributions of magmatic affiliation, consistent with the stable and radiogenic isotopic signatures found (see also Li et al. 2019). In contrast, all the Zn-rich ores of the Lombador orebody show Pb and Nd isotope signatures that are very similar to the signatures characteristic of typical IPB deposits, precluding direct magmatic contributions to the metal budget of the low-temperature end of the NC mineralization spectrum (Carvalho 2016).

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Stratiform tourmalinites: revised genetic models and exploration applications

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Abstract. Stratiform tourmalinites are metallogenically important rocks that locally show a spatial association with diverse types of mineralization, especially sediment-hosted, stratiform Zn-Pb deposits and volcanogenic massive sulphides. Revised genetic models suggest that laterally extensive types of such tourmaline-rich rocks formed mainly by syngenetic processes on or below the seafloor, or later during diagenesis. Stratiform tourmalinites can be exploration guides wherein samples contain base-metal sulphides, high Mn concentrations, or positive Eu anomalies.

1 Introduction

Stratiform tourmalinites are defined as rocks that are concordant with the compositional layering of host lithologies and contain more than 15 volume percent tourmaline (Slack et al. 1984). These distinctive rocks are metallogenically important in locally showing a spatial association with a variety of metal deposits including Cu, Pb, Zn, Ag, Au, W, Co, and U (Slack 1996). Syngenetic or diagenetic origins for stratiform tourmalinites have been proposed in myriad geological, structural, and geochemical studies worldwide (e.g., Bandyopadhyay et al. 1993; Mao 1995; Pesquera and Velasco 1997; Golani et al. 2002; Tourn et al. 2004; Ferla and Meli 2007; Čopjaková et al. 2009; Martínez-Martínez et al. 2010; Yücel-Öztürk et al. 2015; Spránitz et al. 2018). However, detailed field, microtextural, and geochemical studies have also documented epigenetic origins involving metamorphic or magmatic processes (Steven and Moore 1995; Raith et al. 2004; Vial et al. 2007; Yang and Jiang 2012; Pirajno 2013; Mahjoubi et al. 2016; Kalliomäki et al. 2017; Spránitz et al. 2018). Such types of epigenetic tourmalinites are generally distinguished by a lack of lateral continuity (<10 m) along strike, and by proximity to shear zones, veins, or margins of granitic intrusions. This paper is not concerned with metamorphic or magmatic-hydrothermal varieties, but is focused on stratiform tourmalinites, reviewing current knowledge of these rocks and presenting revised models for their genesis.

2 Identification and occurrence

It is important to emphasize that some stratiform tourmalinites can be misidentified as compositionally different rock types (Slack et al. 1984). For example, in weakly metamorphosed terranes, very fine-grained tourmalinite superficially resemble carbonaceous argillite or siltstone as in the Golden Dyke dome of Australia (Plimer 1986), and chert as in the Belt and Purcell supergroups of the U.S. and Canada (Slack 1993); in highly metamorphosed terranes, coarse-grained tourmalinite may be mistaken for hornblende amphibolite as in the Broken Hill district of Australia (Slack et al. 1993). Because of the potential for associated mineral deposits, it is thus crucial during field work and later laboratory studies that stratiform tourmalinites not be overlooked or misidentified.

Host lithologies are dominated by siliciclastic metasedimentary rocks with locally important felsic metavolcanics. Meta-carbonate, metabasalt, and other lithologies are uncommon hosts. Some occurrences are interbedded with iron formation or coticule (fine-grained Mn-garnet-quartz rock). Thicknesses of the tourmalinites may range from <1 cm up to several meters, and include interlaminations with siltstone, argillite, and/or chert. Characteristically, only tourmaline and quartz are essential constituents, together making up >90 vol % of the rock. Textural studies indicate that the tourmaline varies from being randomly oriented, especially in weakly metamorphosed sequences, to strongly aligned in high-grade metamorphic terranes.

3 Metallogeny

The dominant deposit type that is spatially associated with stratiform tourmalinites is sediment-hosted, stratiform (SEDEX) Zn-Pb-Ag ores. Less common are occurrences with Cu- or Zn-rich volcanogenic massive sulphide (VMS) deposits. These and many other metallogenic associations are summarized in Slack (1996). Tourmalinites commonly form beds or lenses <1 m thick in the hanging wall of the deposits, or lateral equivalents along strike. Although not wholly stratiform, alteration zones in both sediment- and volcanic-hosted deposits may contain abundant tourmaline, such as in the footwall tourmalinite pipe of the large Sullivan Pb-Zn-Ag deposit (British Columbia) in which very fine-grained (<10 µm) tourmaline makes up ca. 20 to 60 vol % of the rock (Slack et al. 2000).

4 Geochemical and isotopic signatures

4.1 Whole-rock geochemistry

Many studies have reported on bulk compositions of tourmalinites including data for trace elements (TE) and rare earth elements (REE). Contents of major elements (ME) largely reflect the composition and proportion of tourmaline, whereas TE and REE contents mainly...
reflect accessory detrital minerals such as monazite, ilmenite, rutile, and zircon. In hydrothermal systems with relatively low fluid/rock ratios (i.e., rock-buffered), as recorded in distal tourmalinites (Fig. 1A), ME can be enriched or depleted relative to unaltered host metasediments, whereas TE and REE contents tend to be broadly similar (e.g., Raith et al. 2004). However, in high fluid/rock systems, as shown by proximal tourmalinites (Fig. 1B), ME can be both enriched and depleted, but TE and especially REE may differ greatly due to preferential mobility of some elements, especially light REE (Slack et al. 2000; Čopjaková et al. 2013).

Figure 1. Metasomatic changes (shown in %) for major elements during tourmalinite formation based on Al-normalization relative to unaltered host metasedimentary rocks. A, distal tourmalinites, Broken Hill district, Australia (Slack et al. 1993). B, proximal tourmalinites, Sullivan Pb-Zn-Ag deposit, British Columbia (Slack et al. 2000). Note that in B, data are mainly from stratiform tourmalinites in shallow part of footwall vent complex and exclude data for non-stratiform tourmalinites in deep part of this complex. Abbreviations: ME, molar element; MAI, molar aluminum.

4.2 Boron isotopes

Early insights into the oxygen, hydrogen, and boron isotopic compositions of tourmaline in massive sulphide deposits and tourmalinites (Taylor and Slack 1984; Palmer and Slack 1989) have been greatly advanced by recent studies (e.g., Marschall and Jiang 2011), especially those that report in situ analyses for boron isotopes and major elements (e.g., Pesquera et al. 2005; Trumbull et al. 2011, 2018; Su et al. 2016; Albert et al. 2018). Tourmaline is especially valuable in generally retaining original chemical and isotopic compositions, even in metamorphosed terranes, thus providing a potential record of primary fluid chemistry (Slack and Trumbull 2011; Cabral and Koglin 2012).

Diverse boron sources have been identified in tourmalinites. Although the range of δ11B values for natural reservoirs is now well known, uncertainty still exists in attempts to identify the predominant source. This is particularly difficult for isotopically light boron, for which values in the range of –16 to –4 ‰ may reflect boron derived from granitic magmas, marine sediments, or non-marine evaporites. Importantly, however, very low values of less than ca. –18 ‰ likely record a boron source from evaporites or sediments of non-marine origin (e.g., Palmer and Slack 1989; Romer et al. 2014).

5 Discussion

5.1 Constraints on genesis

High alumina contents of tourmaline (ca. 28-35 wt % Al₂O₃) greatly limit models of tourmalinite formation. The precipitation of tourmaline directly from an aqueous phase, such as metalliferous hydrothermal fluids, requires the transport of significant Al in solution. However, in hydrothermal fluids at low to moderate temperature (<300 °C), Al has appreciable solubility only under low or high pH, and with high contents of fluoride, sulphate, or organic acids (Slack 1993, and references therein). In modern seafloor-hydrothermal systems, Al contents are very low (<0.02 mmol/kg; German and Von Damm 2003) and hence are probably insufficient to permit tourmaline saturation in the vent fluids. However, in high-temperature Si- and Cl-bearing metamorphic and magmatic fluids, Al solubility can be very high (up to ~80 mmol/kg; Manning 2006), thus explaining abundant tourmaline in such settings where fluid B concentrations are also high (e.g., Yardley 2013).

The minimum temperature of tourmaline stability is a further constraint. Although the lowest formational temperature is unknown, a reasonable estimate is 100 to 150 °C, based on data for diagenetic tourmaline overgrowths in sandstones and authigenic grains in cap rocks of a salt dome (Henry and Dutrow 2012). In modern seafloor-hydrothermal systems distal (>100 m) from vent sites, temperatures at or near the sediment-seawater interface are generally <50 °C (e.g., Humphris and Tivey 2000). These and other considerations were the basis for suggestions that tourmaline does not form in modern seafloor environments, instead being derived from an original B-rich gel or colloid precursor (Ethier and Campbell 1977; Slack et al. 1984; Slack 1996).

5.2 Modern seafloor analogs

Modern analogs of tourmalinites are unknown. However, in seafloor environments there appears to be a general affinity of B for Mn, such as on the East Pacific Rise where 300 to 800 ppm B (carbonate-free basis) is preferentially associated with Al-poor Fe-Mn sediments (Bostrom and Peterson 1969). In this setting, B-rich precursors to tourmaline may exist, a possibility supported by the interbedded nature of tourmalinites and coticules in numerous metamorphosed metasedimentary and metavolcanic terranes (Slack et al.
1984; Spry et al. 2000). A related constraint is the low B concentration expected in non-buoyant hydrothermal plumes distal from vent sites, based on the large dilution factor (~10^4) for vent fluids by seawater, as calculated for modern plumes (German and Von Damm 2003). Overall, tourmalinite components that formed at or near the seafloor had sources from (1) hydrothermal plumes: Fe, Mn, Si, B; (2) sediments and felsic volcanics: B, Al, Si, Mg, Ca, Na; and (3) seawater: Si (pre-Cretaceous; Grenne and Slack 2003) and B.

Another potential seafloor site for modern B-rich sediments is at or near high-temperature hydrothermal systems hosted in aluminous sediments or felsic volcanic rocks. Whereas modern sediment-free (basaltic) systems have vent fluids with ca. 350 to 700 µmol/kg B, sediment- and rhyolite-hosted systems have up to 4800 µmol/kg B in vent fluids; seawater has an average of 415 µmol/kg B (German and Von Damm 2003; Yamaoka et al. 2015). The combination of high B in these vent fluids, and availability of abundant Al in the host sediments and felsic volcanics, suggests potential in such environments for modern tourmalinite formation.

In the Red Sea, metalliferous brines in several deep basins have temperatures and B concentrations up to 68°C and 4580 µmol/kg, respectively (Schmidt et al. 2015). Although probably too low for tourmaline growth on the seafloor, such elevated temperatures may permit the formation of a B-rich gel or colloidal. Alternatively, tourmaline could be forming in the subsurface, at higher temperatures, by downward penetration of the brines (cf. Sangster 2002) and subsequent reaction with aluminous sediments.

5.3 Boron metasomatism during diagenesis

The importance of precursor aluminous sediments or felsic volcanic rocks in the formation of stratiform tourmalinites supports a diagenetic origin involving the influx of B-rich hydrothermal fluids. This model is consistent with numerous observations of tourmalinites that preserve sedimentary structures such as graded beds, cross-laminations, and rip-up clasts (Slack et al. 1984; Slack 1996). Within these structures, tourmaline shows preferential replacement of the clay and/or feldspar matrix. A preferred origin (Slack 1993, 1996) involves the migration of B-rich hydrothermal fluids along permeable, sandy beds and the selective replacement of argillaceous beds (or laminae) in the upper parts of unconsolidated sedimentary sequences. This replacement may occur at or near the sediment-water interface, or tens to hundreds of meters below. Such a model is also applicable to permeable felsic volcanics, especially volcaniclastic rocks. The timing of the proposed replacement most likely is during sedimentation or early diagenesis, but a much later timing (e.g., metamorphic) is also possible, if sufficient permeability is maintained for fluid transport over large distances (>100 m) within individual beds or laminae.

5.4 Exploration applications

A first-order exploration guide in stratiform tourmalinites is the presence of base-metal sulphide minerals including discrete grains and inclusions in tourmaline. Occurrence of accessory or minor pyrite or pyrrhotite alone may not be prospective. On a whole-rock basis, tourmalinites with high MnO contents (>1 wt %) present in carbonate or garnet (Fig. 1B), together with positive Eu anomalies (e.g., Lottermoser 1992; Slack 1996), likely reflect exhalative hydrothermal components and thus may be time-correlative units with stratiform sulphide mineralization along strike. Positive Eu anomalies are not a required, however since many ore-related tourmalines lack such anomalies. Tourmalinites without any of these anomalies may not be favorable exploration guides, instead reflecting the diagenetic expulsion of B-rich, but metal-poor, basin fluids.

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The distribution of trace elements in pyrite of carbonate-hosted sulfide deposits of the Kootenay arc of southern British Columbia, Canada

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Abstract. The composition of pyrite from SEDEX and volcanogenic massive sulfide deposits is relatively well established; however, the composition of pyrite from Mississippi Valley-type and spatially related fracture-controlled replacement deposits is not well documented. In this study, we observe contrasting trace element chemistry between the two deposit types in the Kootenay arc. Strongly zoned pyrite from Abbott-Wagner, a fracture-controlled replacement deposit, has elevated Au, As, Cu, Ag, Cd, In, Sn, and Sb values compared to pyrite from Jackpot, a typical Kootenay arc MVT deposit. The inverse is true for Co and Bi. Concentrations of Au in the Abbott-Wagner pyrite range from 0.072 to 6.5 ppm (median = 1.6 ppm) and is lower at Jackpot (0.01 to 0.22 ppm; median = 0.04 ppm). The contrasting signature can partly be explained by their mineralogy - galena, sphalerite, pyrite, chalcopyrite and tetrahedrite at Abbott-Wagner and galena, sphalerite, pyrite, and pyrrhotite at Jackpot. Further studies are required to test this hypothesis.

1 Introduction

Many carbonate-hosted Zn-Pb (±Ag, ±Au) deposits of southern British Columbia are distributed along the Kootenay arc, in two main districts: the Salmo and Duncan camps (Fig. 1). The Jackpot deposit is located in the Salmo camp and the Abbott-Wagner deposit is located north of the Duncan camp. These deposits are hosted by deformed Lower Cambrian shallow water platformal carbonate rocks of the Badshot Formation and its equivalent, the Reeves Member of the Laib Formation. The Kootenay arc carbonate-hosted Zn-Pb (±Ag, ±Au) deposits belong to two distinct categories: (1) stratabound lenticular concentrations of Zn-Pb sulfides (e.g. Jackpot) interpreted as Mississippi Valley-type (MVT), and (2) fracture-controlled replacement Pb-Zn (±Ag, ±Au) sulfides (e.g. Abbott-Wagner).

Pyrite is known to incorporate numerous minor and trace elements (As, Ag, Au, Bi, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Te, Tl, Zn) in its crystal structure, or as micro-inclusions (Gadd et al. 2016). Pyrite is ubiquitous throughout most sulfide deposits in the Kootenay arc. Herein we present laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) data for pyrite from the Jackpot (MVT) and the Abbott-Wagner deposits (fracture-controlled replacement, respectively). Similar studies on other deposits in the Kootenay arc are ongoing to further provide insight on migration and precipitation of metallic elements during mineralization events.

Figure 1. Geologic map of south-eastern British Columbia, Canada, showing the locations of carbonate-hosted Zn-Pb (±Ag, ±Au) deposits within the Kootenay arc (dark blue). Modified from Katay (2017).

2 Geological setting

The Kootenay arc is part of the Kootenay terrane, which lies within the Omineca belt, one of five morphological belts of the Canadian Cordillera (Wheeler and McFeely...
1991; Monger and Price 2002). The Omineca belt consists of variably deformed and metamorphosed rocks of continental affinity that are exposed east of Mesozoic arc and back-arc sequences (i.e. Intermontane belt) and west of deformed Paleozoic continental margin sedimentary rocks (i.e. Foreland belt). The Kootenay terrane comprises dominantly lower to mid-Paleozoic sedimentary and volcanic rocks deposited on the distal western edge of ancestral North America (Gabrielse et al. 1991; Colpron and Price 1995; Paradis et al. 2006).

Most carbonate-hosted Zn-Pb (±Ag, ±Au) deposits are located within the Kootenay arc, an arcuate geomorphic feature within the Kootenay terrane defined by a belt of complexly deformed rocks extending at least 400 km. This arc extends from Revelstoke southwest to across the Canada-US border (Fyles 1964; Fig. 1). The arc lies between the Purcell anticlinorium in the Purcell Mountains to the east, and the Monashee Metamorphic Complex to the west (Figure 1). It consists of a thick succession of thrust-imbricated Proterozoic to early Mesozoic miogeoclinal-platform to deep marine strata of sedimentary and volcanic origin (Brown et al. 1981).

Three phases of folding are recognized within the Kootenay arc. Large amplitude (10 km-scale) west-verging recumbent folds were deformed by two phases of upright, tight to isoclinal folds, under conditions of lower greenschist to lower amphibolite facies regional metamorphism and upper amphibolite facies contact metamorphism (Fyles 1964; Warren and Price 1993). This polyphase deformation produced a pervasive transposition of bedding that locally obscures stratigraphic relationships (Colpron and Price 1995). Colpron and Price (1995) outlined a regionally consistent stratigraphic succession along the Kootenay arc that is summarized below.

The lower part of the stratigraphic section along the Kootenay arc is composed of Eocambrian siliciclastic rocks and carbonate rocks of the Hamill Group and Mohican Formation. These rocks are overlain by the Lower Cambrian Archaeocyathid-bearing carbonate rocks of the Badshot Formation and its equivalent, the Reeves Member of the Laib Formation (Fyles and Hewlett 1959; Fyles 1964). The carbonate rocks hosting the Zn-Pb (±Ag, ±Au) sulfide deposits are conformably overlain by the lower Paleozoic siliciclastic, basal shales and mafic volcanic rocks of the Lardeau Group (Colpron and Price 1995).

3 Sulfide deposits

3.1 Jackpot deposit

Jackpot is a stratabound replacement Zn-Pb sulfide deposit in dolomitized limestone of the Reeves Member, Lower Cambrian Laib Formation (Fyles and Hewlett 1959). It consists of at least four mineralized zones: Jackpot Main, Jackpot Lerwick, Jackpot West, and Jackpot East. It has 943,300 tonnes of indicated ore grading 4.68% combined Pb+Zn with an additional 2.93 million tonnes of inferred and speculative ore (BC MINFILE: https://minfile.gov.bc.ca/).

The main sulfide minerals are sphalerite, pyrrhotite, pyrite, and marcasite, with trace galena. They form concordant lenses and layers oriented parallel to foliation in a matrix of recrystallized and altered carbonate minerals. All minerals show some degree of deformation with pyrite being the least-deformed sulfide mineral.

Pyrite selected for this study are from the Jackpot Main and Lerwick zones. Pyrite occurs as irregular, anhedral to rounded, disseminated crystals and as aggregates of brecciated and fractured crystals enveloped in massive pyrrhotite and its alteration mineral, marcasite (Fig. 2). Sphalerite, which occurs as discontinuous string, is replaced and enveloped by pyrrhotite. The fractures in pyrite are filled with more ductile sulfide minerals, sphalerite and pyrrhotite.

![Figure 2. Photomicrograph of large pyrite (Py) grain surrounded by deformed sphalerite (Sph), pyrrhotite (Po) and marcasite (Mrc) from sample 08-SP-102B of the Jackpot Lerwick zone.](image)

3.2 Abbott-Wagner deposit

Abbott-Wagner is a polymetallic fracture-controlled replacement Zn-Pb-Ag-Au sulfide deposit hosted in the basal part of the Index Formation and the upper part of the Badshot Formation. Mineralization occurs as sulfide-rich quartz veins in calcareous and carbonaceous phyllites and phyllic schists of the Index Formation and as lenses of massive to semi-massive sulfide minerals replacing carbonate rocks of the Badshot Formation. The total historic mineral resource is estimated at 296,650 tonnes grading 7.81% Pb, 6.39% Zn, and 295 g/t Ag (BC MINFILE: https://minfile.gov.bc.ca/).

The replacement mineralization in carbonate rocks consists of clustered and disseminated galena, sphalerite, and pyrite, with trace chalcopyrite and tetrahedrite in quartz-calcite gangue replacing the dolomite matrix and cementing brecciated fragments of carbonate rocks and phyllites.

Pyrite analysed in sample 08-SP-155 is categorized as: 1) relict pyrite occurring as subhedral to rounded grains with embayments in massive aggregates of galena; this pyrite is rich in inclusions of chalcopyrite, sphalerite and carbonates; and 2) disseminated,
euhedral, cubic to cubo-octohedral crystals and irregular clusters of fractured and brecciated anhedral crystals in a carbonate matrix (Fig. 3). The fractures are filled by galena, sphalerite, and chalcopyrite, and pyrite grains are commonly adjacent to sphalerite.

Figure 3. Photomicrograph of pyrite (Py) and sphalerite (Sph) from sample 08-SP-155 of the Abbott-Wagner deposit.

4 Materials and LA-ICP-MS methods

A suite of polished thin and thick sections were made from representative samples from the Jackpot and Abbott-Wagner deposits for petrographic and LA-ICP-MS analyses.

We measured the concentration of Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Mo, Ag, Cd, In, Sn, Sb, Te, Au, Ti, Pb, and Bi in pyrite from the Abbott-Wagner and Jackpot deposits using LA-ICP-MS spot analyses (n = 25) and 2-dimensional element mapping. The analyses were done at the Geological Survey of Canada using an Agilent Technologies 7700x ICP-MS coupled to a Teledyne Photon Machines Analyte G2 excimer laser ablation system (λ: 193 nm) and processed following the method of Lawley et al. (2017). Analyses for both deposits were done on non-deformed anhedral pyrite grains. Detailed methodology is available upon request.

5 LA-ICP-MS results on pyrite

5.1 Jackpot deposit

Pyrite from the Jackpot deposit has higher concentrations of Co and Bi compared to that of the Abbott-Wagner deposit (Fig. 4). The inverse is true for all other elements examined. Concentrations of Au (0.01 to 0.22 ppm; median = 0.04 ppm) and Ag (0.3 to 0.8 ppm; median = 0.15 ppm) are very low at Jackpot. Ni and As are the only two elements that show good positive covariance; the covariance is especially strong at Jackpot Main (R² = 0.84). Notably, As values differ significantly between the Jackpot Main (280-900 ppm, median = 360 ppm) and Jackpot Lerwick (<0.88 ppm, median = 0.4 ppm) zones.

Figure 4. Box and whisker plots of trace element contents in pyrite from the A) Abbott-Wagner, and B) Jackpot deposits.

5.2 Abbott-Wagner deposit

Pyrite from the Abbott-Wagner deposit has elevated Au, As, Cu, Ag, Cd, In, Sn, and Sb compared to Jackpot (Fig. 4). In general, Au is enriched (0.072 – 6.5 ppm, median = 1.6 ppm), and moderately covaries (R² = 0.4 to 0.6) with Ag and Cu. However, this covariance is not always observed on element maps of pyrite from sample 08-SP-155. This is because some pyrite grains show positive covariance of Au with Cu and Ag, and others do not. The same phenomenon occurs between Au and As. Arsenic content varies from 1090 to 11820 ppm (median = 4722 ppm). On element maps, Au (Fig. 5) and As show distinctive rich bands. In detail, however, Au and As bands are not spatially coincident within the pyrite grains, resulting in imperfect covariation. Gold was not observed microscopically in polished thin sections and is most likely lattice-hosted or present as nanoparticles in pyrite.

On element maps, zonation in pyrite shows positive covariance between Cu, Zn, Ga, Ge, Ag, Cd, In, Sn, and Sb; and positive covariation between Ni and Co. Some of these elements, such as Cu and Zn, correspond to chalcopyrite and sphalerite inclusions in pyrite, respectively. Other elements, such as Co and Ni, may be substituting for Fe²⁺ in pyrite.

Silver concentrations vary widely between pyrite grains (0.019 to 56.9 ppm) and within a single pyrite grain (0.4 to 56.9 ppm). Copper and Sb show similar variations. There is strong positive covariance between Ag and Cu (R² = 0.87) and between Ag and Sb (R² = 0.99).
In this preliminary study, we analysed pyrite grains with similar microscopic textures (i.e., irregular anhedral crystals that show no tectonic deformation) from Jackpot, a MVT deposit, and from Abbott-Wagner, a fracture-controlled replacement deposit. Both share the same tectono-stratigraphic setting within the Kootenay arc.

Pyrite from the Abbott-Wagner deposit is rich in Au and As. Gold enrichment does not appear to be related to deformation-induced microstructures, and may occur as nanoparticles in pyrite or be lattice-hosted. Silver, Cu, and Zn are also elevated. These trace elements are characteristic of the polymetallic nature of the Abbott-Wagner deposit and of the mineral association represented by galena, sphalerite, and pyrite, with trace chalcopyrite and tetrahedrite.

Pyrite from the Jackpot deposit has lower trace element concentrations than pyrite from Abbott-Wagner with the exception of Co and Bi. Overall, the trace element content in pyrite of this MVT deposit is low and possibly reflecting recrystallization and brecciation. Significant modification of primary trace element distribution resulting from hydrothermal reworking, recrystallization, and metamorphism has been observed in many sediment-hosted deposits. Another possible explanation is that this trace element signature is characteristic of the type of sulfide deposits (i.e. MVT) of the Kootenay arc. Further studies are required to test this hypothesis.

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Destabilisation of titanite in the Roxby Downs Granite surrounding the Olympic Dam Fe-oxide Cu-U-Au-Ag deposit

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Abstract. Titanite textures and geochemistry have been investigated from the Roxby Downs Granite, host to the Olympic Dam Fe-oxide Cu-U-Au-Ag deposit, South Australia. Three textural subtypes of titanite are documented: primary magmatic (cores and rims); late/interstitial; and secondary (low T recrystallisation). Magmatic cores are defined by enrichment in LREE (~3 wt%), Nb (up to 1 wt%) and Zr relative to rims, which typically contain <1 wt% LREE and Nb, as well as greater concentrations of Al, Ca, Fe and F. Secondary titanite forms as a low temperature hydrothermal overprint on primary titanite, as well as an alteration product of chloritised phlogopite. Titanite breakdown is a ubiquitous feature of the RDG, and occurs through interaction with CO2- and F-rich fluids, forming REE-fluorocarbonates, which are subsequently overprinted by REE-phosphates with increased proximity to the Olympic Dam Breccia Complex. This change is related to interaction with fluids containing appreciable free PO42-, liberated from local fluorapatite dissolution, and represents later/retrograde stages in the formation of the Olympic Dam deposit.

1 Introduction

Titanite is a common accessory mineral in intermediate-silicic igneous rocks and numerous studies have shown its potential to reflect bulk compositions of source rocks and track the physicochemical conditions of evolving magmatic-hydrothermal systems (Wones 1989; Nakada 1991; Piccoli et al. 2000; Frost et al. 2001; Mcleod et al. 2011). The applicability of titanite as a geochemical indicator mineral in magmatic-hydrothermal ore deposits and igneous-metamorphic terranes has also been documented (Buick et al. 2007; Storey et al. 2007; Smith et al. 2009; Ismail et al. 2014; Storey and Smith 2017). Here we report textures and geochemistry of titanite from the ~1595 Ma Roxby Downs Granite, host to the Olympic Dam Fe-oxide Cu-U-Au-Ag deposit, South Australia, in an attempt to further constrain hydrothermal stages preserved in the host rock and thus gain a greater understanding of fluid evolution and deposit genesis.

2 Geological background

The ~1595 Ma Roxby Downs Granite (RDG) hosts the world-class Olympic Dam Fe-oxide Cu-U-Au-Ag deposit, which is located in the north of the Olympic Cu-Au Province on the eastern margin of the Gawler Craton. Rocks of the Hutchison Group (~2000-1860 Ma), Donington Suite (~1845-1810 Ma) and Wallaroo Group equivalents (~1750 Ma) form the Paleoproterozoic basement of the Olympic Dam region (Creaser 1989; Ferris et al. 2002; Jagodzinski 2005). These units are unconformably overlain and intruded by felsic and mafic-ultramafic lithologies of the Hiltaba Suite (HS) and Gawler Range Volcanics (GRV).

Deposition of Cu-U-Au-Ag mineralisation at Olympic Dam is considered to be contemporaneous with regional magmatism at ~1590 Ma (e.g. Johnson and Cross 1995; Jagodzinski 2005; Ciobanu et al. 2013; Courtney-Davies et al. 2016, 2019). Hydrothermal breccias of the Olympic Dam Breccia Complex (ODBC) host the Cu-U-Au-Ag mineralisation and are contained within the RDG. Compositions and textures within the ODBC are gradational, and comprise a continuum from sericite-hematite-altered granite through mineralised, hematite-rich breccias to barren hematite-quartz breccias in the deposit center (Ehrig et al. 2012).

The RDG is equigranular to porphyritic, medium-coarse grained and peraluminous to weakly metaluminous (Creaser 1989; Kontonikas-Charos et al. 2017). Dominant minerals are alkali feldspar (40-50%), plagioclase (20-25%), quartz (20-25%), with minor edenite and phlogopite (5-10%). Magmatic accessory minerals (~5%) include magnetite, titanite, ilmenite, fluorapatite, zircon and allanite. Other minor minerals include: fluorite, tourmaline, uranothorite, REE-fluorocarbonates (parisite, bastnäsite and the unnamed polytype B2S) and sulphides (pyrite, chalcopyrite, galena, sphalerite and molybdenite) (Ehrig et al. 2012; Ciobanu et al. 2017; Kontonikas-Charos et al. 2017, 2018a, b).
3 Results

3.1 Petrography

For a comprehensive summary of primary magmatic titanite textures see Kontonikas-Charos et al. (in review). Secondary titanite appears green in plane-polarised light and is distinguished from primary titanite rims by its irregular zonation (Fig. 1a). It also occurs as an alteration product of phlogopite, forming fine-grained, cleavage-oriented lenticular inclusions enclosed within clinohlore (Fe# ~0.35-0.45), typically along rims and parallel to the basal plane (Fig. 1b).

Partial to complete breakdown of titanite is observed throughout the RDG. Initial dissolution occurs along the crystal face and produces a microporous phase at the reaction interface which propagates towards grain interiors (Fig. 1c). Further destabilisation of titanite produces coarser symplectites of a clinohlore (Fe# ~0.3) + calcite matrix intergrown with hetero-oriented Ti-oxide, Ce-dominant REE-fluorocarbonates (parisite and bastnäsite), and quartz. The predominance of chlorite over calcite in the alteration matrix decreases with sample depth. Most primary titanite shows evidence of such breakdown, and in many cases, large polymineralic pseudomorphs are all that remain.

In granite samples affected by sericite-hematite alteration, titanite is no longer preserved. Rather, complete breakdown of titanite has produced euhedral pseudomorph grains of Ti-oxide and REE-phosphates (monazite, xenotime) + REE-fluorocarbonates within a dolomite and chamosite (Fe# ~0.65) matrix (Fig. 1d). With increased proximity to the ODBC and intensity in alteration, quartz + K-feldspar + sericite (Fe, Mg-rich) ± hematite predominate over chamosite and dolomite in the matrix, whereas REE-phosphates are the sole REE-minerals within the resultant pseudomorphs.

3.2 Geochemistry

Electron microprobe analyses reveal intracrystalline variation in major and minor elements of titanite cores and rims, as well as between late/interstitial and secondary titanite. Brighter BSE cores are markedly enriched in LREE (~3 wt%), Nb (up to 1 wt%) and Zr relative to darker BSE rims. In contrast, rims typically contain <1 wt% LREE (La, Ce, Nd) and Nb, however they are richer in Al, Ca, Fe, and F and calculated OH than cores. Binary plots in Figure 2 illustrate these characteristics and show strong correlations consistent with the coupled substitutions at the octahedral Ti site and 7-fold polyhedral Ca site: (Al, Fe)$^{3+}$ ↔ Ti$^{4+}$ + (OH, F); and Ca$^{2+}$ + Ti$^{4+}$ ↔ REE$^{3+}$ + (Al, Fe)$^{3+}$. Late and secondary titanite are also distinguished by major and minor element variation, defined by progressive increases in F, Al and Fe accompanied by depletion in LREE (La, Ce, Nd), Nb and Y (Fig. 2).

Laser Ablation ICP-MS maps provide a visual insight into the spatial distribution of elements in titanite, either in the crystal lattice (solid solution) or as inclusions. Selected elemental maps are shown for primary, late and secondary titanite (Fig. 3). Zirconium (not shown), REE (Ce, Eu) and Y are strongly correlated and show high concentrations within primary titanite cores. All these elements are significantly depleted in recrystallised and late titanite. Minor dissolution of primary titanite has resulted in the redistribution of REE in irregular inclusions, identified as REE-fluorocarbonates within the REE-poor calcite ± clinohlore and Ti-oxide matrix. Interestingly, some zones within late titanite and recrystallised primary titanite show decoupling of Eu from other REE. Uranium and $^{206}$Pb (not shown) are negatively correlated with Th, and generally concentrate along rims and within late titanite. Recrystallised titanite is almost devoid of Nb and Ta (not shown), however they appear to preferentially partition into newly formed Ti-oxide. Tin and Sc (not shown) show a consistently low abundance within titanite cores, which steadily increases towards grain.


Figure 2. EPMA data binary plots of titanite textural subtypes in the Roxby Downs Granite. Data presented as atoms per formula unit based on 20(O,OH) for titanite. (a) (Al+Fe) vs F, (b) (Al+Fe) vs Ti, (c) (Ca+F) vs (La+Ce+Nd), (d) Nb vs (La+Ce+Nd).
rims. They also strongly correlate with areas of recrystallised titanite. Vanadium (not shown) has a preference for certain zones towards grain boundaries and, like Sc, is concentrated in recrystallised titanite.

**Figure 3.** BSE image and selected LA-ICP-MS element maps for primary, late and secondary titanite. Scale bar is in ppm.

### 4 Discussion

Titanite breakdown is a ubiquitous feature of the RDG. Textural observations support initial fluid permeation along grain boundaries and microfractures at the titanite crystal interface. The microporous matrix represents the first stage in the dissolution process. As the reaction progresses, the chemical components of titanite mix with percolating fluids (likely introducing additional Fe, Al and Mg) and eventually precipitate as pseudomorphs comprising a fine-grained calcite + clinohlore matrix with coarser Ti-oxide + REE-fluorocarbonates (parisite and bastnasite) + quartz. Although the overall precursor grain shape is retained (e.g. pseudomorphic), neither calcite nor clinohlore (the dominant matrix minerals) share any structural similarity with titanite. This explains the extremely fine crystalline nature of the initial matrix, which would be a consequence of complete breakdown of titanite structural bonds. Primary titanite rims are relatively unaffected by dissolution in comparison to cores, indicating hydrothermal fluids were in disequilibrium with the F-poor, REE-Ti-rich cores, and that F and REE contents may influence titanite stability under certain physicochemical conditions.

Fluids responsible were likely rich in CO₂ and F, based on the presence of fluorocarbonates and calcite as alteration products. Similar alteration assemblages in corroded titanite grains have been reported from numerous other granitic rocks (Pan et al. 1993; Morad et al. 2009; Middleton et al. 2013), with inferences for interaction with hydrothermal fluids characterised by high CO₂ and HF activity levels. This is also supported by experimental studies, which indicate that both CO₂ and F promote titanite destabilisation (Hunt and Kerrick 1977; Troitzsch and Ellis 2002).

Suitable element sources in the RDG include the chloritisation of phlogopite (~3 wt% F) which likely produced FCO₃⁻-bearing fluids and released Fe, Al and/or Mg, which can account for the presence of chlorite in the resultant alteration assemblage. A similar source of F has been suggested in other altered granitic rocks (e.g. Förster 2000; Middleton et al. 2013). In addition to phlogopite, albitionisation of adjacent and local plagioclase could also be a suitable source of Al for alteration pseudomorphs which contain chlorite.

The prevalence of REE-phosphates over REE-fluorocarbonates in pseudomorphs, observed in sericite-hematite-altered RDG, would require a change in physicochemical conditions that promotes the availability of free phosphate anions. In the case of the RDG, fluorapatite is the main carrier of PO₄³⁻ and would thus be the most likely source. Previous mineralogical and geochemical studies on these samples (Krneta et al. 2016, 2017) provide substantial evidence for multistage dissolution of fluorapatite and eventual replacement by quartz through interaction with highly acidic, CO₂-rich fluids. The initial dissolution of fluorapatite would thus release PO₄³⁻, as well as Ca²⁺ and F⁻, to the fluid, allowing for precipitation of monazite and xenotime. At this later stage, low temperature and high acidity (low pH) would likely buffer F⁻ in the fluids as HF (e.g. Migdisov et al. 2016). Florencite may also form on behalf of fluorapatite at this stage (Krneta et al. 2016, 2017). The observation of early REE-fluorocarbonate and later REE-phosphate crystallisation is consistent with REE-mineral speciation within the Olympic Dam Breccia Complex (Schmoldt et al. 2017, 2019).

As a significant repository for REE (> 5 wt%) and the dominant RE host in the RDG (unpublished MLA data), the destabilisation of titanite and subsequent element recycling likely contributed to the overall anomalous REE concentrations reported at Olympic Dam. The work presented here further substantiates the utility of titanite and its alteration products to reflect physicochemical changes in intrusion-hosted magmatic-hydrothermal deposits.

### 5 Conclusions

Breakdown of titanite is selective and typically affects primary cores more than rims. The resultant alteration assemblage (clinochlore + calcite + Ti-oxide + REE-fluorocarbonates + quartz) is indicative of interaction with dominantly F- and CO₂-bearing fluids, with additional elements likely scavenged from concomitant alteration of adjacent phlogopite and plagioclase.

With increased proximity to the ODBC, fluorapatite in sericite-hematite-altered RDG samples is favored as the source of PO₄³⁻ for crystallization of REE-phosphates in polymineralic pseudomorphs (after titanite). This is consistent with later/retrograde stages of deposit genesis.

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Skarns in Eastern Pampean Ranges of Córdoba, Argentina

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Abstract. The lithological constitution of the Neoproterozoic-Cambrian metamorphic basement of the Eastern Pampean Ranges of Córdoba (EPRC) has favored the formation of skarns and skarn deposits from the Cambrian to the Carboniferous, covering all the metamorphic-deformational and magmatic cycles. This contribution summarizes the main characteristics of these rocks, making mention of the antecedents published up to now.

1 Introduction

Formerly referred to as “pneumatolitic contact rocks” or “tactites”, the first mention of skarns in the EPRC (Fig. 1) is attributed to Beder (1922) who described the presence of extraordinary crystals of different calc-silicate minerals like garnet, vesuvianite, wollastonite and epidote as aggregates, bands, lenses and single crystals (some garnet crystals as large as 10 cm) in different marble quarries.

The meta-sedimentary basement of the EPRC is linked to an old carbonate-pelitic platform of Neoproterozoic age exposed to metamorphic-deformational episodes of great magnitude (until partial fusion) which conditioned the internal structure and current lithotypes. The most representative metamorphic lithologies of the basement are defined in order of abundance by migmatites, gneisses, marbles, ultramafic and mafic rocks.

From the Neoproterozoic to Lower Paleozoic, three magmatic cycles of greater expression were recorded, corresponding to the Pampean Cycle, the Famatinian Cycle and the Achalian Cycle. The Pampean Cycle, also known as Pampean Orogeny, corresponds to the amalgamation of the Pampia Terrain with the western edge of the Cratón del Río de la Plata. In the EPRC, Pampean magmatic expressions are represented mostly in Sierra Norte de Córdoba and as small plutons outcropping north of the Sierra Grande and Sierra de Altautina. The geochemical signature of this magmatism corresponds to metaluminous to peraluminous I-type granitoids related to an ancient continental arc magmatism in a tectonic regime of subduction followed by collision (Lira et al. 2014) occurring between ~ 540-515 Ma (Baldo et al. 2014).

The Famatinian Cycle (or Famatinian Orogeny) represents the collision of the Precordillera Terrain with the Pampia Terrain between 478-460 Ma (D’Eramo et al. 2014). The granitoids associated with this event are type I, metaluminous, and poor in K. The bodies are small plutons (some kilometers in their maximum extension) of tonalitic, trondhjemitic, granodioritic and granitic composition (TTG, Rapela et al. 1998).

The magmatic expressions that generated greater participation in the formation of skarns in EPRC, are those linked to the Achalian magmatism of Devonian-Carboniferous age. The Achalian Cycle (~ 366-379 Ma) presents the most important magmatic volumetric expressions. The most representative bodies of this magmatism are the Achala and Cerro Áspero Batholiths (ca., 2500 km² and 660 km², respectively) and its related peribatholithic pegmatitic derivatives that cut the metamorphic complex. There are also negligible plutons peripheral to these masses (e.g., Capilla del Monte, 336...
is to review previous work on these rocks in the EPRC, fluid-rock interaction (infiltration and diffusion) with basement (especially marbles) resulted in extensive processes of magmatic differentiation (Lira and Sfragulla 2014, and references therein).

The interaction of these igneous rocks with the basement (especially marbles) resulted in extensive fluid-rock interaction (infiltration and diffusion) with concomitant formation of skarns. The aim of this paper is to review previous work on these rocks in the EPRC, emphasizing the main characteristics and distinctions between each magmatic event.

2 Pampean skarns

Pampean skarns are not well developed in EPRC. The only works published to date on skarns linked to the Pampean environment are those studied by O'Leary et al. (2000) and Espeche et al. (2019). For the Batholith of Sierra Norte-Ambargasta, O'Leary et al. (2000) described a skarn formed from a spessartitic lamprophyre and a quartz-calcite alteration zone in contact with the regional granodiorite. The skarn is constituted by garnet, pyroxene, amphibole, prehnite, epidote and calcite and does not host significant resources. Espeche et al. (2019) referred to a Fe-Cu ± Zn skarn in a marble quarry in Malagueño city formed at the lithological contacts of marbles, gabro-dioritic, tonalitic and alkal-feldspar dikes and amphibolites. These authors attribute two different hypotheses for the origin of the fluids: 1) linked to a non-outcrop post-deformational cambrian intrusive and 2) derived from fluids related to migmatization (and/or granitization) of metasedimentary basement. The formation of metal-bearing skarns would be circumscribed to those areas where protolithic lithologies present, although not necessarily in appreciable quantities, primary (syn-sedimentary) mineralization.

3 Famatinian skarns

During the emplacement of the Famatinian intrusives, some bodies emplaced in rocks of contrasted composition (i.e., marble) in Pampa de Olaen generated centimeter bands of composite barren skarns mostly by calcium plagioclase, clinzoisite, garnet, epidote and titanite. Plagioclase is commonly observed as a pervasive replacement front towards the intrusive, instead of monomineralic bands over the lithological contact. Franchini et al. (1999 and references therein) described in San Marcos Sierra and La Falda, skarns formed from homogeneous marbles, gneisses and schist of Neoproterozoic basement. Skarns are in contact with tonalitic granite and granitic pegmatites, in the case of San Marcos Sierra and with granitic pegmatites with accessories such as beryl, garnet, apatite and limonite from pyrite in La Falda.

4 Achalian skarns

The magmatic expressions that generated greater participation in the formation of skarns in EPRC, are those linked to the Achalian magmatism of the Devonian-Carboniferous age.

The fluids exsolved through the crystallization of igneous rocks related to this magmatism, generated skarns with a mineralogy that clearly reflects the composition of the fluids and is distinctive of the rest of the skarns described above. They are not in contact (at the scale of outcrop) with the parental granitic mass, but it is inferred, from field observations, that the fluids have migrated through large structural discontinuities. These discontinuities may or may not be genetically linked to the location of the granitic masses. There is also evidence of skarns formed from exsolved fluids of pegmatitic bodies in discordant contact with the metamorphic basement as studied by Franchini et al. (1998a, b) in Copina and Cañada del Puerto (Vázquez 1985).

In those regions where the presence of carbonate rocks is abundant, such the Sierra Chica, the interaction of Achalian fluids with these lithologies of such contrasted composition generated large bodies of skarns with the formation of W deposits. There are also evidences of small bodies of scheelitic-epidote skarns formed in mafic rocks belonging to a shear belt of altered ultramafic rock at ∼ 10 km from the northeastern contact of the Achala Batholith. The scheelitic skarns linked to the Achalian magmatism are the deposits of Altautina (Ametrano 1999), Ambul (Hermann 2002), Zinqui (Lyons et al. 1997) and Pampa de Olaen (Jutorán 1965; Valdez 1984, among others). All these deposits share similar characteristics: the associated gangue (or skarn s.s.) commonly forms perfectly developed crystals of sizes that exceed the edge decimeter in some of them (e.g., garnet, epidote, vesuvianite), reflecting a high fluid/rock ratio, conditioning extreme dissolution processes and scheelite is related with retrograde and filling associations. In Pampa de Olaen, elements such as Mn, Zn are abundant both in the prograde as well as in infilling and retrograde associations while elements such Bi, Cu, Sn are randomly manifested. Large amounts of F as filling fluorite and in carrier minerals such as garnets (Franchini and Lira 1998) and vesuvianite, is also a common characteristic. These particularities are similar to those deposits correlated with the global classification of W skarns deposits (Einaudi et al. 1981; Kwak and White 1982; Newberry and Swanson 1986; Kwak 1987; Meinert et al. 2005). In this classification, the geochemical characteristics of the igneous source responsible for the contribution of the acidic fluids carrying the mineralization and other metals fit with the magmatic signatures of the Achalian intrusives.
5 Considerations on the genesis of W deposits.

Studies carried out on the geology and origin of the tungsten deposits sustain that the origin of the calc-silicate rocks (skarns) mineralized with scheelite are linked to impure calcareous rocks associated with a platform pelitic sedimentary package that were metamorphized in the successive metamorphic peaks referred to in each region in particular.

The origin of W was attributed to exhalative processes within an environment of tholeiitic volcanism (Brodtkorb 1991; Ametrano 1999; Gamba 1999; Herrmann 2002; Brodtkorb et al. 2014) without evaluating its geochemical incompatibility. The main argument that supports this theory is the concordance of the calc-silicate lenses with the marbles and amphibolites of the basement and the absence of intrusive bodies (stocks or dikes) in contact with these rocks that allow for zonation or contact metasomatism. However, previous studies carried out (technical-mining reports) in some mining districts defined these scheelite-bearing lithologies as "tactites", "pirometasomatic" rocks or "pneumatolitic contact" rocks, which now refer to skarns (Einaudi et al. 1981; Meinert et al. 2005).

6 Discussion

The lithological constitution of the basement of the EPRC, has favored the generation of exchange reactions by infiltration and the consequent formation skarns. Some skarns are spatially and genetically linked to impure calcareous rocks associated with a platform pelitic sedimentary package that were metamorphized from fluids whose geochemistry allows linking them to exsolved phases of a magmatic source, although this does not implicitly arise in the contact of the skarn (e.g., Pampa de Olaen, Malagueño). Although the published antecedents are widespread, studies concerning the geochemistry and behavior of fluids forming skarns are insufficient and little mention has been made of the metal remobilizing potential in the metamorphic basement of the EPRC.

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Structural controls on sulphide (re)-distribution in Kiruna

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Abstract. In this study, we investigate a potential structural control on sulphide distribution in phyllite from the Kiruna area, northern Norrbotten, Sweden. We use X-ray tomography and X-ray fluorescence analyzed in tandem on a 40 cm section of oriented drill core. Scanning Electron Microscopy and Energy Dispersive Spectrometry are used in combination with optical microscopy to analyze mineralogy and microstructures. The results show that sulphides are distributed along S0 bedding planes, re-distributed along S2 axial planar cleavage planes, and trapped by F2-hinge zones and shear bands visible as elevated sulphide concentrations. The results of this study underlines the strength of X-ray tomography to image 3D geological structures and their relation to mineral distributions.

1 Introduction

The Palaeoproterozoic Kiruna area is the host to a wide variety of metal deposits. In particular, Rhyacian-Orosirian volcanic-sedimentary metasupracrustal belts constitute key exploration targets for iron oxide-apatite (IOA), iron oxide-Cu-Au (IOCG), epigenetic Cu-Au, and syn-exhalative base metal deposits. During tectonism, the total strain was partitioned into these metasupracrustal belts giving rise to crustal scale shear zones that parallel the belt axes and served as conduits for ore-forming fluids. Evidence of fluid-rock interaction is persevered in both regional and local scale and the mineralizations tend to be located in association to the crustal scale structures.

Age constraints on deformation in northern Norrbotten are rare. However, the deformation in this region seems to correlate with known magmatic/metamorphic events at approx. 1.89 Ga and 1.79 Ga (e.g. Bergman et al. 2001) and is considered polyphase (Wright 1988, Bergman et al. 2001, Bergman 2018, Andersson 2019). The majority of results from geological mapping campaigns indicate an early NE-SW crustal shortening (D1), followed by later E-W directed compression (D2), which forms the basis of the present consistent regional understanding in the area.

Recently, new advances in the understanding of the regional structural evolution of the Kiruna area has been made (Bergman 2018, Andersson 2019), and linked to the metallogeny of the region. The deformation is assigned to the inversion (D1-D2), refolding (D3), and further fracturing (D4) of an Orosirian volcanic-sedimentary basin hosting the Kiruna IOA-deposits (Andersson 2019). The IOA- deposits are pre-tectonic in timing and associated to the extensional basin development. In contrast, iron- and copper sulphides are hosted by brittle D2 structures and linked to the compressive brittle-ductile basin inversion (Andersson 2019).

Despite the close association between sulphide mineralization and structures in northern Norrbotten, detailed accounts of the structure-sulphide relations are rare. Instead, structurally controlled sulphide occurrences and deposits are often described in general terms and studied in deposit- or camp-scale (e.g. Bergman et al. 2001, Bergman 2018, Andersson 2019). In this case study, the D2 control on sulphide distribution is further investigated in meso- to micro-scale in order to support the development of robust conceptual models of structural transport- and trapping mechanisms in Kiruna and the wider region. We image the relation between structures and sulphide in dm- to sub mm-scale at 200-µm resolution using a new and innovative method, X-ray computed tomography (CT) and X-ray fluorescence (XRF) analyzed in tandem. This method brings new possibilities for fast and thorough imaging of 3D geological structures and their relations to mineral distributions combined with geochemical data.

2 Local geology

The numerous IOA-deposits and the well-preserved stratigraphic record characterizes the geology of the Kiruna area. The supracrustal pile is dipping and younging to the east (Fig. 1). It constitutes a basal horizon of poorly sorted conglomerates overlain by bimodal volcanic-volcanosedimentary rocks (basaltic-rhyolitic) covered by volcanosedimentary and sedimentary rocks (Frietsch 1979, Martinsson 2004). The supracrustal pile is interbedded by breccia-conglomeratic horizons occurring repetitively throughout the sequence (Frietsch 1979, Andersson 2019). The IOA-deposits are generally hosted by lithostructural boundaries separating compositionally different volcanic rocks.

An approximately N-S aligned structural grain dipping steep to the east, is the most prominent component of the structural pattern in Kiruna. Geological contacts and metasedimentary rocks took up the total strain during reverse shearing with east-side-up kinematics (Wright 1988, Andersson 2019). Competent volcanic units show little or no ductile deformation but show instead evidence of brittle structures developed coeval with the reverse shearing at the contacts and favorable rocks (Andersson 2019).
Geological mapping and drill core logging was conducted during 2017-2018. All structural measurements were collected using a Brunton Geo Pocket Transit and all data was digitized in field on a ruggedized iPad mini device using the Field Move application (Midland Valley Exploration Ltd). One 1173 m oriented drill core (PG81619), intersecting the sedimentary upper part of the supracrustal pile was mapped and sampled.

A 40 cm core sample with a diameter of 51 mm was analyzed by X-ray CT and XRF in tandem at the Orexplore AB facility in Kista, Sweden. The above measurement modalities, together with simultaneous weighing of the sample, enables an assessment of the density variation of the sample, plausible mineralogical composition, and inferred values for non-measured elements – through stoichiometry and a model of the material using minerals as building blocks.

The drill core was cut in appropriate angles to the structural elements. Polished thin sections (30 µm thickness) were prepared at Vancouver Petrographics (VanPetro). Microstructures and mineralogy were investigated using a conventional petrographic polarization microscope equipped with a digital camera (NIKON ECLIPSE E600 POL).

The polished thin sections were coated with carbon prior to analysis with a Zeiss Merlin FEG-SEM-EDS/WDS. Backscattered electron (BSE) imaging was used to find regions of interest. EDS point analysis was performed on the various grains in each section to verify mineralogy. For data acquisition and processing the AZtec software by Oxford Instruments was used.
4 Results

The sericite-chlorite phyllite under investigation represents the uppermost horizon of a heterogeneous volcanic-volcanosedimentary-sedimentary formation that constitutes the hanging wall to the Per Geijer IOA deposits (Fig 1). The phyllite horizon is located at the contact to an overlying 1.5 km thick arenitic unit that was thrust to the west during D2. The phyllite acted as a smear plane during reverse D2 shearing and faulting under brittle-ductile conditions generating faults and mylonite zones. A D3 event responsible for a gentle F3 refolding of the area (Fig. 1) also affected the phyllite horizon producing a S3 crenulation cleavage oriented in high angles to S2.

The sample used as a case example in this study is a whitish-green, partly mylonitized fine-grained rock. The compositional banding constitutes bedding S0 planes defined by sericite + quartz and chlorite. Quartz + calcite veins occur along the mylonitic S2 fabric. S0 is openly to tightly folded by antithetic F2 flanking folds (c.f. Passchier 2001) associated to minute S2 fracture planes and shear bands intersecting the compositional banding (Fig. 2 a, f, g, h). A later S3 crenulation cleavage in sericite or chlorite domains (Fig. 2 b) also affects S0. SEM and EDS analyses in mixed chlorite + sericite + quartz (Fig. 2 d) and sericite + quartz domains (Fig. 2 e)
confirms the mineralogy.

Results suggest that pyrite distribution is mainly controlled by D$_2$ structures. The CT-images reveal that pyrite occurs along S$_0$ bedding planes (Fig. 2 f) and as remobilized pyrite in D$_2$ structures. The D$_2$ structures form structural traps in cm-scale and the largest pyrite accumulations occur in the hinge zones of the antithetic F$_2$ flanking folds (Fig. 2 g) and S$_2$ shear bands (Fig. 2 h). Remobilization of pyrite into minute axial plane parallel S$_2$ offsetting S$_0$ (Fig. 2 f) is also observed and is probably an important transport-type of structural element.

The combined CT-response and XRF-analysis accords with the sericite + chlorite + quartz + pyrite mineralogy of the rock.

5 Discussion

In the competent volcanic rocks of the Kiruna IOA district, Fe- and Cu-sulphides are hosted by brittle D$_2$ structures. These structures have been interpreted as higher order structures developed in response to the brittle behavior of competent units in association to reverse ductile shearing at lithostructural contacts (Andersson 2019). The results in this particular study show that the sulphide distribution in rheologically weak units, such as phyllite, is concentrated in a wider spectrum of D$_2$ structures. In the sericite-chlorite sample used as a case example in this study, pyrite is interpreted to have been transported along S$_0$ and axial plane parallel S$_2$ (Fig. 2 f) and concentrated in F$_2$ hinge zones (Fig. 2 g) and D$_2$ shear bands (Fig. 2 h). These structure-sulphide occurrences are similar to classic examples of structural traps for hydrocarbons (Dolson 2016). However, detailed descriptions of structural traps for metal-bearing fluids are rare from the northern Norrbotten mining district, which is problematic for conceptual modelling of ore forming processes valid for

controlled by fractures and shear bands are shown to be efficient structures to transport and trap metal bearing fluids in meso-scale. The observed structural elements and their ability to transport and trap metal bearing fluids, as interpreted in this study, is summarized in Figure 3. The CT-images (Fig. 2 f-h) confirms the development of F$_2$ in Kiruna as a consequence of reverse shearing and faulting as was suggested by Andersson (2019).

CT-imaging of geological materials is an appreciated geoscientific method for material analysis. Detailed insights into the development of structures in relation to mineralogical and textural features (Kaufhold et al. 2016) proves the strength of the method for structural analysis. The results in this study confirm that detailed structural information can be obtained for materials with relatively low density-contrasts, exemplified by sericite-chlorite in this study. The technique is superior to any standard 2D technique, such as thin section analysis, for the imaging of mineral distributions in relation to structural 3D geometries. The novel method used in the current study is also very useful by its detection of chemical elements and suggestion of plausible minerals.

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Mo mineralization in western Bergslagen, Sweden, marks pre- and late-collisional tectonothermal events during Svecokarelian orogenesis

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Abstract. New zircon U-Pb SIMS and molybdenite Re-Os N-TIMS geochronology results are presented for a mineralized Palaeoproterozoic granite and adjacent skarn zone in western Bergslagen, Sweden. The Mo- and F-mineralized Pingstaberg granite gave a zircon U-Pb concordia age of 1805 ± 9 Ma (2σ, MSWD = 1.5, n = 8). Disseminated molybdenite from the same granite yielded a largely identical Re-Os age of 1801 ± 10 Ma. Molybdenite from the adjacent Kalkåsen-Barnfallet skarn Fe ± Mo zone, which is part of the metasupracrustal sequence hosting the Pingstaberg granite, yielded a Re-Os age of c. 1923 ± 10 Ma. This older age predates syn-orogenic deformation and regional metamorphism (at c. 1.87 – 1.84 Ga), and potentially resolves a syn-volcanic Mo and possibly Fe mineralization event during pre-collisional Svecokarelian orogenesis. The new results add to growing evidence for at least two generations of Mo mineralization in western Bergslagen that mark successive orogenic evolutionary stages and which, based on their differing metal associations, may have exploration significance.

1 Introduction

The Bergslagen region of central Sweden is a classic mining district with a long history of metallic resource exploitation. The district is best known for its Fe and polymetallic base metal deposits, and presently has three active Zn-Pb ± Ag ± Cu ± Au mines. From a metallogenic perspective, different mineral deposit types in Bergslagen display first-order associations with different stages of Palaeoproterozoic orogenesis and related tectonothermalism. For example, syn-volcanic Zn-Pb ± Ag ± Cu ± Au deposits (e.g. Garpenberg) are thought to have formed in local suprasubduction caldera basins at c. 1.90 – 1.89 Ga (Jansson and Allen 2011). In contrast, skarn W-F ± Mo ± Cu deposits (e.g. Wigström, Yxsjöberg) formed during late-collisional (post-subduction?) granite emplacement at c. 1.80 – 1.75 Ga (e.g. Romer and Öhlander 1994). Recent molybdenite Re-Os dating of “Bastnäs-type” skarn Fe-REE-(Cu-Mo-Bi-Au-Be) deposits in western Bergslagen records episodic mineralization at c.1.90, 1.86 and 1.84 Ga, and supports genetic links with early syn-subduction felsic magmatism, and apparently later REE-(Mo)-bearing hydrothermal fluids driven by waning, syn-orogenic plutonism (Holtstam et al. 2014). Further efforts to constrain the character and age of Bergslagen mineral deposits may thus help elucidate broader tectonothermal controls on ore formation, especially for closely juxtaposed systems with differing metal associations and/or mineralization styles.

Figure 1. Summary geology of the Bergslagen region, central Sweden (B, inset map). The study area is also shown (see Fig. 2).

We report new zircon U-Pb and molybdenite Re-Os geochronology results from the Mo- and F-mineralized Pingstaberg granite in western Bergslagen that typifies “late Svecofennian” granites linked to W-F ± Mo ± Cu mineralization. A new molybdenite Re-Os age for the Mo-bearing Kalkåsen-Barnfallet skarn Fe ± Mo zone immediately adjacent to the Pingstaberg granite is also given. Our results more precisely constrain the age of the Pingstaberg granite (and its contained Mo-F mineralization) and tentatively resolve an older, c. 1.92
Ga, phase of Mo (+ Fe?) mineralization with a potentially pre-collisional, syn-subduction origin.

2 Geological setting

2.1 Regional geology

The Bergslagen region comprises c. 1.91 – 1.75 Ga igneous and sedimentary rocks that were episodically deposited, emplaced, deformed and metamorphosed during the Svecokarelian orogenic cycle (Fig. 1; Stephens et al. 2009). Early-stage (c. 1.91 – 1.88 Ga), syn-subduction magmatism produced bimodal mafic and felsic volcanic and gabbroic to granitic plutonic rocks, and subordinate sedimentary deposits, within a juvenile, continental arc-type setting (Allen et al. 1996; Andersson et al. 2006). Subsequent syn-accretionary-collisional events (c. 1.87 – 1.84 Ga) promoted polyphase deformation, regional metamorphism and minor felsic magmatism. A late collisional stage (c. 1.81 – 1.75 Ga) produced a suite of granite-pegmatite intrusions that are locally associated with intragranitic- and exoskarn-style W-F ± Mo ± Cu mineralization (e.g. Ohlsson 1979).

2.2 Geology of the Pingstaberg granite and adjacent Kalkåsen-Barnfallet Fe ± Mo skarn

The Pingstaberg granite is a small (c. 0.7 x 1.5 km), ovoid stock intruding polydeformed, c. 1.9 Ga metasupracrustal rocks near Grängesberg in western Bergslagen (Figs. 1 & 2A). The stock comprises grey to pale pink, fine- to medium-grained, weakly deformed to massive, equigranular biotite granite (Fig. 3A). Locally, pegmatite and quartz-feldspar segregations also occur (Fig. 3B). Fine- to medium-grained (c. 0.5 – 3 mm) molybdenite occurs as irregular disseminations in the granite (c. 1 – 3 vol. %), and forms 2 – 15 mm rosettes in biotite-poor, alkali feldspar ± quartz clots and veins (Fig. 3A-B). Minor fluorite is also disseminated in the granite and associated with pegmatic clots. Geochemically, the Pingstaberg granite is a high-silica, peraluminous, alkali-calcic intrusion with elevated Rb, Y, Nb, U and F concentrations (Billström et al. 1988).

3 Study methods

Mapping and sampling in the Pingstaberg area was
conducted during 2016 and 2017 for about three weeks in total. Zircon U-Pb SIMS geochronology was performed at the Nordsim laboratory, Swedish Museum of Natural History, Stockholm, and followed the procedure detailed in Whitehouse et al. (1999). Analysis of epoxy-mounted zircons was made using a c. 10 µm-diameter O$_2^-$ primary ion beam, and care was taken to avoid visible pits, cracks and inclusions when placing the analytical spots. In total, 68 spots on 45 zircons were analysed, including 26 core-rim pairs.

Following mineral separation at the Geological Survey of Sweden, molybdenite Re-Os N-TIMS geochronology was conducted at the Department of Earth Sciences, University of Durham, using the analytical procedure described in Selby and Creaser (2001). Molybdenite Re-Os ages are given at the 2σ (95%) uncertainty level and incorporate cumulative errors associated with the analytical procedures and 187Re decay constant.

4 Results

4.1 Zircon U-Pb SIMS geochronology

Zircon U-Pb SIMS geochronology results are summarised in figure 4 and a table of the analytical data is available from the lead author. Zircons from the dated granite sample comprised subhedral to euhedral, commonly prismatic to rare stubby crystals (c. 20 – 125 µm in longest dimension). Pre-analysis transmitted light, secondary electron and cathodoluminescence (CL) imaging revealed metamict discolourations, internal fractures and inclusions that are typical for U-rich zircons in c. 1.8 Ga Bergslagen granites. CL imaging also showed oscillatory growth zoning and core-rim domain relationships in most grains, consistent with magmatic crystallisation (cf. Corfu et al. 2003).

![Tera-Wasserburg plot showing U-Pb isotopic data (Pb, corrected) for Pingstaberg granite zircons. Inset plot represents a concordant subset (p > 0.05, n = 8) giving a concordia age of 1805 ± 9 Ma. Plots made using Isoplot 4.15 (Ludwig 2012).](image)

Most of the data are discordant in T-W concordia space and define a quasilinear discordia array with a lower intercept at c. 400 Ma (Fig. 4). This trend and the metamict character of the zircons suggests discordance controlled by partial radiogenic Pb loss (cf. Schoene 2014). A single core domain (green arrow, Fig. 4) yielded a discordant apparent $^{206}$Pb/$^{238}$Pb date of 1887 ± 4 Ma, suggesting inheritance of c. 1.89 Ga source material. Two analyses are negatively discordant although remain on the discordia trend (red arrow, Fig. 4), which may reflect preferential U loss or an older radiogenic Pb component. A subset of eight discordant analyses (inset, Fig. 4) yielded a concordia age of 1805 ± 9 Ma (2σ, 0.50%; MSWD = 1.5), which we interpret as a best estimate for the age of the granite.

4.2 Molybdenite Re-Os N-TIMS geochronology

Disseminated (interstitial), medium-grained (c. 1 – 4 mm) molybdenite from the southwest margin of the Pingstaberg granite (sample ELH170002A; Figs. 2B & 3A) has a Re concentration of 2.3 ± 0.01 ppm and gave a Re-Os age of 1801 ± 10 Ma (2σ, 0.53%). This date is geologically identical to the new zircon U-Pb age given above (Section 4.1) and supports an emplacement age of c. 1805 Ma for the granite.

Disseminated, fine- to medium-grained (c. 0.3 – 3 mm) molybdenite associated with amphibole-garnet ± quartz from the Kalkäsen-Barnfallet skarn (sample CMR160009A; Figs. 2B & 3D) has a Re concentration of 7.1 ± 0.02 ppm and yielded a Re-Os age of 1923.1 ± 10.0 Ma (2σ, 0.52%), which is significantly older than the adjacent granite-hosted molybdenite. The new Re-Os dates thus indicate two temporally and geologically distinct Mo mineralization events in this part of Bergslagen (discussed further below).

5 Discussion

5.1 An accurate and precise ‘older’ age for the Pingstaberg granite

An igneous age of 1781 ± 46 Ma was previously determined for the Pingstaberg granite using zircon U-Pb TIMS geochronology (Billström et al. 1988). This date, although imprecise (± 2.58% at the 2σ-level), provided evidence linking granite emplacement and related Mo mineralization at Pingstaberg to regional, late-collisional tectonothermal events, and refuted earlier suggestions of an older (c. 1.9 Ga) origin for Mo-F-(W) systems in western Bergslagen based on field and mineralogical relationships (e.g. Hellingwerf and Baker 1985).

The new zircon U-Pb SIMS age reported here (1805 ± 9 Ma) is older than the previous c. 1781 Ma TIMS date and more precisely constrains the emplacement age of the Pingstaberg granite. When combined with the new Re-Os age for intragranitic molybdenite at Pingstaberg (1801 ± 10 Ma), a genetic link between c. 1.80 Ga granitic intrusions and proximal Mo-F-(W) mineralization in western Bergslagen is affirmed. The similarity of both ages, acquired using independent isotopic chronometers, also indicates these dates are likely...
accurate. Consequently, other metalliferous granites in Bergslagen with zircon U-Pb 'discordia' ages in the c. 1.78 – 1.75 Ga range may be c. 20 – 30 million years older than presently thought (cf. Woodward et al. 2009). Our geochronology results also highlight the utility of the molybdenite Re-Os chronometer as an alternative to zircon U-Pb dating for high-silica, alkali granites containing both disseminated molybdenite and metamict zircons.

5.2 Potential c. 1.92 Ga mineralization at the Kalkåsen-Barnfallet Fe-(Mo) skarn?

The Re-Os age of 1923 ± 10 Ma for skarn-hosted molybdenite at Kalkåsen-Barnfallet (Fig. 2B) tentatively identifies the oldest known Mo mineralization event in Bergslagen (assuming no disturbance of the molybdenite Re-Os systematics). The sampled molybdenite forms disseminated impregnations in a garnet-amphibole epidote matrix (Fig. 3D) and lacks obvious grain-scale alteration features, although locally (at the outcrop-scale) it has a 'smeared out' or 'entrained' appearance suggestive of remobilisation (Fig. 3C). The determined age, although unexpected considering the skarn's proximity to a c. 1.80 Ga molybdenite-bearing granite (Fig. 2B), may reflect early, 'proto-Svecokarelian' magmatic-hydrothermal events linked to arc magmatism and metasomatic Fe mineralization (cf. Jansson and Allen 2013).

The new c. 1923 Ma Re-Os date overlaps with a weighted average molybdenite Re-Os age of 1904 ± 14 Ma (n = 2; 2σ with full error) for Fe-REE-(Mo) mineralization c. 50 km southeast in the Nora-Riddarhyttan area (Fig. 1; Holstam et al. 2014), and three zircon U-Pb LA-ICP-MS ages ranging from c. 1916 – 1910 Ma for felsic metavolcanic rocks hosting the same mineralization (Linders 2016). Thus, a Mo ± Fe mineralization event linked to pre-accretionary-collisional magmatic-hydrothermal events at c. 1.92 – 1.91 Ga may be geologically plausible at Kalkåsen, although plutonic rocks in this age range from western Bergslagen are presently unknown. Tectonothermal events at that time are further supported by c. 1.94 – 1.91 Ga age signatures in detrital and inherited zircons from across the region (e.g. Andersson et al. 2006).

6 Conclusions

New U-Pb and Re-Os dating of the Pingstaberg granite, an archetypal Mo-F-mineralized granitic stock in western Bergslagen, provide a more accurate and precise timing for its emplacement at c. 1805 – 1801 Ma, and affirms a link with late-orogenic felsic magmatism associated with W-F-Mo ± Cu. A single c. 1923 Ma molybdenite Re-Os age from the adjacent Kalkåsen-Barnfallet Fe-(Mo) skarn tentatively identifies an older (pre-accretionary) Mo ± Fe mineralization event in the area. Combined, the geochronology results suggest closely juxtaposed Mo mineralization in differing settings (skarn vs intragranitic) may represent different tectonothermal events during Svecokarelian orogenesis. Recognition of these temporally distinct generations and metal associations (Fe ± Mo vs W-F-Mo ± Cu) may have exploration significance in this part of the Fennoscandian Shield.

Acknowledgements

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References


Molybdenum metallogeny in the Tauern Window, Eastern Alps, Austria

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Abstract. The Reichenspitze and Alpeinerscharte molybdenum mineralizations are hosted by Variscan metagranites in the Tux nappe of the western Tauern Window, Austria. The Alpeinerscharte mineralization yielded a Re-Os molybdenite age of 306.8 ± 3.1 Ma. Molybdenite is restricted to biotite- and garnet-bearing quartz veins, which are interpreted as metamorphosed argillic alteration selvages in a granite. The Reichenspitze mineralization is hosted by calc-alkaline aplitic A-type metagranites and occurs disseminated and in quartz veins with muscovite and sulfides. The aplitic granite yielded a Rb/Sr age of 292±6 Ma. The mineralization is structurally controlled by intrusion contacts and faults. Associated are sulfides (pyrite and chalcopyrite), a conspicuous Pb-Ag-Bi-Te sulfide and sulfosalt assemblage and a HFSE assemblage comprising apatite, thorite, zircon, and allanite. The mineralization likely represents a metamorphosed and hence remobilized low-grade low fluorine calc-alkaline molybdenum porphyry system developed within post-orogenic to anorogenic Variscan intrusions around 300 Ma.

1 Introduction

The Tauern Window, Austria, hosts a variety of mineralizations, the most important comprising gold, tungsten (scheelite), base metals (Cu, Zn) and molybdenum. Twenty-three molybdenum occurrences are known (Meixner 1952), the largest represented by the Alpeinerscharte deposit where exploration was conducted during World War II (Anonymous 1943; Melcher et al. 1996).

2 Geological overview

The crystalline units of the western Tauern Window include the Zillertal-Riffl system, the Ahorn nappe, and the Tux-Granatspitz nappe. The latter hosts the molybdenum mineralization dealt with in this paper. All units are part of the Subpeninic nappe system, i.e. they formed the distal European margin of the Penninic ocean in which they were overlain by Mesozoic cover series (Schmid et al. 2013). The Tux-Granatspitz nappe mainly comprises the Tauern Batholith, which intruded during the Variscan orogeny within four magmatic pulses at ≥370 Ma, 340 Ma, 300-280 Ma and <280 Ma (Eichhorn et al. 2000; Veselá et al. 2011). Those ages mark the stages of the Variscan orogeny starting with an active margin and ending with orogenic collapse (Eichhorn et al. 2000). Around 215 Ma, increased heat flow possibly related to the break-up of Pangea led to a first hydrothermal overprint (Finger et al. 2017). In the Cenozoic, the units were affected by an eclogite event (Paleocene), a blueschist event (Eocene), and an amphibolite facies regional metamorphism due to the closure of the Penninic ocean (Christensen et al. 1994; Schmid et al. 2004; Schmid et al. 2013; Finger et al. 2017) often referred to as Tauernkrystallisation. Due to extension related to the lateral extrusion of the tectonically higher units and the exhumation of the crystalline units (Ratschbacher et al. 1991), NNE-SSW oriented “alpine joints” hosting the famous Tauerngold and other mineralizations opened.

Figure 1. Tectonic overview of the W part of the Tauern Window. The Reichenspitze and Alpeinerscharte deposits are marked by blue and yellow triangles, respectively. (a) = Tux-Granatspitz nappe; (b) = Ahorn nappe; (c) = Zillertal-Riffl system; green colours = Penninic nappes; blue colours = Subpeninic nappes; those units comprise the Tauern Window. Modified from Schmid et al. (2013).

The metallogeny of the Tauern window is as complex as its history. It starts in the Cambrian with polymetallic VHMS deposits in ophiolites. A major metallogenetic event was the Variscan orogenesis forming metamorphogenic and magmatogenic deposits including the Alpeinerscharte Mo (Mostler et al. 1982; Melcher et al. 1996; Langthaler et al. 2004) and the Felbertal scheelite deposits (Kozlik et al. 2016; Höll and Eichhorn 1998) as most important examples. The molybdenite occurrences are summarized as the “Molybdenum ore district Central Gneiss Supersuite” in the online application IRIS (Weber et al. 2018). Numerous small cupferiferous pyrite mineralizations (“Kieslager”) formed in the Penninic ocean during the Jurassic. The Alpine orogenesis led to overprint and remobilization of many deposits (e.g. U-Cu
mineralizations), due to extensional stress related to the lateral extrusion of the eastern Alps and the unroofing of the Tauern Window. “Alpine” sulfide-rich quartz-gold veins formed during the Miocene (Tauern gold).

3 Reichenspitze area

The occurrence of molybdenite in the Reichenspitze area is known since the 1960s (Karl 1964; Schmidegg 1964), but only attracted the interest of mineral collectors (Walter et al. 2016; Burgsteiner 2017) due to its remote location in a high alpine terrain. Since 2012, exploration fieldwork was conducted by geologists of the Montanuniversität Leoben supported by the Schurfgemeinschaft Zinkwand resulting in a master thesis (Steiner 2018). The area is located in the Tux core (blue triangle in Fig. 1) SW of Krimml directly at the border of the provinces of Salzburg and Tyrol. The mineralization is hosted by calc-alkaline aplitic A-type granites (Haunschmid et al. 1991; Schermaier 1993), which intruded at 292±6 Ma (Rb/Sr dating by Besang et al. 1968; recalculated by Finger et al. 1993) into slightly older Variscan I-type plutons now present as gneisses (Eichhorn et al. 2000) showing S-type affinity due to crustal contamination (Finger et al. 1993). The aplices range from 73-77% SiO₂, and the gneisses from 70-73%, respectively. Both are low in CaO (Fig. 6), and the aplices yield higher K₂O contents (4-6%) than the gneisses (3-4%). The former yield a negative Eu anomaly (chondrite normalized) and are enriched in HFSE. Both lithologies show a pervasive plagioclase saussuritisation following the metamorphic gradient of the Tauernkristallisation (Steiner 2018).

Molybdenite appears as two types in the field: (1) disseminated in the aplitic granite (Fig. 2c), often near the intrusion contact to the granitic gneiss; (2) in sulfide-bearing quartz veins (Fig. 2d), often in the gneisses and only sometimes in the aplitic granite. The latter type appears at higher topographic elevations than the disseminated type. Both types are controlled by faults and intrusion contacts (Fig. 4) and can be traced along the general NE-SW oriented strike in an area measuring 20 km². They occur in several corridors or zones associated with stocks of the aplitic granite. Under the microscope, molybdenite is often located in small (disseminated type) or larger quartz veins (Fig. 2a, b) with muscovite and rare sulfides (mainly pyrite and chalcopyrite). A conspicuous mineralization containing Bi sulfides (bismuthinite), native bismuth, Pb-Bi-Ag sulfosalts (cosalite, illianite, pavonite and others) and Bi tellurides is associated with molybdenite in samples carrying base metal sulfides. Molybdenite is very low in Re (<10 ppm in molybdenite concentrates), but regularly shows blebs of native Bi or Bi tellurides in the 1-10 µm range.

Figure 3. SEM images; a: Typical HFSE assemblage comprising apatite (Ap), thorite (Thr), zircon (Zrn), and allanite (Aln) in quartz (Qz); b: molybdenite (Mol), chalcopyrite (Ccp), and pyrite (Py).

The ore paragenesis comprises assemblages of molybdenite, pyrite, and chalcopyrite (Fig. 3b), with molybdenite being by far the most abundant, and often appearing without the latter two minerals. The aplitic and granitic gneisses carry abundant assemblages of zircon, U-Th-phases, apatite, and allanite (i.e. REE-bearing minerals, Fig. 3a) in the vicinity of the molybdenite mineralization. There seems to be a weak correlation of molybdenite and the abundance of rusty stains (“Branden”, Fig. 4) caused by weathered sulfides.

Figure 4. The aplitic granite (rusty stained appearance) intruded as subvertical dykes and stocks of variable thickness ranging from few meters to 500m with sharp intrusion contacts.
The Mo mineralization likely formed during the pneumatolytic stage of the intrusion of the aplitic granites as a low-grade low fluorine calc-alkaline molybdenum porphyry system and was remobilized during the Neoalpine event, forming a variety of alteration minerals. These include powellite (Ca(MoO₄)), wulfenite (PbMoO₄), betpakdalite-CaCa ([Ca₂(H₂O)₁₁Ca(H₂O)₆][Mo⁶⁺₈As⁵⁺₂Fe³⁺₃O₃₆(OH)]), ichnusaites (Th(MoO₄)₂·3H₂O), nuragheite (Th(MoO₄)₂·H₂O), sardignaite (BiMo₂O₇(OH)·2H₂O), ichnusaite (Th(MoO₄)₂·3H₂O), and ferrimolybdite (Fe³⁺₂(Mo⁶⁺O₄)₃·7H₂O). Metamorphic conditions during the remobilization reached at least upper greenschist facies. Comparable mineralizations have been described from Su Seinargiu, Sardinia (with a very similar alteration assemblage, i.e. Orlandi et al. 2015), and Endako, BC (Selby et al. 2000).

4 Alpeinerscharte deposit

The Alpeinerscharte Mo deposit is located 35 km W of the Reichenspitze area in the Tux core (yellow triangle in Fig. 1). Molybdenite is restricted to quartz veins (Fig. 5) in calc-alkaline I-type granites (Melcher et al. 1996; Langthaler et al. 2004). The molybdenite is intergrown with coarse garnet and biotite at vein selvages (Fig. 5; Melcher et al. 1996). Re-Os dating of molybdenite yielded 306.8 ± 3.1 Ma, and U-Pb zircon dating of the host granites yielded 305.0 ± 6.6 Ma and 306.8 ± 3.8 Ma, respectively (Langthaler et al. 2004).

The subvertical E-W trending quartz veins are concentrated at the ridge between Fußstein and Alpeiner Scharte and reach a maximum thickness of 25 cm, although being normally in the mm – cm range (Melcher et al. 1996). The deposit is interpreted as a late-magmatic, pneumatolytic mineralization formed in a late stage of granite intrusion (Melcher et al. 1996). The original argillic alteration was metamorphosed during the Alpine metamorphic event forming the biotite-garnet vein selvages (Melcher et al. 1996).

5 Comparison and metallogenetic model

Geochemical analysis of metagranites indicates that the Alpeinerscharte I-type granites follow the same differentiation trend as the granites in the Reichenspitze area (Fig. 6). However, the Reichenspitze A-type granites are more differentiated, whereas the Alpeinerscharte I-type granites are similar to the I-type granites in the Reichenspitze area.

The mineralizations are also remarkably similar in mineralogy and texture (Table 1); however, those at the Reichenspitze lack prominent alteration zones around veins, indicating higher temperatures of formation. It is likely, that they represent different levels of porphyry-type late-Variscan intrusions: the Reichenspitze represents a deeper level with mineralization related to the highly differentiated aplitic facies, whereas the molybdenite-quartz veins in the Alpeinerscharte area represent a higher level with stockwork-type ore intruded into less fractionated I-type granites. Although direct radiometric dating of molybdenite in the Reichenspitze area is outstanding, both mineralizations are related to post-orogenic to anorogenic Variscan intrusions (Finger et al. 1997; Eichhorn et al. 2000) caused by wrenching of the Variscan orogen at around 300 Ma (Finger et al. 1997; Eichhorn et al. 2000).

Figure 5. Schematic drawing of the quartz veins at the Alpeiner Scharte. Bio = biotite, Ga = garnet. From Melcher et al. (1996).

Table 1. Comparison of the Mo mineralization at the Reichenspitze and the Alpeinerscharte. If not cited, the data originate from Steiner (2018) (Reichenspitze) and Melcher et al. (1996).

<table>
<thead>
<tr>
<th>Reichenspitze</th>
<th>Alpeinerscharte</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Age</strong></td>
<td>292±6 Ma (Besang et al. 1968; Finger et al. 1993)</td>
</tr>
<tr>
<td><strong>Mineralization</strong></td>
<td>Disseminated and in quartz-muscovite veins</td>
</tr>
<tr>
<td><strong>Paragenesis</strong></td>
<td>Molybdenite, pyrite, pyrrhotite, chalcopyrite, Pb-Bi-Ag-Te phases, U-Th-REE phases</td>
</tr>
<tr>
<td><strong>Enriched elements in mineralized zones</strong></td>
<td>Mo, Cu, Y, Ce, Rb, Th, U</td>
</tr>
<tr>
<td><strong>Depleted elements</strong></td>
<td>Ba, Sr, and Li</td>
</tr>
<tr>
<td><strong>Source</strong></td>
<td>Calc-alkaline aplitic A-type granite</td>
</tr>
</tbody>
</table>
Acknowledgements

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References

The acid phases of the Bushveld Complex – petrogenetic relationships and metallogeny

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Abstract. The acid phases of the Bushveld Complex, comprising the Lebowa Granite Suite, the (upper) Rooiberg Group volcanics and sub-volcanic and/or anatectic granophyres (the Rashoop Suite), remain enigmatic in terms of their petrogenesis, relationship to the mafic Rustenburg Layered Suite, and metallogeny. This paper presents initial results of a study aimed at improving our understanding of the timing and emplacement histories of the acid phases, the source of the magmas, and the formation of a widespread suite of polymetallic, magmato-hydrothermal, mineral deposits that occur in both exo- and endogranitic environments, and formed over a time-span that far out-lives the emplacement history of the magmatic phases themselves.

1 Introduction

Despite decades of research the petrogenetic interrelationships that link the various major pulses of magma emplacement of the Bushveld Complex remain unclear. The principal components of the Complex (Figure 1), namely the Rustenburg Layered Suite (RLS), the Lebowa Granite Suite (LGS), the Rooiberg Group (RG) and sub-volcanic and/or anatectic granophyres (Rashoop Suite - RS), were all emplaced over a brief interval of time (between circa 2060 and 2054 Ma). Whereas the RLS has been extensively studied, the various acid phases of the magmatic province remain enigmatic. The timing and petrogenesis of the acid magmas are poorly understood and a unifying model for the genesis of their Sn-W-Cu-Zn-Pb-Mo-Ag-Au-U-F metallogenic footprint does not exist.

2 Petrogenesis

A compilation of major and trace element geochemistry for the acid phases sheds light on the petrogenesis of a variety of both intrusive and extrusive rocks that broadly conform to an A-type classification:-

- **RG** – rock compositions of the upper, dacitic-to-rhyolitic, Damwal, Kwaggasnek and Schrikkleof Formations (Fig. 1) typically define a single liquid-line-of-descent, which is distinct from those defining the underlying Dullstroom Formation. A hiatus may exist between the emplacement of these two magma pulses, perhaps similar to that which exists between RLS and LGS emplacement.

- **RS** - the majority of granophyres have compositions that coincide with the range of dacite-rhyolite compositions evident in the upper RG. Some ‘pseudogranophyres’, however, have compositions more akin to the basaltic andesites of the lower Dullstroom Formation.

- **LGS** – parts of the Nebo granite have compositions similar to rhyolites of the Kwaggasnek and Schrikkleof Formations, but the Nebo granite also exhibits more fractionated compositions with higher incompatible element concentrations.

- **LGS** – the Bobbejaankop granite is consistently more fractionated than the Nebo granite and typically is emplaced in the apical portions of the
latter.
• LGS - the Klipkloof phase is represented by a dyke-like set of intrusions that are also more differentiated than the Nebo granite and possibly represent the filter-pressed mesostasis after feldspar-dominated fractionation of the latter.
• LGS - the Lease granite is typically the most fractionated part of the RLS and possibly represents a late-stage aplo-pegmatitic phase that often exhibits evidence of fluid saturation and mineralization. In most cases it does not represent the quenched apical portion of a parental Nebo or Bobbejaankop magma chamber.

Figure 2. Diagram illustrating the relationships between the intrusive acid components of the Bushveld Complex (age data from the sources appended).

The Nebo granite represents the mainphase of the LGS, although it too has been intruded as several sheet-like plutons (Verena, Moloto, etc) whose relative ages are uncertain. More differentiated phases such as the Bobbejaankop and Lease granites are likewise undated, but intrude the Nebo granite (Fig. 2). These granites collectively are vertically differentiated – sidewall boundary layer differentiation has concentrated incompatible elements towards the centre of individual intrusive phases, and their roof facies tend towards fluid saturation and mineralization.

A key, but hitherto relatively little studied, unit in the Bushveld province is the extrusive Rooiberg Group. Represented by compositional and volcanological bimodality, it is amongst the largest siliceous extrusive suites in the World and may have formed over a time range spanning both the RLS and LGS.

3 Metallogeny

Mineralization in the Lebowa Granite Suite of the Bushveld Complex is characterised by numerous polymetallic, magmatic-hydrothermal ore deposits represented by a three-stage paragenetic sequence: early magmatic Sn-W-Mo-F ores (600°C>T>400°C), followed by a Cu-Pb-Zn-As-Ag-Au paragenesis (400°C>T>200°C) and then late-stage Fe-F-U mineralisation (<200°C).

The first stage of mineralisation (typified by the endogranitic Zaaiplaats tin deposit) is related to incompatible trace element concentration during crystal fractionation and subsequent fluid saturation of the magma. Evolution of the magmatic fluids, and progressive mingling with externally derived connate fluids, resulted in the deposition of the second stage of mineralisation, often within the same structures as the earlier stages of metal deposition.

The second stage is typified by the fracture-related, endogranitic Spoedwel and Albert deposits as well as the exogranitic, sediment-hosted Rooiberg deposits and is dominated by polymetallic sulphide ores. As the more oxidized, externally derived, fluid component became progressively more dominant, precipitation of hematite, pitchblende and fluorite occurred, again generally along the same fracture systems hosting the earlier sulphide paragenesis.

Small hydrothermal zircons trapped along quartz growth zones from the Spoedwel deposit yield a U-Pb concordia age of 1957 ± 15 Ma suggesting that late stages of mineralization associated with the Lebowa Granite Suite formed up to 100 My after magma emplacement (Robb et al., 2000). By contrast, thermal modelling suggests that magmatic-hydrothermal activity should have ceased within 4 My of emplacement, implying that the mineralization event was short-lived. Resolving this contradiction could be achieved if the early Sn-W-Mo-F paragenesis is attributed to magmatic-hydrothermal processes, but later parageneses were longer-lived and episodic, and possibly linked to Palaeoproterozoic orogenic activity along the margins of the Kaapvaal Craton.

Polymetallic Sn-W-Cu-Zn-Pb-Mo-Ag-Au-U-F mineralization is concentrated in the LGS, but exogranitic styles are also evident both in the RG and RS and the Transvaal Supergroup country rocks. Although mineralization is broadly magmatic-hydrothermal in character, little is understood of the relationship between crystal fractionation and fluid saturation, and the relative partitioning of metals between magmatic and hydrothermal settings. Vectors to potential mineralization are likely to be derived from the understanding and detection of fractionation mechanisms, alteration footprints and zones of depletion caused by metal-rich fluid extraction (Fig. 3). Deciphering these vectors is being carried out at several scales, from district scale alteration zonation to outcrop scale identification of fluid saturation parameters. Vugs in the tin-bearing Bobbejaanop granite, for example, reflect mineralization and alteration processes at the deposit scale. At an even smaller scale zircon microchemistry is proving to be a faithful recorder of the fertility of its parental magma.
This paper explores new ideas related to the petrogenesis and metallogeny of the highly prospective acid phases of the Bushveld Complex. The presence of highly fractionated, fertile A-type granite magmas emplaced at both shallow intrusive and extrusive levels of the crust, together with the accompanying and widespread exsolution of metal-endowed fluid and volatile phases, has resulted in a polymetallic Sn-W-Cu-Zn-Pb-Mo-Ag-U-F mineral endowment, the full extent of which has yet to be realized.

References

Ta-Nb-Sn-W-Au mineralization in the Mesoproterozoic metasediments of the Karagwe-Ankole belt (Rwanda, DRC) and its relation to early Neoproterozoic orogeny and magmatism

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Abstract. A recent renewal of interest and research into Nb, Ta, Sn, W, Li and Au deposits of the Central African Mesoproterozoic Karagwe-Ankole belt (KAB) has led to new insights regarding its metallogenesis. This study provides an overview of the geodynamic framework of the KAB, including its magmatism and mineralization. During compressional deformation, barren quartz veins are intensely folded. A second quartz vein generation developed inside the fold hinges. Reverse faults occur in the hinge zone of such folds. After compression, but still during tectonism, Neoproterozoic granite intrusions (G4) are emplaced. Hydrothermal W-rich quartz veins with a mixed magmatic and metamorphic origin formed after folding and cleavage development. Highly fractionated and often metasomatized pegmatites are enriched in Ta-Nb and Sn. Extensional tectonism is evidenced by boudinaged pegmatites, which post-date vein-type W mineralization. Sigmoidal quartz veins and shear zones are an expression of late tectonic shearing. Gold mineralization at Byumba (Rwanda) could be related to this shear phase, but a hydrothermal magmatic source for this deposit cannot be excluded. Sn mineralization is associated with greisenization of pegmatites and with quartz veins. These Sn deposits originate from magmatic fluids, evolved from pegmatitic melt and post-date folding and faulting.

1 Introduction

The Mesoproterozoic Karagwe-Ankole belt (KAB) stretches from the Kivu-Maniema region in the DR Congo in the south over Burundi and Rwanda to southwest Uganda in the north. It hosts important Nb, Ta, Sn, W, Li and Au mineralization, which occurs associated with lithium-tantalum-cesium family, rare-element pegmatites (Hulsbosch et al. 2014; Melcher et al. 2015), while quartz veins (Dewaele et al. 2016; Pohl and Günther 1991) host Au, Sn and W. After many geological studies carried out in the 1960s, renewed interest in the ore deposits in this part of Central Africa boosted the application of new analytical techniques to gain insights in their metallogenesis (e.g. Hulsbosch et al. 2016; Pohl et al. 2013). These data resulted in a profound knowledge of the ore-forming processes leading to the formation of the Ta-Nb, Sn, W, Li and Au deposits. The studies constrained the origin and age of the deposits, the source of the metals and fluids, and the lithological and structural control on the ore deposits. Although most deposits have been related to a specific stage in the evolution of early-Neoproterozoic granitic intrusions (see reviews in Hulsbosch in press; Pohl et al. 2013), the relationship with the tectonic evolution, although sometimes determined on a local scale (Hulsbosch et al. 2017; Pohl et al. 2013), has not been fully resolved. The aim of this study is to provide a first overview of the relationship between tectonism, granite intrusion and mineralization in the Karagwe-Ankole belt based on the current stage of knowledge.

2 Geochronology

Two main periods of granite intrusion have been identified in the KAB. The first period, which took place between 1400 and 1370 Ma, comprises a large bimodal magmatic event, i.e. the so-called Kibaran event (Tack et al. 2010), and culminated in the intrusion of (1) mafic to ultramafic rocks which have been dated at 1403 ± 14 Ma (SHRIMP U-Pb; Maier et al. 2007) and 1374 ± 14 Ma (SHRIMP U-Pb; Tack et al. 2010); and (2) large volumes of peraluminous S-type granites and accompanying subordinate mafic rocks, which have been dated between 1383 ± 17 Ma and 1371 ± 7 Ma (SHRIMP U-Pb; Tack et al. 2010). The S-type granites are the historically defined G1-G3 generation (i.e. for Rwanda; Gérards and Ledent 1970).

The second period of granite magmatism took place at the beginning of the Neoproterozoic. Their intrusion age has recently been set at 986 ± 10 Ma by SHRIMP U-Pb dating of zircons from the small peraluminous S-type Kasika granite in the Kivu province of DR Congo (Tack et al. 2010). Regionally, they are the so-called G4 generation (i.e. in Rwanda; Gérards and Ledent 1970). Compressional events are reported in the entire “Kibara” region in the early-Neoproterozoic, however the exact timing is debated (Kokonyangi et al. 2004; Tack et al. 2010). This compressional event resulted in upright folding and thrusting of the metasediments of the western part of the KAB (Fernandez-Alonso et al. 2012). Several pegmatite generations have been identified and reflect different stages of fractionation of G4
leucogranites

(Hulsbosch et al. 2014). U–Pb ages were obtained from TNO (tantalum-niobium oxides) forming the primary mineralization of the pegmatites in the Karagwe Ankole Belt. Columbite data from pegmatites in northern Burundi reveal ages of 963 +9/−5 Ma and 968 +33/−29 Ma (Romer and Lehmann 1995). New TIMS and LA-ICP-MS U-Pb columbite–tantalite ages from the KAB range largely from ca. 920 to 1030 Ma, with a maximum around 960–990 Ma (Melcher et al. 2015). Additional new U-Pb columbite ages from the Gatumba-Gitarama area show also a spread in age between 975 ± 8 Ma and 936 ± 14 Ma (Dewaele et al. 2011).

Tungsten mineralization has been dated by Ar-Ar of muscovites hosted by W-rich quartz veins at 992.4 ± 1.5 Ma (Dewaele et al. 2016). This age overlaps with the emplacement of the G4 granites and is slightly older than the ages obtained for pegmatites and associated columbite-tantalite mineralization in Rwanda (Dewaele et al. 2011, 2016). This age is in agreement with the metallocenic model, which relates the W-mineralization to an early fractionation and expulsion of an aqueous fluid from the leucogranites (Hulsbosch et al. 2016). Cassiterite-rich quartz veins in Burundi (Mulehe) have been dated at 951 ± 18 Ma (Rb-Sr muscovite-tourmaline; Brinckmann et al. 1994) and 936 ± 82 Ma (Rb-Sr muscovite; Brinckmann 1988). Sn-mineralised quartz veins from the Rutongo area in Rwanda have been dated at 965 ± 29 Ma (Rb-Sr muscovite; Monteye-Poulaert et al. 1962) and 916 ± 50 Ma (Pb-Pb galena; Monteye-Poulaert et al. 1962).

Central African orogenic gold mineralization has been related to fold-and-thrust belt formation (Brinckman et al. 1994; Koegelenberg et al. 2016). The exact timing of gold mineralization and this deformation is however still highly debated. Two periods of gold mineralization have been proposed for the Western Domain of the KAB, although they are not well constrained. Firstly, sulfide vein assemblages with gold, dated at 908 ± 21 Ma (Rb-Sr muscovite-tourmaline; Brinckmann et al. 1994), are interpreted to be genetically related to the early-Neoproterozoic G4-granite magmatism. Secondly, ferruginous breccia zones with gold dated at 640 ± 28 Ma are interpreted to be related to Pan-African events (Rb-Sr muscovite-tourmaline; Brinckmann et al. 1994). Also muscovite from quartz-sulfide-gold saddle reefs of the Twangiza deposit (Kivu, DR Congo) gave an age of 522 ± 15 Ma (Ar-Ar; Walemba 2001). Alternatively, Pohl and Günther (1991) proposed that Au mineralization is due to deep crustal metamorphism and not related to the G4 magmatism. Timing of metamorphism would be associated with crustal thickening immediately preceding the granitoid magmatism and the metallogenic climax.

3 Tectonic evolution and veining

The Mesoproterozoic strata have been intensely folded often resulting in tight folds. Cleavage is well developed and often almost parallel to the steep bedding. Two cleavage sets can be identified based on their
orientation. Both cleavage sets are parallel to the axial plane of the folds, i.e. represent an axial planar cleavage. Occasionally, crenulation cleavage is observed in mica-rich schists. Reverse faults developed in steep to overturned limbs of folds are therefore developed at the end of the folding. Several meter-thick shear zones developed after folding and are characterized by the occurrence of C-type shear bands. These shear zones are heavily chloritized and host several deformed quartz veins which are parallel to the foliation. Barren and mineralized pegmatites developed dominantly parallel to the bedding, cleavage, bedding-parallel and strike-parallel joints and strike-slip fractures, which developed in relation to the folding (cross-fold joints, e.g. in the Mushi-Ntunga-Rwamagana area). Pegmatites and quartz veins, which developed parallel to the bedding, have been boudinaged, reflecting layer-parallel extension.

Several dominant quartz vein generations developed in relation to the tectonic evolution of the rocks and allow construction of (1) a relative timing of quartz veining and (2) a more detailed paragenetic sequence including the mineralization phases. Quartz veins, which developed parallel to the bedding, have been intensely folded and thus predate tectonic deformation. A second generation of massive quartz veins occurs in the hinge zones of folds where it can be associated with massive pyrite, e.g. Byumba area. In addition, smaller, irregular veins may be present in these hinge zones, but they are more widespread in the metasedimentary rocks. Quartz veins of the 3rd generation occur in fractures related to faulting or along the faults themselves. A fourth generation of quartz veins developed parallel to the cleavage, especially in shales and at the contact between shales and sandstones. In the Byumba area, in cm-thick sandstone layers, these quartz veins do not follow the bedding but crosscut the sandstones at an angle of 45°-60°. The cleavage parallel nature of the veins in the shales and the crosscutting structure in the sandstones gives a sigmoidal or S-shape geometry of the quartz veins. This geometry indicates the veins formed due to shearing along the cleavage. A prominent characteristic is that these veins are also boudinaged, i.e. stretched parallel to the cleavage, which is often sub-parallel or at a small angle to the bedding. Massive quartz veins crosscut the folds and cleavage and all former quartz generations.

4 Paragenetic sequence of veining and mineralization in relation to deformation

The first vein generation observed is parallel to the bedding, has been intensely folded, is not mineralized and crosscut by W-mineralized quartz veins at the Nyakabingo mine. The second vein generation observed are related to the folding and the third vein generation to faulting, often present in the hinge zone of faults. The fourth quartz generation developed parallel to the cleavage and is mineralized in tungsten at the Nyakabingo mine. The Sn-mineralized quartz veins developed as extension veins between boudinaged sandstone layers at Rutongo. An important part of the Sn-mineralized quartz veins developed after pegmatite intrusions and during layer parallel extension. 5 Discussion and conclusion

The paragenetic sequence of the veining and mineralization in relation to deformation can be further integrated within the geodynamic framework, including magmatism. Compressional deformation caused the folding and the development of an axial planar cleavage. Reverse faulting is intimately associated with this folding and occurs close to the fold hinges and in the steep to overturned limbs of the folds, e.g. as observed in the Gitarama-Gatumba section. Existing barren quartz veins became intensely folded and new quartz veins developed in the hinge zones of the folds. Granite intrusions crosscut the folds and are younger (986 ± 10 Ma; SHRIMP U-Pb zircon; Tack et al. 2010). Tungsten-rich quartz veins formed after folding and cleavage development, tungsten had a magmatic source and the hydrothermal fluid had a mixed magmatic and metamorphic origin (Dewaele et al. 2016; Hulsbosch et al. 2016). Tungsten mineralization formed during an early stage of the fractionation of the granitic magma (Hulsbosch et al. 2016). The quartz veins developed along the bedding and cleavage planes, but also along large fractures, which crosscut the folds. The lack of foliated G4 granites further indicate that magmatic activity occurred after the main period of compression but still during late stage tectonism (Hulsbosch et al. 2017). Pegmatites can be boudinaged indicating subsequent extensional tectonism. Tantalum and tin mineralization occur in highly fractionated, often metasomatized pegmatites (Hulsbosch et al. 2014, 2017). Taking into account the former evidence, Ta-Nb and Sn mineralization post-date vein-type W mineralization, and is in agreement with the geochronology of both phases.

A distinct phase of shearing post-dates folding and cleavage development as expressed by sigmoidal veins and shear zones. Silicification as well as intense chloritization is associated with this shearing. Preliminary results suggest that gold mineralization at Byumba could have been formed during this phase. Since this late tectonic stage could well coincide with granite magmatism, a hydrothermal magmatic source of the gold and fluids cannot be excluded and further research is needed.

The main Sn mineralization phase is associated with greisenization of pegmatites and with Sn quartz veins, which post-date folding and faulting as indicated by the structural analysis and geochronology (Pohl et al. 2013). Moreove, these Sn-rich quartz veins are present as inter-boudin veins and are thus related to bedding-parallel stretching of the metasedimentary layers in which they preferentially occur at Rutongo. Sn mineralization in quartz veins has a largely magmatic origin, i.e. fluids exsolved from pegmatitic melt.
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References


Cassiterite as a record of Sn mineral system processes

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Abstract. Cassiterite ($\text{SnO}_2$) is associated with mineral systems enriched in the ‘critical’ metals W, Nb, Ta, Li and In (Chakhmouradian et al. 2015) and is a potential multi-process recorder of these mineralised systems. Cassiterite is known to display complex cathodoluminescent microstructures, however detailed physicochemical models for their formation are yet to be established. Here we present a panchromatic CL, hyperspectral CL and quantitative X-ray element map study of these microstructures in cassiterite, along with observations from EPMA and LA-ICP-MS trace element datasets.

We show that sector zoning imparts a significant control on W and Fe distribution within cassiterite and that CL imaging alone does not reveal the full microstructural history with high Fe, Ta, Nb or W contents in cassiterite. We also show that the previously reported coupled substitution mechanisms for W, Nb and Ta into cassiterite cannot account for the high contents observed in some samples, and that different sectors within the same crystal show different preferred substitutional stoichiometries. Furthermore, we discuss unusual Nb/Ta and Zr/Hf ratios which imply the existence of fractionation processes during hydrothermal-metasomatic Sn mineralisation that can drive the Nb/Ta ratio to large values in excess of chondritic ratios (Nb/Ta >> 100).

1 Introduction

The basis of the cassiterite ‘multi-tool’ is the application of the U-Pb isotopic system for geochronometry, allowing a direct constraint on the age of Sn-bearing mineralised systems. Since the initial attempts at cassiterite U-Pb geochronology (Gulson and Jones 1992) via Isotope-Dilution Thermal Ionisation Mass Spectrometry (ID-TIMS), the development of in-situ analytical approaches such as Secondary Ion Mass Spectrometry (SIMS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has lead to a flurry of recent cassiterite geochronological studies (Liu et al. 2007; Yuan et al. 2011; Zhang et al. 2013, 2015, 2017; Li et al. 2016; Carr et al. 2017; Neymark et al. 2018; Cheng et al. 2019).

The power of in-situ analytical methods over bulk mineral techniques is their ability to target distinct growth histories within single grains. These separate growth stages are usually identified via cathodoluminescent (CL) imaging. However, cassiterite is well known to show complex CL microstructures and the chemical nature of these structures, and models for how they physically arise, are poorly constrained (Hall and Ribbe 1971; Farmer 1991; Wille et al. 2018).

In order to start unravelling the various physicochemical processes recorded by these microstructures, we compare panchromatic CL images, hyperspectral CL maps and quantitative X-ray element maps with an Electron Probe Microanalysis (EPMA) and Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) trace element dataset, which we present as a baseline with which further analytical studies on cassiterite may be compared.

2 Oscillatory and sector zonation

The chemical basis for the CL response in cassiterite has been previously reported as a yellow 520-565 nm Ti activated emission and a blue 420-465 nm W activated emission (Hall and Ribbe 1971; Farmer 1991). While intrinsic luminescence may play a role in the CL response of natural cassiterite crystals and cannot be discounted, the strong correlation between chemistry and CL signature observed (Hall and Ribbe 1971, Farmer et al 1991) suggests that the microstructures observed via CL imaging techniques are dominantly due to the distribution and incorporation of minor components of Ti, Fe, Nb, Ta and W into the cassiterite lattice.

Figure 1. Panchromatic CL image of a cassiterite crystal from Saltwater Creek, Tasmania, showing three main types of CL microstructures. a) Oscillatory zonation. b) CL-dark sector zonation. c) CL-bright cross-cutting features. White corners refer to region in X-ray element map in Figure 2.
In our study, we compared panchromatic CL images (e.g., Figure 1) and hyperspectral CL maps with quantitative X-ray element maps (e.g., Figure 2) and found that the CL response in cassiterite is due to a complex interplay of Ti, Fe, Nb, Ta and W. Titanium does indeed activate a CL emission in cassiterite, but only up to a threshold of 0.4 at% before concentration quenching occurs. The presence of Fe, Nb, Ta or W also quenches the CL response. The blue W activated emission of Hall and Ribbe (1971) appears to only exist at sufficiently low W contents (<0.1 at%) which also occur with moderate Ti contents (~0.2 at%), implying that the presence of W itself does not result in CL activation but instead modifies the Ti emission.

Three distinct styles of CL microstructures are generally reported in the literature; variably coarse to fine scale oscillatory zoning, CL-dark sector zonation, and CL-bright features that cross-cut the oscillatory and sector zoning (Hall and Ribbe 1971; Farmer 1991; Carr et al. 2017; Wille et al. 2018). We found that the oscillatory zonation is mostly due to fine-scale oscillations in Fe and Ti, with minor contributions from W, Nb and Ta.

Figure 2

We also report two distinct CL-dark sectors; zones enriched in Fe (Figure 1a) and with low contents of W (Figure 2) and zones enriched in W (Figure 1b) and with low contents of Fe (Figure 2). These two CL-dark sector zones are in many cases indistinguishable in panchromatic SEM-CL imaging, but hyperspectral CL may be able to distinguish these zones via subtle differences in their emission spectra (i.e., their colour).

The CL-bright cross-cutting features (Figure 1c) are rather uniform in their composition, despite the variable chemistry of their host cassiterite crystals. Titanium contents are range between 0.1 to 0.2 at%, with Fe, Nb, Ta and W contents well below 0.1 at%. These microstructures appear to represent late-stage annealing/fracture healing processes, with chemical re-equilibration. In some samples, small inclusions of iron-oxides are present which may represent a local sink for the Fe, Nb, Ta and W contents ejected from the re-equilibrated lattice.

### 3 Substitution mechanisms in cassiterite

The Fe-enriched sector zones may be explained by a coupled Fe$^{3+}$+OH$^-$ substitution mechanism previously described by Möller et al. (1988), along a limited solid solution series with the poorly described ‘varlamoffite’ species with the formula Sn$_{1-x}$Fe$_x$O$_{2-x}$(OH)$_x$ (Sharko 1971; Jambor et al. 1995). The W-enriched sectors however remain unexplained by existing models for coupled W-Fe substitution mechanisms (Möller et al. 1988). The W-rich sectors of some cassiterite crystals require a component of either coupled W$^{6+}$+W$^{4+}$+Fe$^{2+}$ or 2W$^{5+}$+Fe$^{2+}$ to maintain charge, or a component of direct W$^{4+}$ substitution (Figure 3).

![Figure 3](image3.png)

A similar behaviour is exhibited in some Nb-rich samples, with stoichiometries only explainable by some component of Nb$^{4+}$ alongside the well reported 2Nb$^{5+}$+Fe$^{2+}$ substitution mechanism (Möller et al. 1988). In addition, the sector zones of a cassiterite crystal from Blue Tier, Tasmania, show two different stoichiometries depending on the growth face present during incorporation (Figure 4).
4 Trace element fractionation ratios

The bulk rock Zr/Hf and Nb/Ta ratio of Sn-mineralised granites are well recognised to exhibit low values highly fractionated from typical crustal rocks (Ballouard et al. 2016). While the exact processes that cause this fractionation are debated (Stepanov et al. 2016), cassiterite would be expected to have Zr/Hf and Nb/Ta ratios similar to the bulk rock values of the host granite, and in many greisen-hosted cassiterite crystals this is indeed the case. However, distinct regions within some crystals exhibit ratios that appear to return to near chondritic values for Nb/Ta (~30), and some samples show ratios well beyond the chondritic ratio (Figure 5). A similar trend is seen in the Zr/Hf ratio, though no analyses exceed the chondritic ratio.

Cassiterite crystals from pegmatitic systems show an overall trend towards further highly fractioned low values, but some analyses within each crystal define trend in Nb/Ta ratios towards higher values. These higher Nb/Ta analyses correlate well with the CL-bright cross-cutting features.

5 Conclusions

The complex microstructures usually observed in cassiterite under CL illumination provide a detailed record of various processes operating in the mineralising system during cassiterite precipitation and growth. This work opens up new research questions surrounding the physical kinetics of cassiterite crystal growth, and its impact on the chemical and isotopic systematics of cassiterite trace element geochemistry.

Further research into the chemical and isotopic properties of these microstructures will allow for detailed mineralisation models for any primary cassiterite bearing mineral assemblage. This will in turn further refine our understanding of Sn mineral systems, and processes that lead to enrichment in metals ‘critical’ for 21st century technology.


Cassiterite deposition triggered by fluid mixing: evidence from in-situ $\delta^{18}$O-$\delta^{11}$B analysis of tourmaline from the San Rafael tin deposit, Peru

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Abstract. We present a combined study of oxygen and boron isotopes ($\delta^{18}$O and $\delta^{11}$B) measured in situ in tourmaline from the giant San Rafael tin deposit (Central Andean Tin Belt, Southeast Peru) to trace fluid processes during the magmatic-hydrothermal transition leading to tin mineralization. The results show that magmatic and pre-ore hydrothermal tourmaline has similar $\delta^{18}$O-$\delta^{11}$B values, which are consistent with crystallization in a continuously evolving magmatic-hydrothermal closed system. In contrast, syn-ore hydrothermal tourmaline has $\delta^{18}$O-$\delta^{11}$B values defining a linear array interpreted as the result of mixing with external fluids, thus indicating an opening of the hydrothermal system during the ore stage. Quantitative fluid modeling shows that a Rayleigh fractionation process in a closed system reproduces closely the $\delta^{18}$O-$\delta^{11}$B compositions of magmatic and pre-ore tourmaline, whereas mixing of a hot and saline (500°C, 45 wt% NaCl eq) tin-rich magmatic fluid with a heated meteoric fluid (250°C, 0 wt% NaCl eq) explains the observed $\delta^{18}$O-$\delta^{11}$B compositions for syn-ore tourmaline.

1 Introduction

Primary Phanerozoic tin (Sn) and/or tungsten (W) mineralization is mostly associated with reduced and highly evolved granitic magmas that were generated in orogenic belts by melting of tectonically thickened sedimentary sequences (Romer and Kroner 2016). Granite-related Sn±W deposits dominantly consist of cassiterite±wolframite-bearing quartz veins hosted by the apical part of granitic intrusions or extending into surrounding country rocks (Černý et al. 2005). The ore-bearing hydrothermal fluids and metals are generally considered to be of magmatic origin and cassiterite deposition is interpreted to result from several processes, including fluid cooling, boiling, fluid-rock interaction, and mixing with external fluids (Heinrich 1990). Here, we traced hydrothermal fluid evolution by using the isotopic composition of tourmaline, which is a common boron-rich mineral in granite-related Sn-W deposits and a robust chemical and isotopic monitor of ore-forming processes (Slack and Trumbull 2011).
We present a combined study of oxygen and boron isotopes measured in situ in tourmaline from the giant San Rafael Sn deposit (Peru) to trace fluid processes occurring at the magmatic-hydrothermal transition and leading to tin mineralization.

2 Geological setting

The world-class San Rafael lode-type tin deposit (>1 Mt Sn) is located in the northern part of the Central Andean Tin Belt extending from southeast Peru to Bolivia and northern Argentina (Fig. 1A). Mineralization consists of a NW-trending quartz-cassiterite-sulfide vein system hosted by a late-Oligocene (ca. 25 Ma) peraluminous S-type granitic complex and by surrounding Ordovician shales of the Sandia Formation (Fig. 1B-C; Kontak and Clark 2002, Mlynarczyk et al. 2003, Gialli et al. 2017).

Description of the early hydrothermal alteration stages is presented in Gialli et al. (2019). The deposit is characterized by volumetrically important presence of tourmaline, both of magmatic and hydrothermal origin (Mlynarczyk and Williams-Jones 2006). The following three major tourmaline generations have been distinguished (Harlaux et al. 2018): (i) Tur 1 is magmatic tourmaline found in peraluminous granites as quartz-tourmaline nodules and disseminations (Fig. 2A-B); it is texturally homogeneous and has dravitic composition (X\(_{\text{Mg}}\)=0.49-0.61); (ii) Tur 2 is pre-ore hydrothermal tourmaline formed during post-magmatic subsolidus alteration and veining-brecciation (Fig. 2C-D); it shows primary banding and overgrowth textures at microscopic scale and ranges in composition from dravite to schorl (X\(_{\text{Mg}}\)=0.22-0.98); (iii) Tur 3 is syn-ore hydrothermal tourmaline forming widespread microscopic veinlets and overgrowths, partly cross-cutting the previous tourmaline generations (Fig. 2E-F); it has schorl-foitite composition (X\(_{\text{Mg}}\)=0.08-0.55) and is locally intergrown with cassiterite, chlorite and quartz from the ore stage.

3 Results

We analyzed the \(\delta^{18}\text{O}\)-\(\delta^{11}\text{B}\) compositions of different tourmaline generations (Tur 1 to Tur 3) in situ by secondary ion mass spectrometry (SIMS) at the SwissSIMS facility, University of Lausanne. Our results (Fig. 3A) show that Tur 1 and Tur 2 have similar \(\delta^{18}\text{O}\) (10.6‰ to 11.6‰) and \(\delta^{11}\text{B}\) (-11.5‰ to -6.9‰) values. In contrast, Tur 3 has lighter \(\delta^{18}\text{O}\) compositions (4.9‰ to 10.2‰) and in part heavier \(\delta^{11}\text{B}\) compositions (-9.9‰ to -5.4‰). We also measured in situ the \(\delta^{18}\text{O}\) compositions of magmatic and hydrothermal quartz showing equilibrium textures with tourmaline in order to estimate crystallization temperatures (Fig. 4). Quartz-tourmaline oxygen isotope compositions yield equilibrium temperatures of 485-618°C for magmatic quartz-tourmaline nodules (Tur 1, average 555±44°C), and 429-487°C for pre-ore hydrothermal quartz-tourmaline veins (Tur 2, average 455±30°C). This indicates temperatures of ca. 450-500°C for the magmatic-hydrothermal transition, which is in agreement with previous fluid inclusion data (Kontak and Clark 2002, Wagner et al. 2009). Considering the upper values for quartz-tourmaline isotopic equilibrium, crystallization temperatures of about 600°C for Tur 1 and 500°C for Tur 2 can be estimated. No quartz was found directly intergrown with Tur 3, but previous works reported homogenization temperatures of about 350°C for primary fluid inclusions hosted in cassiterite (Wagner et al. 2009), temperature taken here as representative for the crystallization of Tur 3.
equilibrated with water at the same temperatures. The lowest values of $\delta^{18}$O=11.5‰ and $\delta^{11}$B=-9.5‰ point to a single fluid end-member (“fluid A” in Fig. 3B) that fits the typical isotopic compositional range of a magmatic-hydrothermal fluid derived from a S-type magma. The magmatic origin of this fluid is also supported by the high salinity (40-55 wt% NaCl eq) and high temperatures (350-500°C) of primary fluid inclusions hosted in the early quartz-tourmaline veins (Kontak and Clark 2002, Wagner et al. 2009). The isotopic composition of water equilibrated with Tur 2 hosted in the enclosing shales has different $\delta^{18}$O- $\delta^{11}$B values, pointing to a fluid end-member having $\delta^{18}$O=14‰ and $\delta^{11}$B=-6‰. Such a fluid composition may correspond to a contact-metamorphic fluid equilibrated with the shales or a magmatic-hydrothermal fluid that interacted with the metamorphic host-rocks. Isotopic composition of water in equilibrium with Tur 3 plots along a well-delineated array ranging from $\delta^{18}$O=8.4‰ and $\delta^{11}$B=-6‰ to $\delta^{18}$O=3.2‰ and $\delta^{11}$B=-2.1‰. These oxygen isotopic compositions are also consistent with the bulk $\delta^{18}$O values (3.3‰ to 8.1‰) of quartz, cassiterite, and chlorite from the main ore stage equilibrated with water at 350°C. This linear $\delta^{18}$O-$\delta^{11}$B array can be interpreted as a mixing line between a magmatic-hydrothermal fluid end-member having $\delta^{18}$O=11.5‰ and $\delta^{11}$B=-9.5‰ (“fluid A”) and another fluid end-member having $\delta^{18}$O=0‰ and $\delta^{11}$B=0‰ (“fluid B” in Fig. 3B). The latter can be interpreted as groundwater of meteoric origin equilibrated with the host-rocks.

4.2 Quantitative modeling of fluid evolution

Quantitative modeling of tourmaline $\delta^{18}$O-$\delta^{11}$B composition has been performed for fluid evolution scenarios considering fluid mixing as well as cooling, Rayleigh fractionation, and fluid-rock interaction (Fig. 3C). In each scenario, the starting magmatic-hydrothermal fluid was assumed to have a temperature of 500°C, a salinity of 45 wt% NaCl eq, $\delta^{18}$O=11.5‰, and $\delta^{11}$B=-9.5‰. Simple cooling of such a fluid down to 250°C results in a trend of increasing $\delta^{18}$O and decreasing $\delta^{11}$B, which do not reproduce the isotopic compositions of tourmaline. A Rayleigh fractionation process results in a trend of near-constant $\delta^{18}$O and increase in $\delta^{11}$B, which reproduces closely the isotopic compositions of Tur 1 and Tur 2 hosted in granites with fractionation grades of 10% to 90% of the initial magmatic fluid at constant temperature. Fluid-rock interaction involving oxygen and boron isotope exchange between a magmatic fluid and typical Early Paleozoic Andean shales ($\delta^{18}$O=18‰, Bindeman et al. 2016; $\delta^{11}$B=-6‰, Kasemann et al. 2000) produces a trend of increasing $\delta^{18}$O and $\delta^{11}$B for moderate water/rock ratio of ~0.5, which is consistent with the isotopic compositions of Tur 2 hosted in shales. A model involving fluid mixing between a hot and saline magmatic-hydrothermal fluid (500°C, 45 wt% NaCl eq, $\delta^{18}$O=11.5‰, and $\delta^{11}$B=-9.5‰) and a cooler meteoric fluid (250°C, 0 wt% NaCl eq, $\delta^{18}$O=0‰, and $\delta^{11}$B=0‰) reproduces the full range of isotopic values for Tur 3.

Figure 3. A) Plot of $\delta^{18}$O vs. $\delta^{11}$B composition of tourmaline from the San Rafael tin deposit determined by SIMS. B) Calculated $\delta^{18}$O vs. $\delta^{11}$B composition of water in isotopic equilibrium with tourmaline assuming formation temperatures of 600°C for Tur 1, 500°C for Tur 2, and 350°C for Tur 3 (see text). The field for S-type granites is from Trumbull and Slack (2018) and Harris et al. (1997). Calculated $\delta^{18}$O values for water in equilibrium with ore and gangue minerals from the pre-ore stage (Qtz: n=16, Tur: n=7) and the main ore stage (Qtz: n=13, Cst: n=14, Chl: n=5) are from Wagner et al. (2009), Prado Flores (2015) and this study. C) Modeling of $\delta^{18}$O vs. $\delta^{11}$B composition of tourmaline based on different fluid evolution scenarios (cooling, Rayleigh fractionation, fluid-rock interaction, and fluid mixing).
This suggests that Tur 3 records variable degrees of mixing with 10% to 80% of pre-heated meteoric fluid. If the initial δ¹¹B composition of the magmatic-hydrothermal fluid was -8.5‰ or -7.5‰, the results are similar.

Figure 4. Plot of δ¹⁸O values for coexisting quartz (Qtz) and tourmaline (Tur) from the San Rafael tin deposit. Isotherms are calculated using fractionation factors for quartz-tourmaline from Zheng (1993).

5 Conclusions

In situ oxygen and boron isotope analysis of tourmaline allowed to effectively trace the fluid evolution of the San Rafael magmatic-hydrothermal system. The similar δ¹⁸O-δ¹¹B values for Tur 1 and Tur 2 are consistent with crystallization driven by Rayleigh fractionation in a continuously evolving magmatic-hydrothermal closed system, likely under lithostatic pressure conditions. In contrast, the δ¹⁸O-δ¹¹B linear array observed for Tur 3, interpreted as the result of mixing with external fluids, indicates an opening of the hydrothermal system during the main ore stage, likely related to a transition from lithostatic to hydrostatic pressure conditions. Mixing of a hot, saline, and reducing Sn-rich magmatic fluid with a cooler and more oxidizing meteoric fluid resulted in destabilization of tin-chloride complexes, which is the decisive parameter for cassiterite precipitation (Schmidt 2018). Therefore, the δ¹⁸O-δ¹¹B compositions of Tur 3 unambiguously demonstrate that fluid mixing was the key process triggering cassiterite deposition in the giant San Rafael Sn deposit.

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Late Cretaceous (~80 Ma) magmatic-hydrothermal event associated with Sn polymetallic mineralization in the Nanling Range, South China

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Abstract. The Nanling Range of South China is the most important W–Sn mineralization belt in the world. Mesozoic W–Sn mineralization in the Nanling Range dominantly occurs during the Late Jurassic (160–150 Ma). However, based on our detailed field investigation and zircon studies, a Late Cretaceous (~80 Ma) magmatic-hydrothermal event has been differentiated from the Jurassic main mineralization stage in some typical Sn polymetallic deposits such as Xianghualing and Xitian. Zircon internal textures, trace element contents and Hf isotopic compositions indicate that the Cretaceous zircons are late stage hydrothermal zircons. They may have crystallized from a late fluid medium generated from deep Cretaceous magmatism which is not visible at shallow depths in the region. The Cretaceous zircons are small, euhedral prismatic in shape and completely dark in CL images, with abundant disseminated hydrothermal mineral inclusions (HREE phosphates, quartz and thorite). Moreover, the high ΣREE, Y, Nb, Ta, Th and U contents, Nb/Ta, 176Lu/177Hf and 176Yb/177Hf ratios and low Hf and Ti and Hf/Y ratios in the Cretaceous zircons indicate they crystallized from a more evolved, but lower temperature fluid. We proposed that responding to the Late Cretaceous Sn-dominated metallogenic event in South China, an ~80 Ma magmatic-hydrothermal activity occurred in the Nanling Range.

1 Introduction

South China is characterized by widely exposed granites and intensely developed mineral resources of Mesozoic age. The Nanling Range in the central part of South China hosts an economically important W–Sn polymetallic ore belt that contains more than 60 % of the world’s total W reserves and about 20 % of the Sn reserves. Most of the W–Sn polymetallic deposits are located in the central Nanling Range, an area of ~6,600 km² in Hunan and Jiangxi provinces. The Nanling Range of South China is the most important W–Sn mineralization belt in the world. Mesozoic W–Sn mineralization in the Nanling Range dominantly occurred during the Late Jurassic (160–150 Ma). These deposits are typically enriched in W, Sn, Mo, Bi, Pb, Zn, Cu, Ag, Nb, and Ta, and, in some areas, Pb and Zn are the dominant metals. Mesozoic large-scale magmatism and associated ore formation in South China peaked during three intervals: at ca. 230–210 Ma, 160–150 Ma, and 90–70 Ma. Compared to the well-studied Jurassic ore-forming events, the Late Triassic and Late Cretaceous mineralization stages have been less thoroughly investigated to date, especially in the Nanling Range.

One of the most representative Sn-polymetallic ore fields in the Nanling region, the Xianghualing Sn-polymetallic ore field is located in southern Hunan Province. Two Jurassic granite stocks (Laiziling and Jianfengling granites) are associated with the Sn-polymetallic mineralization and their geological and geochemical features have been extensively investigated and debated over the past two decades. However, their genesis remains controversial. Given the multi-stage magmatic evolutionary processes and variable granitic rock types in these plutons, more precise dating work on a broader range of samples is required. The Dengfuxian and Xitian W–Sn polymetallic ore fields in eastern Hunan Province were newly discovered during the latest phase of exploration in the Nanling Range (from 1999 to the present). These two ore fields are spatially and temporally associated with the Dengfuxian and Xitian granitic complexes and are considered to have a great potential for exploration of W–Sn, Cu–Pb–Zn, and Nb–Ta resources. The Dengfuxian ore field has total Sn + WO₃ and Ta₂O₅ + Nb₂O₅ resources of 68 kt and 10 kt, respectively. In addition, Pb, Zn, Cu, Mo, Au, and fluoride are byproducts with economic value. In the Xitian ore field, the total Sn and W reserves are estimated at 586 kt and 46 kt, with a grade of 0.26–0.36 % (Sn) and 0.28–0.63 % (WO₃), respectively. A synthesis of the geochemical and minerogenic evolution of the Dengfuxian and Xitian W–Sn ore fields has been hindered by a lack of systematic dating of the ore mineralization events and constraints on the physico-chemical conditions of the ore-forming fluids. Despite considerable study since their discovery, the fluid chemistry and mineralization history of the Dengfuxian and Xitian ore fields remain incompletely understood. Previous research constrained the peak W–Sn metallogenic epoch to 160–150 Ma, which is consistent with contemporaneous magmatic activity.
However, recent studies have proposed another mineralization event at 233–225 Ma. Even though W–Sn ores are widely hosted in both Triassic and Jurassic granites of the Dengfuxian and Xitian complexes, the nature of Triassic magmatism and its relationship to local polymetallic mineralization in these ore fields are still under debate. Moreover, no Late Cretaceous magmatic and mineralization ages have been reported from the two ore fields to date. The prolonged history of crystallization of these granitic complexes complicates an understanding of their relationship to the major ore mineralization events.

2 Method

Magmatic and hydrothermal zircons were separated from altered granites from some typical Sn polymetallic deposits. Zircon separation was carried out using standard techniques, with individual crystals hand-picked using a binocular microscope, mounted in epoxy resin, and polished to expose the grain center. Cathodoluminescence (CL) images were taken for all zircons at Beijing GeoAnalysis Co., Ltd., using an energy dispersive spectroscopic (EDS) system and a CL3+ detector and operated at 15 kV and 20 nA. In addition, back scattered electron (BSE) imaging of zircons was carried out at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences (Wuhan). By examining these photomicrographs, zircon internal structures were studied and hydrothermal mineral inclusions were identified. Grains without visible fluid/mineral inclusions and cracks were chosen for U–Pb and Hf analysis. Zircon U–Pb isotopic and trace element analyses were analyzed in situ using LA-ICPMS at the GPMR. Laser sampling was performed using an excimer laser ablation system consisting of a GeoLas 2005 with an Agilent 7500a ICPMS used to acquire ion-signal intensities. Laser energy and frequency were 70 mJ and 8 Hz, respectively. The beam diameter is 32 μm for most zircons, with a 24 μm used for small grains (< 50 μm wide). Standards were run at the same spot size as the samples. Helium was used as the carrier gas with argon used as the make-up gas and the carrier gas with argon used as the make-up gas and helium was used as the make-up gas with the same spot size as the samples. Helium was used as the carrier gas with argon used as the make-up gas and helium was used as the carrier gas with a laser beam density of 5.3 J/cm² at the sample surface. The ablation spots for Hf isotope analyses were situated over or close to the U–Pb age analysis positions on each grain. Interference of 176Lu on 176Hf was corrected by measuring the intensity of interference-free 176Lu, using the recommended 176Lu/175Lu ratio of 0.02669 (De Bièvre and Taylor, 1993) to calculate 176Lu/177Hf. The isobaric interference of 176Yb on 176Hf was corrected using a recommended 176Yb/172Yb ratio of 0.5886 (Chu et al., 2002). Detailed operating conditions and analytical methods for LA-ICPMS and LA-MC-ICPMS are described in Hu et al. (2012). Three different standards zircons (91500, TEM and GJ-1) were measured to correct Hf isotopic values. As the primary reference material, 91500 was analyzed twice every 8 unknowns and both GJ-1 and TEM standard zircons were analyzed twice at the beginning and ending of the run. The 176Hf/177Hf results obtained for 91500 are within error (0.282307 ± 0.000014 (95% conf., n = 14) of the recommended Hf isotopic values (0.282306 ± 0.000004) (Wiedenbeck et al., 2004). The analysis of GJ-1 and TEM yielded the 176Hf/177Hf ratios of 0.282008 ± 0.000019 (95% conf., n = 4) and 0.282690 ± 0.000022 (95% conf., n = 4), respectively, which agree with the recommended values (0.282013 for GJ-1 and 0.282677 for TEM, Hu et al., 2012). Off-line selection and integration of analyte signals, and mass bias calibrations were performed using ICPMSDataCal (Liu et al., 2010). A decay constant of 1.867×10⁻¹¹ y⁻¹ was adopted for 176Lu (Soderlund et al., 2004). The initial 176Hf/177Hf ratio, denoted as chf(t), was calculated relative to the chondritic reservoir with a 176Hf/177Hf ratio of 0.282785 and 176Lu/177Hf of 0.0336 (Bouvier et al., 2008). Single stage Hf model ages (TDMC) were calculated relative to the depleted mantle with a present day 176Hf/177Hf ratio of 0.28325 and 176Lu/177Hf of 0.0384 (Vervoort and Bilcher-Toft, 1999), and crust Hf model ages (TDMA) were calculated by assuming a mean 176Lu/177Hf value of 0.015 for average continental crust
Cretaceous zircons indicate they crystalized from a late fluid medium generated from deep Cretaceous magmatism which is not visible at shallow depths in the region. The Cretaceous zircons are small, euhedral prismatic in shape and completely dark in CL images, with abundant disseminated hydrothermal mineral inclusions (HREE phosphates, quartz and thorite). Moreover, the high ΣREE, Y, Nb, Ta, Th and U contents, Nb/Ta, $^{176}$Lu/$^{177}$Hf and $^{176}$Yb/$^{177}$Hf ratios and low Hf and Ti and Hf/Y ratios in the Cretaceous zircons indicate they crystalized from a more evolved, but lower temperature fluid. We proposed that responding to the Late Cretaceous Sn-dominated metallogenic event in South China, a ~80 Ma magmatic-hydrothermal activity occurred in the Nanling Range. This supplementary mineralization was superimposed on the main Jurassic ore-forming stage, enhancing Sn-polymetallic mineralization in the region. It can be concluded that Cretaceous Sn-dominated mineralization was significantly developed after the Jurassic intensive W–Sn mineralization in South China, not only in the southeastern Yuannan and northwestern Guangxi areas but also in the Nanling Range. The occurrence of the Late Cretaceous Sn metallogenic event identified in the Nanling Range further highlights the importance of systematic studies of the Nanling W–Sn belt. The Mesozoic W–Sn mineralization in Cathaysia Block of South China can be divided into three stages: Late Triassic (230–210 Ma), Late Jurassic (170–150 Ma), and Late Cretaceous (120–80 Ma). Guided by the major Mesozoic W–Sn ore-forming events occurring in the Cathaysian Block of South China, a multi-stage genetic model has been proposed for the Xianghuailing and Xitian granitic-mineralogic system: Stage I: Triassic initial enrichment stage (~220 Ma). In concert with the Triassic prelude W–Sn mineralization in the Nanling Range, the ~220 Ma concealed magmatism in the Xianghuailing area could also have provided the initial concentration of W–Sn for later mineralization. Stage II: Jurassic main mineralization stage (~150 Ma). Corresponding to the Jurassic intensive magmatism in South China and triggered by the increased uplift of lithospheric mantle, the ~150 Ma-magma was derived from partial melting of the lower crust, subsequently contaminated by Silurian sedimentary formations and Triassic magmatic rocks, resulting in a Sn-enriched magma. The evolved magma then underwent heavy fractional crystallization and fluid differentiation, causing the major Sn-polymetallic mineralization in the Xianghuailing area. Stage III: Cretaceous superimposed stage. Responding to the Late Cretaceous Sn-dominated metallogenic event in South China, at ~80 Ma, magmatic-hydrothermal activity occurred in the Xianghuailing and Xitian area. This supplementary mineralization was superimposed on the main Jurassic ore-forming stage, enhancing Sn-polymetallic mineralization in the region.

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Late-stage Sn-polymetallic hydrothermal overprint of the Pöhla-Hämmerlein skarn, W-Erzgebirge, Germany

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Abstract. The Pöhla-Hämmerlein skarn deposit, situated in the W-Erzgebirge (Germany), represents a potentially economic Sn-In-polymetallic mineralization hosted by an amphibole-pyroxene-garnet-dominated calc-silicate skarn. Macro- and microscopic analyses, including mineral liberation analysis (MLA), electron-probe micro analysis (EPMA), and mineral geochemistry, as well as δ34S analyses, point out that the Sn-In polymetallic mineralization results from a late-stage hydrothermal overprint of the skarn lithologies. Cassiterite is the main Sn-bearing phase and crystallized co-genetically with sulfides (mainly sphalerite, arsenopyrite, chalcopyrite) in veinlets that crosscut the skarn. Sphalerite as well as rare In-Zn-Cu-S phases are the main hosts for In. Mineral geochemistry and EPMA analyses of sulfide phases show only insignificant variation and suggest a single hydrothermal event. Sulfur isotopic analyses of pyrite-arsenopyrite-sphalerite-chalcopyrite assemblages (0–2 ‰ VCDT) indicate a magmatic origin of the hydrothermal fluids. Hidden late-Variscan post-collisional granites and/or lamprophyres are regarded as possible sources for hydrothermal fluids.

1 Introduction

The Pöhla-Hämmerlein skarn deposit was discovered in 1969 during uranium exploration by the Soviet-German SDAG Wismut. It represents a potential economic Sn-In-mineralization hosted in calcic skarn (Fig. 12). The resource has been estimated to contain c. 22.1 Mt @ 0.2 wt.% Sn and 15.9 Mt @ 130 ppm In (Anglo Saxony Minerals Ltd. 2018). In our study, we want to provide new insights into the mineralogy and the genesis of the Sn-In-bearing mineralization of this deposit.

2 Geological background

The Hämmerlein deposit is hosted in Variscan metamorphic rock units of the W-Erzgebirge (Baumann et al. 2000), belonging to the Saxo-Thuringian Zone and situated at the northern margin of the Bohemian Massif. The metamorphic units consist mainly of schists (greenschist- to amphibolite facies), gneisses, and metacarbonates (Rötzler and Plessen 2010). Peak of metamorphic conditions was reached at around 340 Ma (Kröner and Willner 1998).

The region features several geochemically distinct groups of late-orogenic granites, subvolcanic dikes, and microgranites. A further occurrence are lamprophyres intruding into the metamorphic rocks between 327 and 290 Ma (Seifert 2008; Tichomirowa and Leonhardt 2010). In spatial relation with the magmatism, different types of magmatic-hydrothermal ore deposits like greisen, skarn, and polymetallic veins occur (Baumann et al. 2000). Units are crosscut by networks of local to regional faults, the most prominent being the Gera-Jáchymov Fault Zone.

The Pöhla-Hämmerlein skarn layer forms an irregular shaped elongated body (Fig. 12) of amphibole-pyroxene-garnet-dominated calc-silicates, sandwiched in between two-mica schist of the Jáchymov group, and is located above a granite body of Eibenstock type (Schuppan et al. 2012).
3 Methodology

For this study, we analyzed 113 samples, gathered from the underground Pöhla-Hämmerlein mine (Fig. 13) between 2015–2017, using optical microscopy, SEM-MLA (TUBAF), EPMA (HIF), mineral geochemistry (ICP-MS by ActLabs), and δ34S isotopic analysis (stable isotope lab at WWU Münster).

4 Results

4.1 Petrography

Results from this investigation have been combined with previous studies (Schuppan et al. 2012; Wolf 1995) and compiled into a paragenetic chart (Fig. 14). We could identify four main mineralization stages:

The first stage (skarn stage) consists of early anhydrous (e.g. diopside, andradite) and later hydrous silicates (e.g. hastingsite, epidote). This stage is barren of economic mineralization.

The second stage is characterized by magnetite that occurs as massive (up to 2 m width) flat dipping lenses (Figs. 15, 16). It is usually accompanied by amphiboles, e.g. hastingsite.

The third stage comprises massive sphalerite (sphalerite-I), which is often intergrown with massive magnetite, but also occurs as independent flat dipping elongated lens-like structures (cf. Figs. 15, 16). Locally, sphalerite-I shows exsolutions of chalcopyrite. Relative timing of the magnetite and sphalerite stages is uncertain.

The last stage is characterized by oxidic and sulfidic minerals, accompanied by variable amounts of fluorite and chlorite, and minor scheelite. Oxides comprise hematite/martite and cassiterite, sulfides comprise arsenopyrite, chalcopyrite, sphalerite (sphalerite-II, often with chalcopyrite exsolutions), pyrite, minor marcasite, galena, and others. Both oxide and sulfide phases are intergrown with each other and occur in crosscutting veinlets (up to a few mm) and smaller nests within the skarn (Fig. 17).

Microscopic analyses reveal that the Sn-In-polymetallic mineralization of the deposit is linked to these veinlets and smaller nests (Figs. 15, 16), including Sn-In-polymetallic phases dispersed in the other lithologies.

4.2 Mineral chemistry

Arsenopyrite, chalcopyrite, and pyrite generally show stoichiometric compositions. Sphalerites show a larger variety, especially regarding Fe and In contents. Only sphalerites with 3–7 wt.% Fe feature In contents above 1 wt.%. Cu and In in sphalerite correlate positively (Fig. 18). Major and trace element composition of 15 sphalerite concentrates show 5.9–13.9 wt.% Fe, 50–4,700 ppm In, 0.1–0.7 ppm Ge, 0.7–4 ppm Ga, 2,900–4,500 ppm Cd, 80–55,000 ppm Cu and 1–360 ppm Ag (Fig. 19).
Distribution of $\delta^{34}S$ isotope ratios in sphalerite, chalcopyrite, arsenopyrite, and pyrite is limited to a narrow range of 0 to +2 ‰ VCDT. These values are in the range of other polymetallic skarns in the area (e.g. St. Christoph mine, Fortuna mine, cf. Stoltnow et al. 2019). They overlap with several vein-hosted polymetallic deposits of the greater Erzgebirge (Fig. 20).

5 Discussion

The Pöhla-Hämmerlein deposit is an example for late-stage Sn-In-polymetallic hydrothermal overprinting of skarn lithologies. This led to possibly economic mineralization of an in itself uneconomic skarn body. Microscopic analyses confirm that cassiterite and sulfides (except for early sphalerite-I) are co-genetically precipitated with quartz-chlorite-fluorite in veinlets that crosscut the amphibole-pyroxene-garnet skarn as well as the associated massive magnetite-sphalerite. In the calc-silicate skarn, finely-dispersed cassiterite+sulfide mineralization replaces silicates adjacent to veinlets, indicating a pervasive hydrothermal overprint along these fluid pathways. There, precipitation of the Sn-In-polymetallic phases is likely controlled by the chemical composition and physical rock properties of the calc-silicate skarn lithologies.

Indium occurs only in sphalerite-II and unidentified (Zn-Fe-In-Cu)-S phases (cf. Bauer et al. 2017). The very narrow range of $\delta^{34}S$ isotopes in sulfides indicates a single S source. Sulfur isotopes of sphalerite-I and sphalerite-II are in the same range (Fig. 20), suggesting co-genetic fluids responsible for sphalerite formation. They overlap with other vein-hosted polymetallic deposits in the Erzgebirge region that have been attributed to magmatic origin, likely associated with late-Variscan magmatic pulses like post-collisional small intrusion of Li-F granites and lamprophyric dyke intrusions (Seifert 2008). Therefore, S isotopes analyses of this study potentially support a magmatic linkage.

We found no evidence for a two-stage Sn mineralization (Jeske and Seifert 2017; this study) as proposed by Lefebvre et al. 2019.
6 Conclusion

The Pöhla-Hämmerlein Sn-In-polymetallic skarn deposit shows how hydrothermal overprinting is the single event for the formation of a potential economic veinlet-style mineralization in a calc-silicate skarn. While it remains difficult to establish the exact timing of events and to pinpoint the source of metals, analyses reveal several indications for a magmatic influence and link the deposit formation to the post-collisional emplacement of the Li-F small intrusion granites and lamprophyre dikes.

Figure 18. Bivariant plots of EPMA analyses of sphalerite-I and II.

Figure 19. Trace element distribution in bulk sphalerite concentrates.

Figure 20. δ34S isotopic distribution in bulk sulfides (Erzgebirge-values from Bauer et al. 2019 and references therein).

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The South-West England metallogenic province: concentration of tungsten by hydrothermal processes for future critical raw materials supply

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Abstract. South-west England is presently undergoing tungsten-tin (W-Sn) exploration and has recent open pit W-Sn production (2015-18) from Drakelands Mine. The majority of the W-Sn mineralization is hosted by Variscan granite plutons. Hydrothermal tungsten-tin mineralization is overwhelmingly associated with muscovite granite while tin-absent tungsten mineralization may be associated with two-mica granite. This contribution provides an overview of tungsten-tin deposits of South-west England and discusses ongoing research. Wolframite is the dominant tungsten ore mineral and exhibits variable major and trace element composition. Fluid inclusion microthermometric analysis indicates that this is controlled by the source and temperature of fluids (resulting in variation in salinity and homogenization temperature). We describe here data that will be expanded upon and used to determine the associations, occurrence and characteristics of tungsten mineralization.

1 Introduction

Granite-greisen hydrothermal systems are key sources of tungsten mineralization (Brown and Pitfield 2014). The ore mineral assemblage of these systems is dominated by wolframite ((Fe,Mn)WO$_4$) ± cassiterite (SnO$_2$) but it can contain a broad range of minerals including sulfides and other minor metals such as bismuth. Production of tungsten from greisen systems associated with the Variscan granite in South-west England occurred during the late 19th and 20th centuries and more recently has been the focus of both exploration (Kit Hill/Redmoor) and production (Hemerdon) (Fig. 1). A new minerals safeguarding policy, developed by Cornwall Council (2018), has highlighted the potential economic importance of reviving the mining industry.

Tungsten is a key critical metal, according to the EU (European Commission 2017), the USA (Dept. of the Interior 2018) and the UK (BGS 2015) being of considerable economic importance and at potential risk of supply interruption. The outlook for tungsten is unclear due to uncertainty in its future use in lightbulbs and how electric vehicles may disrupt the automotive industry (Roskill, 2019). However, with several mines expected to cease production in the near future, the need to source new primary raw materials remains (Roskill, 2019).

Recent research has resulted in new conceptual models for the interplay between host rocks, fluid inputs and magmatic sources, and controls on W and Sn deposit formation (Fekete et al. 2016; Lecumberri-Sanchez et al. 2017; Myint et al. 2018; Michaud and Pichavant 2019). Deposits in South-west England have been selected to test these models.

2 Geological setting

Tungsten-tin and tin-tungsten deposits are present in a metallogenic belt, stretching across Western Europe and Eastern North America, which formed during, and immediately after, Acadian-Variscan-Appalachian orogenesis (Romer and Kroner 2016).

South-west England lies within the Rhenohercynian zone of the Variscan fold belt. It comprises Devonian-Carboniferous metamorphosed sedimentary and volcanic lithologies (Shail and Leveridge 2009). Generation and emplacement of the peraluminous granites of the Cornubian Batholith occurred in the Early Permian (Chen et al. 1993; Chesley et al. 1993). These granites have been classified from G1 to G5 according to their mineralogy, texture and geochemistry (Simons et al. 2016).

The granites formed due to partial melting of a Sn-W enriched sedimentary source during post-orogenic
extension (Alexander et al. 2019; Simons et al. 2016); this tectonic setting has been used to describe the associated mineralization as ‘Cornwall-type’ (Romer and Kroner 2016). Tungsten-tin mineralization (Fig. 1) is overwhelmingly associated with muscovite (G2) granites in the region (Simons et al. 2017). These granites are typically small stocks and cupolas and include classic greisen localities such as Cligga Head, St. Michael’s Mount, Hemerdon and Kit Hill/Redmoor, from here on called ‘Redmoor’ (Fig. 1). Tungsten mineralization (with limited tin mineralization) in south-west England also occurs in veins (± greisen) such as in the Vincent and Bray Downs deposits, associated with the G1 two-mica Bodmin Moor Granite (Simons et al. 2016), and in veins (± greisen) associated with the Castle-an-Dinas granite intrusion.

2.1 Tungsten deposits

The main ore minerals in these granite-greisen systems are wolframite and cassiterite, with gangue minerals typically comprising quartz, feldspar, tourmaline, mica and sulfides, including arsenopyrite, chalcopyrite, pyrite and bismuthinite (e.g. Fig. 2). Samples for laboratory study were collected from various localities with known tungsten mineralization.

Hemerdon Ball Granite (Fig. 1) is a G2 muscovite granite cupola and dyke (Simons et al. 2016), separate to the Dartmoor Granite. It hosts an endogenic greisen-bordered sheeted vein system with wolframite-cassiterite mineralization, which was recently exploited (2015-18) at the Drakelands Mine. Evidence for coeval deposition of cassiterite with wolframite has not been found at Hemerdon. This decoupling of tungsten and tin that was exploited for tungsten during World War II. The wolframite and cassiterite are found in several generations of sub-parallel and cross-cutting quartz veins up to 0.5 m thick. Wolframite crystals are typically large (4–8 mm wide, and up to 20 mm long (Smith et al. 1996; this study) and grow from the vein edges. Cassiterite occurs as subhedral to euhedral crystals (2–10 mm) or as fine-grained masses (Smith et al. 1996). The average grade of the deposit is c. 0.2% W+Sn across the sheeted veins (Dines 1956; Moore and Jackson 1977).

St. Michaels Mount is a G2 muscovite granite cupola (Simons et al. 2016). The overall dimensions of the granite are unknown but the endogenic greisen-bordered sheeted vein deposit is at least 75 m in width and traceable for at least 250 m on the granite foreshore. Dominy et al. (1995) reported that the ore minerals are not associated with one another: cassiterite occurs at the vein walls, while the greisen-hosted wolframite is found predominantly in the core of the veins.

Additional samples were collected from Bodmin Moor where mineralization is vein hosted but not well constrained. Samples from Bray Downs (locality ‘Buttern Hill, Fig. 1) and Vincent mines were collected from waste material near old mine workings.

3 Geochemistry

Wolframite is characterised by highly variable compositions, from ferberite (the Fe-rich end member) to hüobnerite (the Mn-rich end member); wolframites from south-west England have compositions typically around the hüobnerite-ferberite-divide (Michaud and Pichavant 2019).

The composition of single crystals of wolframite from Cligga Head and Redmoor was determined at Camborne School of Mines (CSM) using electron microprobe analysis. Mineral composition is depicted using the H/F ratio (Michaud and Pichavant 2019) against atoms per formula unit of tungsten (W) and probable at 0.18% WO₃ and 0.03% Sn (Wolf Minerals 2015).
describes variation both within crystals and between deposits. Wolframite from the endogranitic Cligga Head deposit has higher H/F ratio than wolframite from the exogranitic Redmoor deposit.

Figure 3. H/F ratio versus the atoms per formula unit of tungsten (W) (hübnerite>50)/ferberite ratio, defined as 100 atoms of Mn/(Fe+Mn)) (Michaud and Pichavant 2019) for one wolframite crystal from Cligga Head and one wolframite crystal from Redmoor.

LA-ICP-MS analyses of wolframite from Hemerdon, Cligga Head, Redmoor, Bodmin Moor and St. Michael’s Mount were undertaken at the British Geological Survey (BGS). The trace element concentrations determined during LA-ICP-MS analysis (Fig. 4) demonstrate the variability of composition of wolframite across the region. Wolframite from Hemerdon is relatively enriched in Mo, Sb and Bi compared to that from Cligga Head, Vincent and Bray Downs. Cligga Head wolframite differs significantly in its Nb/Ta ratio and As contents. Petrographic characteristics of the Cligga Head samples reflect the observed chemical variation, with arsenopyrite a common accessory mineral.

From the unaltered core to the rim of the wolframite crystal from Hemerdon, there is an increase in Mo (from <1 to 135 ppm), As (from <1 to 104 ppm), Sb (from <1 to 130 ppm) and Bi (from <1 to 1600 ppm). Ta, Nb, Sn and Ti are typically higher in the unaltered core of the crystal. The presence of russellite (an alteration product of bismuth and tungsten minerals, Bi₂WO₆) along the grain boundaries of some wolframite crystals from Hemerdon could account for the high Bi content (up to 1600 ppm) in the wolframite rim. LA-ICP-MS data for Mn and Fe content indicates that there is a significant reduction in Mn content (from 63000 to 3000 ppm) around the altered rims of the wolframite, demonstrating that it would have a low H/F ratio.

Figure 4. Average trace element composition (raw data) of single representative crystals of wolframite from Bray Downs, Cligga Head, Hemerdon and Vincent (locations as in Fig. 1).

4 Fluid inclusion microthermometry

Fluid inclusion microthermometric analysis was carried out at the BGS (quartz) and Geo Forschungs Zentrum (GFZ) in Potsdam (wolframite) on representative samples from selected deposits across the region.

At St. Michael’s Mount, primary fluid inclusions hosted in quartz (from both vein and greisen samples) and wolframite and cassiterite (both in vein samples) have a homogenization temperature range of 250–400 °C and a salinity range of 0–14 wt.% NaCl equivalent (Campbell and Panter 1990; this study). Published fluid inclusion data for Castle-an-Dinas is sparse, with one recorded homogenization temperature of 250 °C in quartz (Little 1960) and no associated salinity data. Homogenization temperatures of primary inclusions for both quartz and wolframite determined in this study indicate a high homogenization temperature (380–440 °C) and a salinity range of 3–19 wt.% NaCl equivalent. Fluid inclusion microthermometric data from Cligga Head indicate that there is a difference in homogenization temperature for cassiterite (on average hotter, maximum temperature of 397 °C) and wolframite (on average cooler, maximum temperature of 365 °C) (Campbell and Panter 1990). Fluid inclusion data for Hemerdon has thus far focused on quartz in association with both wolframite and cassiterite with an average homogenization temperature of 400 °C and an average salinity of 15 wt.% NaCl equivalent (Alderton and Harmon 1991; Shepherd and Miller 1988; Shepherd et al. 1985).

5 Discussion

The mineralogical, geochemical and microthermometric data presented above show the variability in tungsten deposits across the south-west England Cornubian Batholith.

The H/F ratio variability in the crystal from Cligga Head (42–86) is due to chemical zonation. The H/F ratio for Cligga Head (Fig. 3) is higher than that previously reported (35–40; Charoy 1979; Michaud and Pichavant 2019) suggesting overall variability within the deposit. The presence of hübnerite is an indicator of a magmatic control on W precipitation (Michaud and Pichavant 2019) and this higher H/F ratio is consistent with the magmatic origin of the ore fluid (Smith et al. 1996).
The H/F variability in the crystal from Redmoor (Fig. 3) shows a variation in Fe and Mn distribution, with an unaltered core of ferberite (29–39) and a reduction in Mn content around the altered rim of the crystal (10–15). Michaud and Pichavant (2019) suggest a ferberite H/F ratio < 50 indicates the precipitation of wolframite at Redmoor might be as a result of a fluid-rock buffered pathway (Lecumberri-Sanchez et al. 2017); the exgranitic nature of the deposit may account for this.

Fluid inclusion homogenization temperatures from greisen deposits (both ore and gangue minerals) range from 250–440 °C and are accompanied by a salinity range of 1–19 wt.% NaCl equivalent. The difference in cassiterite and wolframite homogenization temperature in Cligga Head has been accounted for by earlier precipitation of cassiterite and subsequent cooling and precipitation of wolframite (Campbell and Panter 1990).

We will determine the patterns of variation in chemistry and homogenization temperature as a function of occurrence and granite-association for selected deposits in South-west England to develop an appreciation of the effect of source of fluids and metals on mineralization style.

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Textures in ore exploration: smoking gun or red herring?

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Abstract. Textures are an important indicative feature in mineral exploration and the trained eye of the geoscientist may help to save substantial exploration expenses and even help point towards a potential discovery.

Textures reflect PTX formation conditions of magmatic, metamorphic and sedimentary rocks, specifically their strain-stress regime or tectonic deformation, their alteration products and their mineralisation. Some textures reflect extreme disequilibrium - famous examples are rapakivi textures or orbicules.

This contribution focuses on igneous textures controlled dominantly by fluid processes. Textures from macro- to micro-scale offer insights to reconstruct the formation history of primary rocks and their alteration sequences. Alteration textures may reveal multiple fluid fronts or prograde and retrograde processes including pseudomorphic (first replacement) and tropomorphic mineral assemblages (second overprinting and replacement of preceding alteration facies). In the most extreme cases only SEM CL or high resolution techniques like TEM allow the unravelling of relic textures otherwise hidden during optical microscopy.

1 Magmatic crystallization

The primary textures of igneous rocks reflect the environments in which their magmas solidify, which marks the end-point of changing PTX conditions from source environment over segregation and ascent to emplacement. The architecture of igneous systems is largely controlled by the geodynamic setting of magma generation and by the tectonic framework during intrusion (strain-stress regime) and the physical and chemical parameters of magmas (rheology, viscosity, nucleation and growth driving crystal size distribution), that vary in space and time and evolve during volcano-plutonic evolution from batholith to pluton scale. The spectrum of igneous textures (Figs. 1, 2) signifies that natural magmas approach the equilibrium state from conditions that may begin far from it, and they may be quenched before they achieve it.

Disequilibrium features stored in xenoliths and enclaves, specifically cumulates or orbicules, are powerful tools to reconstruct magma trajectories. For sub-volcanic igneous bodies that often serve as fluid channels, there is the added uncertainty of the extent to which they preserve their original igneous character. Re-equilibration of mineral phases along PTX pathways and subsolidus morphologic changes among crystals may create specific textures indicative of fluid saturation, hinting at fertility of ore-bearing magmas.

Figure 2. Hand-specimen photographs of rapakivi feldspars from (a) Altenberg microgranite, (b) Land’s End biotite granite (from Müller et al. 2008) interpreted by undercooling of overheated melts.

Figure 1. Left: Schematic illustration of the development of granitic textures at individual stages of magma ascent, emplacement and cooling. Right: Proportions of individual quartz grain fractions; positions of individual granite samples are related to the following magmatic phenomena—phenocryst accumulation, textural coarsening, rapid devolatilization and quenching. In the samples W1, ZP2, ZP5 and ZP6 (example from Czech Erzgebirge), the proportion of small grains is nearly constant (~50%) indicating similar nucleation rates in interstitial melt (Stemprok et al. 2008).
2 Magmatic-hydrothermal transition

The intrusion of granitoid magmas (evolved Li-F granites and porphyry systems) into subvolcanic levels is controlled in part by rapid uplift of the crust and exhumation. Rapid cooling and crystallization of these intrusions results in magma quenching and intense fracturing of the carapace in many cases. Due to the so-called “autoclave effect”, a quenched glassy carapace (later recrystallized) is able to sustain overpressures (internal fluid pressures as high as 3-5 kbar) that greatly exceed local lithostatic pressures. Confined to the carapace, the melt crystallizes inward and although initially undersaturated in water, it eventually becomes fluid saturated. This results in late-stage volatile separation beneath the carapace (Figs. 3-4) The passage of the granite system through the water-saturated liquidus boundary involves a volume increase and change in fluid composition (Burnham 1979).

![Figure 3](image3.png)

Figure 3. Model for the concentric formation of unidirectional solidification textures (USTs, stockscheider pegmatites, line rocks) within crystallizing carapace of granite (Halls 1994).

Multiphase granitic intrusions often show a textural sequence (fine-grained, porphyritic to seriate to equigranular textures), in many cases associated with pulses of explosive brecciation and greisen stockworks, characterizing the crystallization regime. Rapid crystallization of these intrusions is characterized by quench textures, such as embayment and skeletal growth of quartz (visible in SEM-CL images), particularly in dikes and in cupolas of the intrusions. Pegmatitic, miarolitic and rhythmical layered textures (e.g., comb quartz layers and other unidirectional solidification textures - USTs) indicate stages of fluid saturation (Kirkham & Sinclair 1988).

![Figure 4](image4.png)

Figure 4. Line rock (oscillatory zoned albite-quartz rock, with minor lepidolite and amblygonite), Argemela, Portugal.

Micrographic intergrowths of quartz and K-feldspar also reflect undercooled conditions that may have been related to rapid release of a fluid phase (i.e., pressure quenching). Nucleation-controlled phenomena, including variations in granite textures, however, can result from a multiplicity of causes. Extensive fracture stockworks and breccia pipes around the tops of intrusions, which indicate explosive rupture of an impermeable barrier by the short-term, self-healing igneous system, are characteristic of fluid-saturated rare-metal granites.

Closed system conditions in the melt reservoir below the carapace enable fluid saturation, disequilibrium reactions between separated magmatic volatile phases and crystals and melt, and thus catalyze a more effective fractionation. Such volatile-rich, highly evolved magmas result in granitic rocks with non-chondritic Y/Ho and Zr/Hf ratios and REE patterns that commonly show the lanthanide tetrad effect. The enrichment of magmatic volatile phases is reflected in H2O-, F-, Cl-, B-, Li-, and P-bearing minerals and C-H-O-enriched micro-inclusions associated with the formation of ore-bearing melts (brines, residual melts that form pegmatites). Subsequent brecciation due to degassing allows channeling and accumulation of the mineralization (Seltmann 1994).

Confluence of many physical and chemical factors such as magma composition, oxidation state, depth and timing of exsolution of a magmatic vapor phase (MVP), permeability and intensity of fluid circulation may lead to high mineralization efficiency. Fractionation affects the composition and reactivity, rather than the volume, of magmatic fluids for generation, mobilization and deposition of ores. Granitic rocks associated with porphyry copper deposits are much less fractionated, but they produce much larger volumes of magmatic fluids. Rare-metal granites produce smaller volumes of magmatic fluids (than other less fractionated melts), but these fluids can be much more concentrated, particularly in incompatible ore elements removed from melts into the magmatic volatile phase(s).

Liquid-liquid immiscibility (i.e. liquation of F,Si-rich vs. P,Al-dominated granitic melt portions) and separation of
a MVP due to rapid pressure release are typical characteristics of mineralized shallow felsic intrusions and related magmatic-hydrothermal transition processes.

Typical signatures of late-magmatic stages are:
* laccolithic bodies formed through repeated dike-in-dike intrusions caused by rheological (density) contrasts,
* existence of intra-mineralization "vein dikes",
* occurrence of magmatic topaz, Li-mica or muscovite, tourmaline orbicules, and snowball quartz (Fig. 5).

Additionally, subsolidus characteristics for crystal-fluid interactions in granites are, for instance, microclinization, albitization, secondary muscovite, and other disequilibrium features (resorption, zonal growth, oscillation zoning). Accessories then often exhibit, due to interaction with a highly reactive fluid phase, hydration, metamicritization, inhomogeneity, and fluorination. Multiple alteration processes cause pseudomorphic and tropomorphic replacement textures.

Rhythmic alternations in magmatic-hydrothermal transition processes in fluid-saturated melts result in textures such as rhythmic layered pegmatite-aplite zones, marginal pegmatites / stockscheiders, USTs, mioralitic cavities and magmatic foliation (Figs. 6, 7, 8).

USTs, for example, form due to repeated oversaturation and oscillatory release of silica-rich hydrothermal fluids in the melt (Fig. 6) and, besides the most common comb quartz, the oscillatory layering may involve albite, K-feldspar, tourmaline, topaz, apatite, aegirine and others.
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3 Textures as tool in mineral exploration

Rapid changes of the physicochemical conditions and focused fluid flow due to specific structural controls are main factors responsible for mineralization associated with shallow intrusions. The association of mineral deposits with granites that contain fluid saturation textures suggests that magmatic fluids contributed to the hydrothermal system. The presence of alternating fluid saturation textures in a cupola system indicates that considerable fluctuations in pressure and temperature occurred in the magmatic-hydrothermal system. These textural features help constrain pressure and temperature conditions used in modeling fluid-rock reactions and the genesis of granite-related ore deposits. Using a complex pattern of signatures to evaluate textural and chemical characteristics of the anatomy of plutons allows in most cases conclusions to be drawn as to their ore-bearing potential and to aid mineral exploration.

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References


Mineral paragenesis, geochemical changes and fluid evolution vis-à-vis greisenization at Degana tungsten deposit, India

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Abstract. The Degana Granite in NW India hosts a typical vein-type tungsten deposit. The mineral paragenetic studies infer crystallization of topaz and biotite at the magmatic stage, followed by albitionization and K-feldspathization. The development of quartz veins induced greisenization in the adjacent host granitic rocks, which resulted in enrichment of a number of elements including Fe, Mg, Li and W. These veins mark the incursion of metal-carrying fluids that evolved through immiscibility of H₂O-CO₂ fluids.

1 Introduction

Wolframite-bearing greisen-quartz veins, and associated greisenized granitic rocks, are an important class of hydrothermal ore deposits. The Degana W deposit in NW India represents a similar ore system of the highest W reserve (~3440 t) in the country – it is essentially an endogreisen-type of ore deposit. Besides a number of studies on Degana deposit (Pandian and Varma, 2001, and references therein), a number of aspects such as - mineral paragenesis, gains/losses of elements (during greisenization) and fluid evolution, remain poorly understood. The present study aims to propose a genetic model for the Degana deposit based on mineral paragenetic, mineral-chemical, whole-rock and fluid inclusion studies.

2 Geology of Degana deposit

The Aravalli-Delhi fold belt (ADFB) is a prominent lithotectonic feature of NW India. Along the western margin of ADFB, a number of Neoproterozoic granitoid intrusives are known, among which leucogranites at Degana are known for W mineralization. The Degana Granite (DG) is a massive, sub-porphyritic to porphyritic and variably greisenized intrusive unit. The DG occupies most of the Rewat hill and western part of the Tikli hill (Fig. 1). An otherwise leucocratic and feldspar-bearing poorly greisenized Degana granite (PGDG) becomes increasingly greisenized and melanocratic (greisenized Degana granite; GDG) in the median part of Rewat hill; in this part of the hill it is devoid of Na- and K-feldspars, rather quartz phenocrysts are common. A number of greisen-quartz veins (GQVs) traverse through DG, which seem to have intruded through nearly vertical fracture/joint planes striking NW-SE. The GQVs are known for remarkable depth persistence (~300m) (Lahiri, 1966) and are bordered by muscovite-rich greisen selvages ranging in width from a few cm to more than a metre. In PGDG, the randomly oriented greisen veins define the lower grade stockwork-type mineralization. The breccia rock that is variably greisenized, comprises phyllite xenoliths (often greisenized along rims) with feldspar-bearing fine (to medium) grained granitic groundmass that acted as a cementing melt (for caught-up xenolith fragments)
occupying the inter-fragmental space. Additionally, a leucocratic (biotite-poor) aplitic phase occurs as plugs, veins and dikes that hosts stockwork-type greisen veinlets.

3 Mineral Paragenesis

Petrographic studies infer four stages of mineral growth, namely - magmatic, sodic, potassic and greisen stages. As a result of greisen alteration, the former three stages are poorly retained in GDG. Mineral paragenetic relationships were delineated based on consistency of crystallographic orientation using a quartz plate under crossed nicols accompanied with slow rotation of the objective stage. Idiomorphic to subhedral grains of topaz (Fig. 2a) and strongly pleochroic grains of biotite define the magmatic stage. The albitic replacement of topaz and biotite represents the sodic stage, wherein the topaz commonly occurs as dismembered relics. This was followed by potassic stage showing pronounced effects in PGDG, in the form of perthitic K-feldspar phenocrysts enclosing skeletal topaz (Fig. 2b), plagioclase and biotite. A post-potassic albitic stage is occasionally observed, as evidenced by irregular or random-shaped albic growth in perthitic phenocrysts. Moderate to intense muscovitisation of biotite, sericitic replacement of topaz (Fig. 2c) and silicification define the greisen stage. The strongly muscovitised biotite is in close association with interstitial wolframite (and rare cassiterite). Extremely melanocratic GDG show effects of intense H+ metasomatism by means of wholly-bleached and muscovitised biotite, formation of sericite associated with fluorite and strong flooding of quartz that commonly replaced biotite and feldspar. The growth of secondary, fine-grained topaz at the expanse of sericite-muscovite is well evident. (Fig. 2d). In PGDG, the greisen veinlets define the greisenization phase. In these veinlets, the median quartz vein comprises fine-grained topaz, sericite and wolframite; this median quartz-rich zone is enclosed by a surrounding halo of darker (greisenized) tone comprising quartz, sericite (+fluorite) and fine-grained disseminated wolframite.

4 Mineral Chemical Studies

With increasing degrees of muscovitisation, the biotite become weakly pleochroic. This is accompanied by loss of Fe and gain of Si and Li in protolithionite and zinnwaldite. In lithian micas, Li commonly replaces Al by means of exchange vector [Li3 Al-1 \(\square\)-2], thereby decreasing the octahedral vacancies (Hawthorne & Černý 1982). In contrast to this, in the present study, the mica composition in DG indicates a linear positive relationship between Li and \(\square\)Al, this can be justified by the substitution: 2ViLi+ = ViFe2+ + Vi\(\square\). The ternary plot in \(\square\)Fe2+-\(\square\)Li+-\(\square\)Al3+ system (not shown here), mica from PGDG to GDG show a complete set of compositions between trioctahedral siderophyllite and intermediate zone between trilithionite and lithian muscovite. This intermediate zone is referred to as ”mixed form" by Foster (1960); some studies have shown the Li-bearing micas to plot in this zone (e.g. Marchal et al., 2014). A continuous linear trend between siderophyllite and ”mixed form" corresponds to solid solution between trioctahedral and dioctahedral micas, as reported by Monier and Robert (1986). Previous experimental studies suggested that the miscibility gap between trioctahedral and dioctahedral micas shrinks progressively with increase in Li and F contents. With regard to the overall compositional changes in mica among PGDG and GDG, the following exchange mechanisms may be assumed: (1) \(\square\)Li \(\square\)Al \(\square\)Fe2+-2, which implies a charge balance within octahedral sites, and (2) \(\square\)Li \(\square\)Al \(\square\)Si4+-\(\square\)\(\square\)Fe2+-3 \(\square\)Al3-, which maintains charge balance between tetrahedral and octahedral sites and an increase in dioctahedral character.

The plagioclase grains in PGDG consistently show an albite composition (\(X_{Ab} = 0.87 \text{ to } 0.99\)). The perthitic K-feldspar with albite lamellae (\(X_{Ab} = 0.73 \text{ to } 0.99\)) shows \(X_{Or}\) ranging between 0.81 and 0.99. The topaz of magmatic and secondary origin does not show any compositional differences. The wolframite grains show high Fe/Mn ratio and classify as ferberite, occasionally of Nb-rich nature. The greisenized rims of phyllite xenoliths contain rutile that show minor presence of W (0.01 - 0.25 wt%) and Sn (0.01 - 0.31 wt%).

Figure 2. Photomicrographs of Degana Granite illustrating the mineralogy and textures: (a) euhedral magmatic topaz in PGDG; (b) K-feldspar replacing topaz during K-feldspathization; the inset panel shows the uniform colour of topaz grains using quartz plate under crossed nicols, which suggests that these relic grains represent a magmatic topaz; (c) Sericite replacing magmatic topaz during greisen stage of alteration; (d) A residual biotite grains that is intensely sericitised; the inset panel shows replacement of sericite by extremely fine-grained topaz developed during advanced stages of greisenization. (All the scale bars are of 200 microns).
5 Mass balance studies

In order to constrain the geochemical gains and losses during greisenization, mass balance calculations were carried out following Grant (1986). The trace elements are widely used as a reference frame due to their immobile nature. In the present study, many of such elements (like Sr, Ba, Hf, Ti and Ga) are present in low concentrations and thus the associated nugget effect prohibits their use. Some trace elements (like Zr, Nb, Cs and Bi) show marked variations between unaltered and greisenized units of DG. It may be noted that the overall melt-fluid regime in Degana seems to be oversaturated in silica. This gains support from the fact that the whole-rock silica content throughout the DG always exceeds 69 wt% (up to 74 wt%). Moreover, petrographic studies clearly suggest that alteration processes were accompanied by silicification resulting in quartz flooding. The quartz-saturated nature of fluids can be attributed to interaction of fluid with leucogranitic rocks. On this basis, we assume Si to be immobile. Any errors in this assumption are minimized by the fact that the variations in SiO\textsubscript{2} concentration are minimal as against other elements; also, SiO\textsubscript{2} is present in abundance in all the samples.

Mass transfer calculations were done using average of unaltered DG as the protolith and SiO\textsubscript{2} as the reference frame; the isocon for a representative sample is shown in Fig. 3. As compared to unaltered variants of DG, the greisenized rock units show gain in Mn, Mg and Fe; in contrast, the loss of Na and K is evident. Among trace elements, Li, W, Sn, Zn and Bi show enrichment, on the other hand, Cu, Ba, Sr, U, Zr and Th seem to be leached out as a result of greisen alteration. The overall patterns of gains and losses in GDG are more or less replicated in greisen veinlets (within PGDG) as well.

As the REE contents are low, most of them (except for Lu, Tb, Tm and Ho) show irregular variations, possibly due to minor nugget effects. It may be noted that both PGDG and GDG show peraluminous nature (A/CKN - 1.6 to 2.3 and 2.0 to 6.6, respectively) and high normative corundum contents (2.5 to 5.7 and 3.9 to 12.7, respectively).

6 Fluid inclusion studies

In doubly-polished wafers of PGDG, GDG and GQVs, three types of fluid inclusions were observed - H\textsubscript{2}O-CO\textsubscript{2} (type-I), CO\textsubscript{2}-rich (type-II) and halite-bearing H\textsubscript{2}O-NaCl (type-III). Three types of fluid inclusion assemblages (FIAs) were commonly observed: (1) FIA-1: cluster of type-I inclusions with fairly consistent H\textsubscript{2}O/CO\textsubscript{2} ratio in magmatic topaz within PGDG; (2) FIA-2: separate clusters of type-II and type-I (less common) inclusions in quartz (of apparently pre-greisen stage) within PGDG; and (3) FIA-3: highly populated and commonly found clusters comprising type-I (with varying H\textsubscript{2}O/CO\textsubscript{2} ratio) and type-II inclusions in intercrystalline quartz within GDG and GQVs, likely entrapping greisen-stage fluids. The secondary topaz in GDG rarely contain type-I (or type-II) inclusions of extremely small size (<8 um). It may be noted that quartz-hosted secondary inclusions of type-I and type-II nature are common, although are too small (< 8 um) for heating-freezing runs; moreover, such fluids are likely related to late-deformation and do not represent the late magmatic or greisen-related fluid regime, which this study intends to outline.

In either type of FIAs, the type-I and type-II inclusions show melting of solid CO\textsubscript{2} at around -56.6 °C. The melting of CO\textsubscript{2}-clathrate for type-I inclusions in FIA-1.
was imperceptible and thus measured at a slow heating rate of 2 °C per minute; it occurs in the range of 2.8 – 5.8 °C furnishing salinity estimates of 7.7-12.1 wt% NaCl equivalents. These topaz hosted H₂O-CO₂ inclusions show homogenization of carbonic fluid component into vapor phase in the range of 23.8 - 29.0 °C. The clathrate melting in quartz-hosted CO₂-rich (H₂O/CΟ₂ < 0.2) inclusions (in both FIA-2 and FIA-3) is often practically invisible - in such cases the disappearance of clathrate was estimated based on change in the convexity of inclusions (in both FIA-2 and FIA-3) is often practically corresponds with the H₂O/CΟ₂ ratios. Inclusions with the range of 395 - 461 °C (and define FIA-3), homogenize in contrasting 39 successfully homogenized (without decrepitating) in Out of a total of 116 numbers of type-1 inclusions, only 7 Discussion and Conclusions

7 Discussion and Conclusions

The distribution of greisenized rocks in Rewat hill indicates that greisen-quartz veins control the greisenization and ore enrichment. Mineral paragenetic studies bring out some interesting observations. The pre-greisen alteration events (albitisation and potassic alteration) are recorded throughout the granitic rocks in Degana, probably facilitated by late-magmatic fluids localized along grain boundaries and impersistent microfractures. The overall paragenetic sequence differs from the one proposed by Pollard (1983) for greisen systems. Pollard (1983) ascribed development of topaz to post-magmatic greisen stage, after the sequential K- and Na-feldspathization stages. The late development of sodic alteration stage is attributed to enhanced F contents in residual melts that shifts its composition towards Ab-rich corner of Qz-Ab-Or ternary system. Contrastingly, in the present study, topaz attains stability not only during the magmatic stage, but sodic alteration stage precedes the potassic stage. Topaz is clearly the earliest-crystallizing phase occurring as euhedral grains and this early stabilization of topaz may be justified based on the results of experimental studies by Weidner and Martin (1987). They argued that in a peraluminous melt, topaz may precede the formation of feldspars and quartz only under high pressure conditions (>4 kbar); indeed, a number of studies support this argument (eg. Haapala, 1997). Thus, the onset of topaz formation, which is a major consumer of F from the melt, might have allowed the residual melt to attain early saturation in albite, as observed in Degana granite.

The enrichment of Fe, Mg, Li, and W along with a number of other elements is well evidenced, based on mass-balance and mineral chemical studies. In both GQVs and GDG, the predominance of type-I inclusions with variable H₂O/CΟ₂ ratios and their homogenization at comparable temperatures in contrasting modes provide compelling evidence for H₂O-CΟ₂ immiscibility in greisen fluids. However, there are no evidences of such immiscibility in the aqueous-carbonic fluid regime that prevailed during development of magmatic topaz.

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Thallium as an indicator of regional fluid flow? A case study from SW England

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Abstract. Gbase regional geochemical stream sediment, soil and water surveys have delineated significant Tl anomalies in SW England. The western anomalies are related to granite phases and vein Pb-Zn mineralisation. The eastern anomalies correlate spatially with Pb-Zn-Sr in red beds and carbonates. Thallium is inferred to be hosted in Rhaetic and Liassic black shale units and is suggested to indicate regional Pb-Zn-Sr-Tl fluid flow in the early Jurassic.

1 Introduction

Multi-element geochemistry of very dispersed, low abundance, elements has become possible and routine with improvements in XRF and particularly the widespread use of low detection limit ICP-MS. These techniques allow their use in delineation of mineral forming systems. Case studies, either of mineralised areas or of individual elements, are however limited. Thallium is particularly useful as it can be both lithophile and chalcophile; largely held in feldspar as a lithophile element and in pyrite or galena as chalcophile. This change in behaviour can be used to track pathways of Tl leached (along with base metals) from feldspars and the element redeposited near or in mineral deposits.

Although Tl has been widely known as a pathfinder for Carlin-style Au, and SHMS and some MVT Pb-Zn type deposits for some time (Ikramuddin et al. 1983; Large and McGoldrick 1998; Graham et al. 2009). More widespread application has been limited until recently by the cost of specialised procedures needed to reduce detection limits to Clarke concentrations.

This study uses data from the British Geological Survey GBase multi-element, stream sediment, partial water and soil data as well as the TellusSW constituent (BGS 2018) in a well mineralised area of western England. An initial driver to investigate Tl was the soil map of England and Wales which shows parts of eastern Somerset and Avon have the most anomalous Tl in England and Wales (Rawlins et al. 2012).

2 Background geology, mineral deposits and data

2.1 Geology

The area is underlain by a variety of mainly Paleozoic and Mesozoic sediments and intrusives deformed by Variscan events. Pre-Permian geology shows a distinct difference between largely marine sediments west of Taunton (Fig. 1) and shelf limestone and coal-bearing sediments more typical of central England to the east. In the west the sediments are intruded by S-type granites of Permian age. These are all overlain by continental red-bed sediments of Permian and Triassic age. These are further overlain by Jurassic marine black shales and calcareous sediments and Cretaceous Chalk in the east. More details can be found in Brenchley and Rawson 2006.

Geological interpretation used a modified and coverage of based on BGS 1:50000 coverage ( Digimap 2018).

2.2 Mineral deposits

The western part of the area hosts the Cornubian Sn-W-Cu deposits discussed by Alderton (1993). In contrast deposits in the eastern part are less well described. The limestones and overlying sediments of the Mendips host Zn-Pb-Cd deposits described in detail by Burr (2015). These Pb-Zn occurrences are however not limited to the Mendips and can be found as far north as Chipping Sodbury where they are Sr-rich. Strontium deposits are a feature of the area, notably at Yate, where significant celestite is stratabound in upper Triassic sediments (Nickless et al. 1976).

2.3 Data collection and preparation

Results from the TellusSW soils and stream sediment samples were released to complement those of the TellusSW airborne geophysical survey (TellusSW 2014). Gbase stream sediment data were used for the rest of SW England (Gbase 2017).

Stream sediment, water and soil geochemistry were obtained using samples collected and analysed using standard GBase protocols of BGS (Johnson 2005). Stream sediment and soil samples were analysed using X-ray fluorescence on pressed pellets. Water samples were analysed by a ICP-MS, and ion chromatography (Rawlins et al. 2003).

Soil data were used as point locations but stream sediment data and waters for the TellusSW area were plotted as drainage catchments derived from point data kindly provided by BGS. These catchment plots are much more indicative of the overburden sources of the sediments than plotting as points or contouring (Moon 1999). Catchments were manually checked for consistency before linking to the Gbase attribute geochemical data.
Figure 1. Stream sediment XRF Ti overlain on selected geology, n=5305.

Figure 2. Shallow soil XRF Ti overlain on selected geology, n=1420
3 Thallium Data

3.1 Overview stream sediments and soils

Coherent data are available for both soil and stream sediment XRF data, although background concentrations are higher than those of ICP-MS (Belzile and Chen 2017; Rader et al. 2018).

Both stream sediments and soils show Tl anomalies in sections of the Cornubian granites, especially in later topaz-rich phases. The strongest anomalies in the western part are associated with crosscourse Zn-Pb deposits, notably East Wheal rose, Wheal Betsy (W of Dartmoor) and the polymetallic Redmoor W-Sn-Cu-Pb deposits. An area E of Dartmoor, near Teignmouth, underlain by Permian sediments, and known, in part, to contain cross-course mineralisation is also anomalous.

However, the most extensive anomalies are in the NE and were coincident with similar regional soil anomalies shown on the regional soil maps of Rawlins et al. (2012).

3.2 Water samples

Water samples from the western (TellusSW) area were analysed but not from the eastern area. These ICP-MS data show similar distributions to stream sediments increasing confidence in the latter. They are also in agreement with the more limited water data of Law and Turner 2011.

3.3 North Somerset and Avon data (detailed area, Fig.1)

The distribution of stream sediment Zn reflects known Pb-Zn mineralisation. This is well known from the Carboniferous Mendips limestone (E-W in the S of Fig. 3) but is also hosted in other Carboniferous limestone as well as Permian conglomerates, Rhaetic shales and Jurassic shales and limestones. Stream sediment strontium indicates the major upper Triassic deposits in the Yate area (Fig. 4), as well as some celestite associated with Zn-Pb. The location of the former Avonmouth Zn smelter is shown on Fig. 3 to eliminate any anthropogenic influence.
Comparable plots of Tl highlight similar regions as well as some areas underlain by the Lias. When examined in detail by extracting the lithological unit of individual catchments and plotting as box plots, the predominant units enriched are mapped as Penarth Gp (Rhaetic) and Lias. Both units are known to have black shales and the Lias is known to be enriched in Mo, Se, as well as Tl (Thornton et al. 1969; Morigi et al. 2015). However Tl concentrations are much higher in the current area and there is no correlation of high Tl concentrations with Mo. In order to remove background sedimentary concentrations, a ratio Tl/Mo (×100) was used (Fig. 5).

3.4 North Somerset and Avon interpretation

Stream sediments and soils are consistent with a regional Pb-Zn-Sr-Tl mineralising event in which fluid deposited minerals in differing receptive stratigraphic units. Lead-Zn in carbonates and calcareous conglomerates, Sr in Triassic evaporite beds, and Tl in sulphide reduced units. Haggerty et al. (2007) argue for a Jurassic age for the event based on Pb isotopic evidence. This is consistent with the silicified mineralised Harptree Beds of Liassic age. Rankin et al. (unpub) prefer a Triassic age. Fluid inclusion data of Rankin et al. at Chipping Sodbury indicate a temperature of <100° C.

The occurrence of thallium anomalies in Rhaetic-Liassic black shales are consistent with Wogelius et al. (1997)’s model of a hydrothermal fluid movement on regional faults, which are shown on underlay in Fig. 5. Thallium would then be precipitated in reducing environments. The source of the thallium could be accounted for by leaching of (? Devonian) sandstone at depth.

The occurrence of Tl in sulphidic sediments overlying mineralisation is similar to the location of Tl anomalies in the major Zn deposit at Navan, Ireland (Walker 2010). Lead-zinc deposits in Triassic carbonates in Poland are also well known to be Tl-rich (Karbowska et al. 2014).

Further work is required to confirm the mineralogical host of Tl in north Somerset/Avon.

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An updated genetic model for metamorphosed and deformed, c. 1.89 Ga magnesian Zn-Pb-Ag skarn deposits, Sala area, Bergslagen, Sweden

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Abstract. This contribution presents an updated view on the genesis of stratabound Zn-Pb-Ag mineralization in the Sala area, Bergslagen, Sweden. Integrated legacy and new geological, geochemical and geophysical data reveal that the deposits are hosted by a complex array of magnesian skarn-altered zones in dolomitic marble. These mineralized zones parallel early faults and metavolcanic interbeds in the host marble, and converge downwards in the stratigraphy adjacent to a 1.89 Ga calc-alkaline granite-granodiorite batholith. Prograde alteration involved formation of early barren ferroan diopside- and forsterite-bearing skarns. Mineralization is mainly associated with subsequent alteration to tremolite, chlorite, serpentine, magnetite and calcite. The hydrous associations overlap mineralogically with assemblages formed during subsequent greenschist facies regional metamorphism between 1.87 Ga and 1.8 Ga. However, ferroan diopside and forsterite are unique to the alteration system, and indicate mineralization in conjunction with an early, high T, metasomatic alteration event at 1.89 Ga. The Sala deposits can be classified as Zn skarn deposits, albeit atypical in the magnesian nature of the skarns and the lack of minerals with essential Mn. The Fe and Mn content in magnesian silicates and carbonates is however sufficient to induce clear enrichment haloes of these elements around the deposits. The magnesian nature of the skarns probably reflect formation in a shallow marine continental back-arc tectonic setting, and an importance of seawater in early pre-skarn alteration stages, such as dolomitization.

1 Introduction

The Sala area is one of the classic mining areas in the Bergslagen mining district of southern Sweden. Several stratabound polymetallic sulphide deposits are hosted by dolomitized and hydrothermally altered stromatolitic limestone, including the c. 5 Mt Sala Zn-Pb-Ag deposit; Sweden’s most historically important silver mine. The marble unit has also been mined for calcite and dolomite, and high quality dolomite for industrial applications is still mined at Tistbrottet directly west of Sala mine (Fig. 1).

The Sala deposit belongs to a sub-type of stratabound marble- and skarn-hosted deposits in Bergslagen. Current understanding based on field evidence and cross-cutting relationships suggest these deposits formed in an early, subseafloor setting at c. 1.89 Ga, when submarine strata were buried and intruded by porphyritic rocks and granitoids. The deposits have many mineralogical and textural similarities to metasomatic skarn deposits (e.g. Allen et al. 2003; Jansson and Allen 2015). However, an overprint by regional metamorphism and deformation during the Svecokarelian orogeny at 1.87-1.80 Ga complicate ore genetic interpretation, in particular the distinction between early ore-related silicates and silicates formed during the regional metamorphic overprint. Analogous to classic discussions on the genesis of Broken Hill-type deposits, metamorphism has induced uncertainty on whether minerals such as diopside and garnet formed metasomatically in conjunction with ore formation, or later when lower temperature alteration assemblages were metamorphosed.

The Sala area is particularly favorable for addressing this problem, since the metamorphic grade only reached upper greenschist facies, as opposed to amphibolite or granulite facies elsewhere in Bergslagen. Furthermore, the area contains some of the most texturally well-preserved rocks in the region. This contribution presents an updated genetic model based on a recent drill core logging and mapping campaign complemented by microscopy and analysis of numerous samples for whole-rock lithogeochemistry and mineral chemistry.

2 The Sala Area

The Sala area is located in the central part of Bergslagen. It is dominated by c. NW-trending, gently plunging F₁ folds that are overprinted by open, NE-trending F₂ folds. The eastern part of Fig. 1 is characterized by zigmoidal, parasitic F₁ folds whereas the western part is a culmination of F₁ folds, interpreted as a F₁ synclinorium. The western limb of this synclinorium is truncated by a prominent, WSW-dipping shear zone with inferred dextral and reverse displacement.
Towards the east, the marble unit is truncated by a large calc-alkaline granite-granodiorite batholith; the Sala-Vänge batholith. Ripa et al. (2002) presented two ages of 1891±6 and 1890±6 Ma of magmatic crystallization, overlapping within error with the age of a dated volcaniclastic interbed in the marble. Shearing and granitoid emplacement have led to that metavolcanic rocks belonging to the original stratigraphic footwall being only present in the SW part of Figure 1. In terms of original volcanic facies, the footwall can be subdivided into a lower succession of stratified, rhyolitic-dacitic siltstone-sandstone with local volcaniclastic breccia intervals and an upper c. 300 m thick unit of feldspar+quartz-phryic rhyolitic pumice breccia. Deposition of the limestone (now marble) occurred during a lowstand in volcanism during which...
growth of stromatolitic limestone was intermittently interrupted by deposition of resedimented volcaniclastic debris (Allen et al., 2003). A succession of metamorphosed polymict rhythmic volcanic breccia-conglomerate and rhyolitic silt-sandstone overlie the marble. The breccia-conglomerate units commonly have erosional lower contacts and locally carry clasts of former limestone. Pumice clasts become more common stratigraphically up-section.

3 The alteration system

The sulphide deposits mainly occur as breccia infill, vein networks and disseminations in skarn-rich dolomitic marble (Fig 2A). Jansson (2017) showed that sulphides have locally replaced and mimicked original stromatolitic laminae. The main ore minerals are sphalerite and galena accompanied by pyrrhotite and pyrite. A plethora of Ag-, Sb- and Hg-bearing minerals accompany the base metal sulphides, such as freibergite, silver amalgam, dyscrasite, mirgryite, allargentum, pyrrhotite, magnetite and very rarely grossular-andradite garnet and dravite tourmaline. Dolomitic marble carrying associations of these minerals define c. 200 m wide haloes around most known deposits (Fig. 1). These haloes coincide with weak but consistent whole-rock Fe and Mn enrichments and positive magnetic anomalies imparted by ubiquitous accessory magnetite and pyrrhotite. Using these geochemical and geomagnetic criteria, complex branching geometries are suggested for the alteration system, ranging from discordant to semi-concordant relative to stratigraphy. Jansson (2017) showed that this pattern reflects a combination of cross-stratal fluid flow along early faults and fluid flow along the contacts of numerous volcanic interbeds in the limestone precursor. F1 folding transposed these alteration zones with the result that they are now sub-parallel in plan view. The alteration zones converge down-stratigraphy and towards the contact of the Sala-Vänge granitoid (Fig. 1).

Clinopyroxene-bearing skarns occupy a central position in the altered zones, including Glasgruvan (Fig. 1) which is the type-locality of the eponymous ‘salite’; an old term for ferroan diopside. Locally, clinopyroxene can be seen to have formed as an open-space infilling in zoned vein networks and breccias where it exhibits a bladed habit (Fig 2B). Early clinopyroxene display complex growth zoning, reflecting variable Fe, Mg and Mn contents (Di66.6Hd2.8Jhn0.6, Fig. 2C).

More peripheral in the haloes, forsterite (Fo96Fay4) is the main anhydrous skarn mineral; a mineral which hitherto has been neglected at Sala (Fig. 2D). The altered dolomite and the magnesian silicates have elevated Fe and Mn, and the associated magnetite carry up to 3.10 wt.% MnO. This is the mineralogical manifestation of aforementioned geochemical and magnetic haloes. However, minerals with essential Mn are lacking at Sala.

Sjögren (1910) found that the ore sulphides have locally perfectly pseudomorphed fibrous tremolite crystals, further highlighting the link between mineralization and retrograde alteration. However, the final stages of retrograde alteration appear to have been barren, except for with respect to amalgams, antimonides and native forms of Ag, Sb and Hg (e.g. Kieft et al. 1987). In Sala mine, this is best reflected by transgressive zones of talc, serpentine and chlorite that occupy a central part of the mineralized system, yet are essentially barren. The strong spatial relationship of these zones to ore have led most observers to interpret them as fossil conduits for hydrothermal fluids (e.g. Sjögren 1910, Jansson 2017). Their barren nature most likely reflect focused retrograde alteration by highly reactive, acidic and siliceous fluids that were poor in metals and/or sulphur. The high content of mechanically weak silicates in these zones resulted in ductile shear zones during subsequent deformation. Strain partitioning by these zones may be the reason why relatively well-preserved rocks can be found in the area near the Sala mine and adjacent dolomite mines.

The Sala-Vänge batholith has a sharp contact towards the alteration system, but is itself virtually unaltered. At the Bronäs deposit (Fig. 1), irregular bodies of weakly sericite-altered feldspar+quartz-porphyritic rocks with chilled margins intruded highly altered and mineralized dolomitic marble directly adjacent to sulphide mineralization. These features can be reconciled if emplacement of these intrusions post-dated mineralization, yet occurred along the same structures that originally channeled the mineralizing fluids.

4 Conclusions

Despite the tectonometamorphic overprint, we recognize that intrusive-related, metasomatic processes were involved in the genesis of the polymetallic sulphide mineralization in the Sala area. The common association of sulphides with retrograde minerals is similar to typical metasomatic skarn deposits (e.g. Meinert et al. 2005). Similar to Zn skarns worldwide, the Sala deposits appears to be structurally controlled and
to have formed away from intrusive contacts. On the other hand, the skarn parageneses are more magnesian than in typical Zn skarn deposits, which typically formed in calcitic rocks and where the alteration silicates are more Fe- and Mn-rich. Most likely, these differences reflect the unusual submerged, intra-continental back-arc tectonic setting of skarn deposits in Bergslagen. This meant involvement of modified seawater in early, pre-skarn alteration stages, such as dolomitization of original calcitic limestone and hydrothermal alteration of volcanic rocks. Nevertheless, the Sala deposits can be included in the larger family of Zn skarn deposits as defined by e.g. Meinert et al. (2005). The results support other studies elsewhere in Bergslagen (e.g. Jansson and Allen, 2015), concluding that despite the complex regional metamorphic overprint, contact metasomatic processes related to 1.89 Ga intrusions can still be recognized.

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Stanniferous silicates in an exotic scheelite skarn close to the Felbertal tungsten mine, Eastern Alps, Austria

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Abstract. A unique type of W-(Sn) skarn mineralisation is reported from a tungsten prospect about 8 km south of Felbertal scheelite mine in the Alps. Scheelite is hosted in calc-silicate rocks consisting of stanniferous clinozoisite, quartz, plagioclase, calcite and chlorite. Tin is exclusively incorporated in the lattice of clinozoisite and titanite. Concentrations of up to 3.00 mass% SnO₂ in clinozoisite are the highest values recorded for this mineral so far. Substitution of (Al, Fe)³⁺ by (Sn, Ti)⁴⁺ in clinozoisite is balanced by incorporation of Fe²⁺. The skarn assemblage records a regional metamorphic overprint. Formation as a distal magmatic skarn is discussed.

1 Introduction

Tungsten exploration in the 1960s to 1980s in the Eastern Alps resulted in discovery of numerous scheelite showings but also of the world-class Felbertal scheelite deposit (annual production 2016 1200 t WO₃). A peculiar aspect of scheelite mineralisation in the Eastern Alps is the paucity of Sn. Mineralised systems containing Sn in addition to W are extremely rare; e.g., only traces of Sn are found in the Felbertal deposit and Sn is lacking in all other scheelite occurrences in the Eastern Alps.

A remarkable exception to this is Messelingscharte (~8 km S of Felbertal) that was re-explored in 2015 by Wolfram Bergbau und Hütten AG. There, the main mineralisation is a Sn-bearing scheelite skarn, which was not identified correctly when it was discovered in the 1960s. The particular feature is that Sn is hosted in Ca-silicate minerals and not in cassiterite.

This study presents information on the geological setting, the skarn petrography and mineralogical data of the stanniferous silicates. Sn-bearing silicates are known from magmatic skarn deposits, but there are very few comparable examples documented in the international literature. It will be argued that this mineralisation type is comparable to distal granite-related magmatic skarns.

2 Geological setting

The study area is situated in the central Tauern Window in the Eastern Alps. The geological units relevant for W-(Sn) mineralisation are metamorphosed Cambro-Ordovician basement units and Permo-Carboniferous metagranites (Zentralgneis). The pre-Variscan metamorphic units include two metabasite dominated units, the Basal Amphibolite (Basisschiefer) and the Habach Complex that are separated by the Basal Schist unit.

The Basal Amphibolite comprises amphibolites and meta-gabbros of debated protolith age (pre-Variscan vs. Variscan) showing enriched MORB-like geochemical signatures typical of back-arc magmas (Ordosch 2017; Vavra and Frisch 1989). The overlying metavolcano-sedimentary sequence is referred to as the Basal Schist (Basisschiefer). The poly-metamorphic Habach Complex consists of various pre-Variscan meta-igneous rocks, clastic metasediments and Variscan metagranitoids (e.g. Höck 1993). It is subdivided into the Lower Magmatic Series (LMS), Upper Magmatic Series (UMS) and the Habach phyllite. The Lower Magmatic Series, a dismembered meta-ophiolite, consists of amphibolites, metagabbros, meta-ultramafic rocks and minor meta-sediments and Early Cambrian I-type metamagranitoids (Höll and Eichhorn 2000). The Upper Magmatic Series is an arc sequence including various metamorphosed basic to acidic calc-alkaline volcanic rocks grading into the Habach phyllites.

The Felbertal tungsten deposit consists of a metamorphosed stockwork of deformed quartz-scheelite veins, mineralised shear zones with strongly foliated quartz-scheelite ores and disseminated scheelite mineralisation in the host rocks. It was interpreted as a polygenetic strata-bound scheelite deposit (Höll and Eichhorn 2000). A conspicuous orthogneiss ("K1 Gneis") derived from an evolved 340 Ma granite played a key role in formation of the Felbertal deposit (see review in Raith et al. 2018).

3 W-(Sn) skarn mineralisation

Scheelite is predominantly present in massive, non-foliated clinozoisite-rich calc-silicic skarn rock and amphibole schist. The skarn bodies occur as irregular pods and nests up to 2.0 x 1.5 m in size within the amphibolites of the Basal Amphibolite unit. The skarn is composed of clinozoisite (50%), quartz (20%), plagioclase (15%), scheelite (6%), calcite (5%) and minor to accessory chlorite, titanite, apatite, zircon, pyrite and chalcopyrite. Two types of clinozoisite can be distinguished. Clinozoisite 1 is coarse-grained forming prismatic to irregular subhedral crystals. The assemblage is stanniferous clinozoisite + scheelite + (stanniferous) titanite + quartz + plagioclase + calcite. Clinozoisite 2 is finer-grained and occurs in the assemblage clinozoisite + chlorite + quartz ± calcite; it often forms euheudal crystals inter-grown with quartz. The minerals show a mosaic texture indicative of metamorphic recrystallisation. Transitions of Clinozoisite 1 to 2 are also documented.
Titanite is fine- to medium-grained forming euhedral (sphenoidal) to anhedral, granular textured grains. Euhedral titanite is very common at the contact of the skarn rock to amphibole. Scheelite is of variable grain size and shows unduolose extinction and optical zoning. Normally, the core of larger scheelite crystals is yellow fluorescent grading into a blue rim.

Amphibole schist forming thin (cm) irregular, discontinuous layers is commonly associated with the skarn, especially at the contact with the host amphibolite. It is composed of medium-grained hornblende (50%), quartz (30%) and biotite (20%). Accessory minerals are pyrite, apatite, scheelite, chlorite, and titanite. In addition to the skarn, scheelite has also been observed in deformed scheelite quartz veins/veinlets and stringers hosted in foliated amphibolite and in mylonitic quartz veins.

4 Sn-bearing silicates

4.1 Clinozoisites

Mineral chemical compositions were analysed by EPMA in WDS mode at Montanuniversität Leoben; for analytical conditions see Ordosch (2017). Clinozoisite is characterised by an average molar Al/Fe³⁺ of 4.4 and Sn contents reach up to 3.0 mass% SnO₂. Concentrations of Na₂O, K₂O and MgO are generally very low, MnO can reach up to 0.67 mass% and TiO₂ up to 1.60 mass%.

Petrography and mineral chemical data allow distinction of two types of clinozoisite. Clinozoisite 1 comprising coarse-grained, irregular grains is higher in Sn and often shows an irregular intra-grain zoning (Fig. 1). High Sn/Ti domains normally occur as relict intra-grain domains that are incompletely replaced or overgrown by low-Sn clinozoisite (Clinozoisite 2); the latter also forms distinct euhedral, small crystals that clearly represent newly formed metamorphic grains. These grains are Sn-poor/free and there is no internal chemical zonation visible. Clinozoisite displays two chemical populations. The low-Sn population is characterised by ≤0.3 mass% SnO₂ (=0.01 apfu Sn; typical values 0-0.1 mass%). The high-Sn population reaches values of 3.00 mass% SnO₂ (=0.094 apfu; typical values 0.5-1 mass%). The high-Sn population mostly corresponds to Clinozoisite 1.

From crystal chemical considerations it is assumed that Sn⁴⁺ and Ti⁴⁺ are incorporated at the octahedral sites of clinozoisite/epidote where they may substitute for (Al, Fe)³⁺ at the M3 site. For charge balance equivalent amounts to Sn⁴⁺ and Ti⁴⁺ of divalent cations must be incorporated according to the following substitution: 2(Al,Fe)³⁺ ⇔ (Sn,Ti)⁴⁺ + (Fe,Mg,Mn)²⁺.

4.2 Titanite

Titanite mineral formulae were calculated on the basis of 1 Si + OH. In backscatter electron images titanite shows patchy irregular internal zoning (Fig. 3). Occasionally, micro-inclusions of cassiterite are observed. The patchy zoning is defined by element variations between Sn-Al- rich and Ti-Fe-rich intra-grain domains. Comparable irregular patchy zoning has been reported from zircons. It can be explained as disequilibrium texture caused by in-situ fluid-related mineral dissolution-precipitation during metamorphism. By this process earlier formed Sn-rich titanite transforms to Sn-poor titanite.

Values of xₐ₁ = Al/(Al+Fe+Ti+Sn) for titanite range from 0.075-0.236 with a median of 0.125; i.e. all titanites are classified as low-Al titanites. Titanite has a very variable content of SnO₂ ranging from 0.07 to 6.48 mass% (median 2.29 mass%). Statistically only one population of titanite can be identified in the data set.
Incorporation of Sn is according to simple Sn\(^{4+} \leftrightarrow\) Ti\(^{4+}\) substitution; i.e. solid solution of titanite-malayaite CaSnSiO\(_4\)(O,OH,F) (Takenouchi 1971).

\[
\text{Sn-rich titanite}
\]

Figure 3. BSE image of titanite. The brighter zones are Sn-rich. Arrow points out micro-inclusion of cassiterite (white).

\[
\begin{align*}
\text{Regression line: } y &= -0.99 + x + 1.07 \\
R^2 &= 0.94 \\
N &= 39
\end{align*}
\]

Figure 4. Bivariate plot of Ti\(^{4+}\)Sn vs. Al\(^{3+}\)Fe\(^{3+}\) (apfu) illustrating substitution of Sn in titanite.

The maximum analysed is 3.00 mass% SnO\(_2\) (=0.094 apfu), which is the highest value ever recorded in the literature to the knowledge of the authors. Worldwide, only a few other occurrences of Sn-bearing clinozoisite/epidote are known. Stanniferous clinozoisite/epidote was reported from massive skarns and skarn veins in Cornwall, UK (Alderton and Jackson 1978; van Marcke de Lummen 1986) and Cassiar district, British Columbia, Canada (Mulligan and Jambor 1968).

Tin-bearing calc-silicate bodies and veins were described from the St. Just aureole in the Land’s End granite, Cornwall (Alderton and Jackson 1978). The irregular-shaped discordant calc-silicate bodies and veins are composed of Ca-rich garnet, diopside, hornblende, epidote, ± axinite, ± tourmaline, ± accessory calcite, quartz, titanite and sulphides.

Tin-bearing epidote from the Chycornish Carn skarn vein is associated with hornblende, axinite, tourmaline and accessory titanite etc. Cassiterite is generally absent in all these calc-silicate veins and the Sn carriers are silicates. The skarn veins were interpreted as high-temperature (c. 500°C) metasomatic rocks predating Cu-Sn mineralisation in the tin lodes. An external; i.e. granitic, source of elements like Sn and Be has been envisaged.

Sn-bearing clinozoisite (up to 2.84 mass% SnO\(_2\)) was moreover described from The Crowns, also in the contact aureole of the Land’s End granite. There, it is part of the retrograde skarn assemblage including stanniferous epidote, cassiterite, amphibole, titanite/malayaite and chlorite and overprinting earlier grossular/andradite-rich skarn (van Marcke de Lummen 1986).

Stanniferous epidote has been reported from Fe-rich pyroxene skarns in the Cassiar district, British Columbia, Canada. These tin skarns belong to a mineralised belt with several Be, Sn, W and Mo occurrences that are spatially linked with granite batholiths in the Western Cordillera. The main constituents are Sn-bearing clinopyroxene, amphibole, epidote, garnet, calcite, quartz and accessory titanite; tin is incorporated in andradite, malayaite and epidote and amphibole (Mulligan and Jambor 1968; Scribner et al. 2017). Interestingly, at none of these localities scheelite has been reported as part of the Sn-bearing assemblage and even cassiterite is rare.

All these reported skarns are connected to granite-related magmatic hydrothermal systems. It is therefore tempting to postulate a similar genesis for Messelingscharte although there are no geological indications for a nearby intrusive contact there. However, it must be kept in mind that the Cornish Sn-(W) granites are post-orogenic whereas in the central Tauern Window pre-Alpine W-(Sn) mineralisation has been overprinted by Alpine tectonics and regional metamorphism. Thus, the Alpine orogeny likely blurred many of the primary features.

5 Discussion

5.1 Comparison with other localities

As documented in this study, clinozoisite from Messelingscharte incorporates high quantities of Sn\(^{4+}\).

Calc-silicate rocks, often collectively referred to as skarns, can form in different geologic environments by
various processes: isochemical formation of calc-silicate rocks with internal fluid buffering, local fluid exchange at the contacts between shales and limestones producing reaction skarns reactions and finally true magmatic skarns with infiltration of external magmatic hydrothermal fluids (e.g. Einaudi et al. 1981). This ambiguity is especially true for scheelite bearing calc-silicate rocks. In addition to magmatic tungsten skarns there are smaller sub-economic tungsten deposits in regional metamorphic calc-silicate rocks unrelated to granites (e.g., Eastern Alps, Raith 1991).

However, the vast majority of W mineralised calc-silicate rocks are magmatic tungsten skarns commonly forming proximal calcic exoskarns but also distal skarns developed along faults and major shear zones. Such magmatic W skarns (e.g., Cantung, Canada or King Island, Australia) are typically associated with evolved granites but they are normally Sn-free (Meinert et al. 2005). In Sn-W-F-Be skarns Sn may be incorporated in silicates (titanite, garnet, amphibole, ilvaite) during the later skarn stages (e.g. Mt. Lindsey, Australia, Kwak 1983).

The mineral assemblage of the clinozoisite-dominated skarn at Messelingscharte is comparable to lower temperature (retrograde) skarn assemblages. The lack of the high-temperature garnet-clinoxyroxene assemblages can be explained with the distal position of skarn formation which is further corroborated by the lack of a contact aureole and nearby granite intrusion. The regional geological setting of Messelingscharte also supports the model of distal skarn formation. Discordant scheelite-bearing quartz veins and stringers could represent feeder zones for skarn-forming magmatic hydrothermal fluids.

The world-class Felbertal scheelite deposit is located only about 8 km north of Messelingscharte. Recent studies confirmed the Variscan age of this deposit and the genetic link with c. 335-340 Ma evolved granites (K1 Gneis) in the deposit (Kozlik et al. 2016). The hypothesis that the W deposit Felbertal and W-(Sn) mineralisation at Messelingscharte are part of a common magmatic-hydrothermal system related to Variscan magmatism has still to be tested in the future.

6 Implications

The unique W-(Sn) skarn reported here is the first record of scheelite mineralisation associated with tin in the Eastern Alps. Tin is exclusively incorporated in the lattice of clinozoisite and titanite and not present as cassiterite; thus, it is difficult to detect during exploration. The element association W-Sn supports a granitic provenance of the ore forming fluids thereby supporting magmatic-hydrothermal models of W mineralisation in the Felbertal area.

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Skarn mineral paragenesis at Delitzsch tungsten occurrence, Central Germany: proximal and distal mineral zoning

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Abstract. Determining the local mineral paragenesis and spatial relations of mineral zones is crucial for understanding the structure of intrusion related skarn systems. In the current study archive material from a 1970's drilling program is being used for extensive relogging and detailed petrography. Three main factors control the mineral zonation of the Delitzsch skarn: I) available host rock element inventory II) fluid permeability and reactivity of the host and III) it's distance to the igneous intrusion. The observed systematic mineral zonation has a skewed character with a lateral and vertical component. Laterally it is following a reactive marble layer dipping west at an angle between 45 to 60°. Vertically it is zoned with respect to the interaction of fluids and different host lithologies (hornfels, marble, intrusive rocks). Five main skarn types can be distinguished based on mineral paragenesis and texture. The skarn is forming zones that are often developed concentrically with respect to the vertical and lateral extension. The skarn types might therefore be used for vectoring mineralized sequences occurring proximal to the contact between intrusive rocks and calcic exoskarns.

1 Overview

Defining large scale mineral zones and structures is crucial for understanding intrusion related skarn systems. Amongst other more advanced methods, mapping and petrography of mineral textures and paragenetic relations are the most basic components in explaining the dynamics leading to the formation of skarns (Einaudi 1981; Fonteilles et al. 1989; Kerrick 1977; Meinert et al. 2005; Newberry 1982). The studied mineral occurrence is located in the state of Saxony, Central Germany, less than 5 km southwest of Delitzsch city. The area was subject to more than 70 deep exploration drillings starting in the late 1960s. In 1990 the project was stopped due to political reasons and economic considerations. No modern research of the mineralized contact-metasomatic rock sequences has been published in English language (Schenke 1995). The aim of the current study is therefore a) the establishment of detailed description of mineral zones and further b) defining vectors for genetic implications and mineralization. Today archive material from the drilling program is available in different conditions. Eight drill cores with a total skarn intersection of more than 300 m are subject to detailed macroscopic investigations and over 200 petrographic polished sections from a dozen drill holes have been studied up to date. Emphasis was put on creating east-west profiles although drill density is limited to a maximum of three cores on a section. Careful petrography is supported by SEM-EDX analysis using a JEOL JSM 6300 with Bruker X-Flash 5010 detector (123 eV energy resolution) and automated mineralogy using a Hitachi TM4000 Plus with “Advanced Mineral Identification and Characterization System” (AMICS). ICP-MS geochemical data for related igneous rocks and metasomatic skarns was available from previous work. EPMA studies on relevant zoned minerals like garnet, clinopyroxene and scheelite are planned in the future. A first publication with a detailed petrographic description including direct LA-ICP-MS U-Pb dating of garnet is in preparation.

Figure 1. Position of the Delitzsch tungsten skarn occurrence in context to the European Variscides (modified from Krüger et al. 2013).

2 Regional geological conditions

The skarn system is positioned at the northernmost margin of the Saxothuringian segment of the central European Variscides in close relationship to the
neighbouring Variscan volcanic arc (Rheic suture) of the Mid-German Crystallin Rise (Fig. 1). A kinked southwest to east trending sedimentary belt (syncline Delitzsch-Torgau-Doberlug) consisting of Cadomian-consolidated Neoproterozoic sediments, Cambrian and Carboniferous sediments were intruded by an igneous intrusion. The area is surficial covered by 100 to 120 m of poorly consolidated Cenozoic glacial and fluvio-glacial sediments. Host rocks of the partly mineralized skarns are alternating carbonatic and pelitic sedimentary sequences of the Lower Cambrian Zwethau-Formation. Intermediate to mafic volcanic and volcano-clastic rocks are interlayered with these sediments. A post-Variscian dated (300-311 Ma) igneous rock suite comprised of diorites, granodiorites and late aplites (Delitzsch pluton) intruded the sedimentary rocks. As a result, the alternating layers of carbonates and pelites of the Zwethau-Formation underwent intense contact metasomatism. Limestones, dolomitic limestones, pelites and pyroclastics were converted to calcite marbles, dolomite marbles, biotite hornfels and calc-silicate marbles. Infiltration metasomatism appears with the subsequent induction of large volumes of magmatic-hydrothermal fluids in permeable reactive lithologies. Today, the altered sediments with interlayered exoskarns dip westwards in an angle between 60° to 45° roughly parallel to the intrusive contact. As a result, metasomatic skarns occur in a depth between 100 m to 600 m in a roughly 300 m wide zone along a 3 km north-south extension between igneous rocks and contact metamorphosed sediments. The largest continuous metasomatic skarn zones are documented in the investigated southern part of the occurrence. Here, an extensively converted calcite marble sequence with an apparent thickness of 25 to 35 m is developed in-between hornfels. The unit is delimited to the west by compact, impermeable, and less reactive biotite hornfels in the hanging wall and footwall. To the east the marble unit is completely converted to skarn with discordant intrusion contact in the foot wall accompanied by intense endoskarn formation.

A prognostic ore content of 11 460 MT grading at 0.4 % WO3 was published by Schenke (1995). The number was later reduced to a third of the original value considering the low drill density and uncertain processability of the ore.

3 Skarn zoning

The observed mineral paragenesis are primarily zoned in dependence to I) available host rock element inventory, II) fluid permeability and reactivity of the host and III) it’s distance to the igneous intrusion. Several complex types of mineral zones can be differentiated based on mineral paragenesis and mineral ratios. The term distal and proximal skarn can be used almost synonymous for low and high intensity skarn forming processes.

Due to the inclination of the metasedimentary host, the most distal skarn is found in the west at the highest depth of up to 600 m. To the east, proximal skarn is found directly outcropping beneath Cenozoic cover at around 100 m depth. The intrusive contact might exhibit a steeper dip than the metamorphic layering of the sediments, hereby increasing the distance between skarn and intrusion from 0 m in the east to more than 75 m to the west. The observed mineral zoning of the investigated drill cores appears skewed due to the geological structure and the combination of vertical and lateral zonation. Vertical skarn zoning in a drill hole profile is obviously present due to changes in lithology and the interaction between magmatic hydrothermal fluids and different host rock lithologies during contact metasomatism. Lateral zoning predominantly occurs along the largely metasomatized carbonate sequence with decreasing intensity in distance to the intrusive contact from east to west.

Generally, the skarn is prominently thicker in the proximal zone close to the intrusive contact compared to the distal zone at the marble front. Exoskarn originating from calcic educts is most abundant. Five main types of skarn can be distinguished (a) brown compact fine crystalline garnet-clino.pyroxene skarn (or skarnoid) (b) greenish-grey quartz-clino.pyroxene-garnet skarn with prominent euhedral crystals floating in quartz matrix (c) medium to coarse crystalline reddish-brown to dark green garnet-skarn with chlorite, calcite and quartz interstitials (d) patchy red-brown to grey albite-doped garnet-clino.pyroxene endoskarn (e) reddish irregular garnet-clino.pyroxene exoskarn or skarnoid at the marble front with vesuvianite or prehnite. Locally, a more detailed subdivision can be performed. For example, garnet-clino.pyroxene skarn (a) might locally have lost most clino.pyroxene due to carbonatization forming calcite, actinolite and chlorite. 1.5 m thick granodiorite apophyses intruding the siliceous metasediments can form a dark red garnet skarn which bears little similarity with the corrosive network of endoskarn (d) at the contact between plutonic intrusion and carbonate rich metasediments. Skarn type (a) and (e) were historically called garnetfels (Granatfels) due to their compact appearance and fine grained mineral size without clearly visible garnet crystals. Granatfels was previously interpreted as reaction skarns forming from localized elemental exchange. Today it can be described as a skarnoid type, forming from slow fluid-rock interaction in less permeable rock sequences.

In the hanging wall and footwall of the metasomatic skarn, bedding parallel clino.pyroxene-prehnite-garnet bands are developed in impermeable, compact, and generally non-reactive biotite hornfels. These can be traced up to a distance of at least 150 m away from the skarn. Due to the very localized character of the bands, these are interpreted as metamorphic skarn bands resulting from contact metamorphic triggered diffusion reaction along former fine carbonate layers inside hornfels. They may reach a thickness of 1 m but usually form thin bands of 2 to 8 cm. Rarely, the original carbonate rock is still preserved at the centre of the band whereas a several cm thick, light brown garnet-clino.pyroxene skarn is developed in contact to siliceous rock. Hornfels is bleached (loss of biotite) to light grey in contact to high intensity proximal metasomatic skarn.
Bleaching occurs irregularly, cross cutting bedding parallel textures as schlieren or plumes.

Distal skarn is characterized by mineral zones of skarns alternating with pure, well recrystallized calcite marbles or lesser silicate marbles. The contact between skarn and marble is very sharp with a transition zone of not more than 5 cm. Metasomatic calc-silicate zones form several irregular finger shaped apophyses of 20 cm to 2 m reaching into the carbonate wall rocks giving some sections an almost brecciated appearance. The distal skarn (e) is comprised of reddish brown, slightly pinkish calcic garnet with dominant grossular component close to the marble front. Garnet is the main mineral component (more than 70 %) generally forming an anhedral isotropic crystal mass. Euhedral crystal boundaries are sometimes developed close to interstitials. The second most abundant mineral phase is hedenbergitic clinopyroxene which occurs as fine crystal aggregates or single crystals overgrown by grossular. The garnet to pyroxene ratio in the distal skarn is around 10:1 to 5:1. Diagnostic for distal skarn at the marble contact is the occurrence of yellowish-brown vesuvianite as subhedral crystals intergrown and sometimes overgrown by garnet. Rarely these minerals occur in some cm distance to the skarn-marble contact in the marble. Particular thin skarn apophyses might contain prehnite or muscovite. Scarc e wollastonite with yellowish UV-fluorescence was observed as subhedral lamellar or radiating crystals overgrowing garnet-clinopyroxene skarn at the marble contact. Sulphides rarely occur and are comprised of sphalerite and galena. Skarn sections are more abundant at the hanging wall and footwall boundary, whereas the centre of the altered marble rarely expresses a metasomatic overprint. Close to the hydraulic impermeable hanging wall hornfels, a more continuous, well crystallized andradite dominated skarn (c) with interstitial calcite, chloride, minor magnetite, and sulphides like pyrite and chalcopyrite forms. Garnet is greenish brown with a yellowish tint and often expresses optical anomalous behaviour with oscillatory or sector anisotropy.

Generally, the distal skarn (a or c) is barren of scheelite. Comparably high contents (up to 0.5 % WO₃) were rarely documented in historical reports close to the footwall or hanging wall, sometimes along fractured compact garnet-clinopyroxene skarn (a).

Proximal to the intrusive contact a much thicker skarn sequence with an apparent thickness of up to 60 m is developed. Original carbonate educts were completely converted to a massive skarn succession. The increase in thickness compared to the 25 to 30 m of primary carbonate metasediments could be explained by lithological changes or stacking through faulting. Currently this is supported by little evidence. Texturally it can be explained by the transformation of less reactive hornfels sections to garnet-clinopyroxene skarn (a) in the hanging wall and footwall of the carbonate beds. Whereas the core zone of the profile is dominated by well crystal lized, coarse grained garnet skarn (c), zones of euhedral quartz-clinopyroxene-garnet (b) to anhedral garnet-clinopyroxene skarn (a) are enveloping the sequence concentrically. The apparent thickness of skarn (a) is higher in the footwall with zones as large as 20 m to 30 m. Granular garnet skarn replacing the carbonate sequence has an apparent thickness of 30 m. In two drill cores, massive granular garnet skarn (c) is directly outcropping beneath the cenozoic discordance and has a direct intrusive contact, with formation of massive endoskarn (d). As a result, no shell of (a) and (b) type garnet-clinopyroxene skarn is developed.

Figure 2. Simplified characteristic rock texture exhibited by garnet-clinopyroxene skarn (a) and quartz-clinopyroxene-garnet skarn (b). Both rock types envelop the granular garnet skarn core zone (c) concentrically.

The outer shell of the proximal skarn consisting of massive compact garnet-clinopyroxene skarn (a) has a brown to reddish brown, rarely light or dark brown homogenous colour (Fig. 2). Textures sometimes appear irregular or cloudy, because of cross cutting reddish or bright late garnet plumes or schlieren. Late garnet might also form discrete bands or veins filled with quartz or calcite rimmed by euhedral red garnet crystals. Clinopyroxene occurs on angular interstitials overgrown by garnet. The ratio of garnet to pyroxene is around 10:1 to 20:1. If altered to calcite, actinolite, and quartz this ratio increases to 50:1. Other minerals occurring interstitially are calcite, chloride and minor quartz. In clinopyroxene rich areas titanite occurs dispersed. The outer limit of the (a) garnet-clinopyroxene skarn bordering bleached clinopyroxene hornfels can host epidote, prehnite, albite, siderite as well as more abundant chloride. In the footwall K-feldspar occurs on bands or veinlets. Garnet shows divers composition along the andradite-grossular series with a ratio of Fe to
Occasionally peculiar greenish-grey, mostly fine or medium grained quartz-clinopyroxene-garnet skarn (b) interlayered with minor garnet-clinopyroxene skarn (a) occurs next to the coarse grained main skarn zone (c). It is composed of massive quartz crystals overgrowing minute euhedral clinopyroxene crystals or aggregates and euhedral garnet. Macroscopically the rock exhibits granular and banded texture. Garnet may form aggregates with interlayered clinopyroxene similar to skarn (a). The ratio of garnet to pyroxene is 1:2 to 10:1 in garnet rich bands. Some intervals have exceptionally high epidote, chlorite or actinolite contents. Actinolite forms from the degradation of clinopyroxene in these specific zones. Garnet has fine inclusions of pyroxene or carbonatized pyroxene and often exhibits slight anomalous optical anisotropy in the outer rims.

Typical granular, medium to coarse crystalline garnet skarn (c) is forming the core zone of proximal skarn. Grain sizes are commonly larger in the centre compared to hanging wall and footwall. Colours are generally ranging from light brown to dark brown and green to dark green. The granular texture of the skarn is clearly visible due to zonal structure of individual minerals with light core zones and more intensively coloured rims. Texture of the rocks is often massive and not oriented but rarely appears banded by colour changes of light to dark browns and greens. In rare cases, coarse grained (>2 cm) euhedral dark red and dark green, zoned garnet is floating in a quartz matrix along several 50 cm thick bands in the centre of the skarn zone (c).

The coarse grained garnet skarn (c) has a simple mineralogy compared to the distal skarn at the marble front (e) or the enveloping skarns (a) and (b). Garnet is the main rock forming mineral with 75 to 90 % total volume. The amount of garnet might drop to 60 % in the main rock forming mineral with 75 to 90 % total volume. The mineralization is disseminated along calcite, chlorite, and quartz interstitials in the transition between the core zone (c) and the garnet-clinopyroxene skarn (a). Subhedral to anhedral crystals have been preferably precipitated along bands in fine to medium grained granular garnet skarn zones. WO3 contents commonly range between 0.2 and 0.6 %. Compact well crystallized quartz-rich garnet skarns rarely host more than 0.1 %WO3. Scheelite only occurs as minor anhedral inclusions in garnet in coarse crystalline garnet skarn (c) and only accessory in late quartz-calcite veinlets in garnet-clinopyroxene shell (a). In the endoskarn zone (d) scheelite occurs as large fractured amoeboid minerals dispersed along a K-feldspar-albite-calcite veinlet that is developed.

In the recent study it was demonstrated that the tungsten skarn occurrence Delitzsch in Central Germany displays a systematic complex mineral zonation. Patterns for distal and proximal skarn zones have been established that might be useful for a vectoring purpose. Highest WO3 grades were observed in the proximal skarn close to the intrusive contact. Vectoring of distal and proximal skarn mineral zones could therefore proof useful in directing future exploration for the strategic metal.

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**References**

District-scale geochemical signatures of calc-silicate skarn minerals from the Pb-Zn (± Ag, Cu) distal skarn deposits in Madan, Bulgaria

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Abstract. The distal skarn bodies of the Madan ore field provide a unique case study on the chemical evolution of a metasomatic mineralizing system at the regional scale. Despite the lack of a known causative intrusive body, chemical zonation in the skarn bodies suggests more proximal metasomatic replacement and mineralization towards the south. Hosted in marble lenses of the basement rocks, skarn pyroxene crystals show an increase in Fe/Mn ratio by an order of magnitude over a 15km N-S transect. Despite this district-scale trend, pyroxene compositions exhibit a wide range of concentrations at the deposit scale, where the Fe/Mn ratio is controlled by sequential crystallization during skarn formation. These trends correspond with local shifts in grain size and Fe/Mg ratio, and are observed at sample locations across the entire district.

Epidote and other Al-bearing alteration phases, hosted primarily in gneiss, can be sorted into two distinct groups based on major element geochemistry. One phase, Al-rich clinzoisite, maintains the major element chemical signature of the aluminous host rocks, while the second, ferriepidote, forms in veins that cut across the former. Previous work suggests that the secondary epidote may be the coeval metasomatic product of the calc-silicate skarn which formed in the marble, providing additional information for the regional scale chemical patterns.

1 Introduction

The Madan ore field (Fig. 1) in southern Bulgaria is endowed with Pb-Zn (± Ag, Cu) polymetallic deposits expressed as vein, skarn, and carbonate replacement mineralization (Bonev, 1984). The largest of these are hosted by distal pyroxene skarn bodies, the distribution of which is controlled by the intersections between a series of NW trending mineralized faults and marble lenses hosted within the metamorphic basement sequence of the Central Rhodopian dome (Marchev et al., 2005).

In the Madan region, the Central Rhodope Mountains are composed of exposed amphibolite and granulite metamorphic units which were exhumed during post-collisional extension beginning regionally in the Eocene (Bonev et al., 2013). These metamorphic units can be subdivided into: i) an upper unit (Madan), in which marble and amphibolite lenses up to 5-10m thick can be seen as a part of the amphibolite grade metapelitic sequence (Bonev, 1984, Burg, 2012), and ii) a lower unit (Arda), higher grade, with relics of UHP metamorphism, with few or no marble horizons (Marchev et al., 2005). The two tectonic terranes are separated by a low-angle detachment fault, which formed as part of the early extensional regime (Marchev et al., 2005; Burg, 2012, Bonev et al., 2013).

Locally, magmatism associated this extension began with the intrusion of the ~42 Ma Smilian granite (and equivalents to the east), which is interpreted to be displaced by the Central Rhodope detachment (Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004, 2013). Later, rhyolite dikes and ignimbrite deposits were emplaced starting at ~32 Ma and into the Paleogene (Harkovska et al., 1998, Kolkovski et al., 2000; Ovtcharova et al., 2003; Kaiser-Rohrmeier et al., 2004).

Figure 1. a. Map of Bulgaria. b. Simplified geologic map of the Madan ore field (modified from Vassileva et al., 2014).
A rhyolite dike has been used to place an upper age constraint on distal skarn formation based on the cross-cutting relationships with the older dike dated at 31.41 ± 0.39 Ma (U-Pb; zircon; Hantsche et al., 2017). Using late-stage white mica, post-skarn sulfide mineralization in the ore field has a minimum age constraint of 29.95 ± 0.23 Ma (Ar-Ar; sericite; Kaiser-Rohrmeier et al., 2004).

The regional geologic constrains on skarn formation are important to understand the metalogenesis of the district, and the formation of the calc-silicate skarns that host the largest Pb-Zn (± Ag, Cu) ore bodies in the district. The regional geochemical signature of the skarn silicates can help vectoring towards more proximal deposits within the mineralized system.

Skarns

The skarn bodies of the Madan ore field are dominated by Mn-rich clinopyroxene, with garnet skarns observed only as rare occurrences in the southern part of the district (Marzian). The pyroxenes grow as elongate crystals in radial clusters that form dense spheroids with minimal porosity. These skarn bodies are observed in the marble horizons within the Madan tectonic unit, where they are commonly located adjacent to fluid pathways, such as faults, veins, and lithological contacts (Bonev, 1984, Vassileva et al., 2009). Pyroxene skarns extend away from such surfaces into the marble lenses at distances of 10's of meters away from the fluid conduit (Vassileva et al., 2009). More rarely, sub-horizontal and sub-vertical skarn morphologies can be found hosted in marble.

Retrograde alteration of the pyroxene skarn bodies is associated with replacement by amphibole, rhodonite, carbonate, quartz, adularia, and rare garnet. This alteration is often followed by, or is simultaneous with, sulfide precipitation, including sphalerite, galena, pyrite, and chalcopyrite, accompanied by later generations of quartz, calcite, and sericite.

In the aluminous rocks, the skarn-stage alteration is dominated by epidote replacement of the host minerals, but is accompanied by rare garnet occurrences. The degree of epidotization corresponds to the distance from the local fluid source (i.e., the vein). Retrograde alteration is present as new epidote crystallization accompanied by sericite and weak sulfide mineralization (sphalerite, galena, pyrite, and chalcopyrite).

2 Methods

We have sampled 7 active and ancient mines (Fig. 1) to observe the district scale variations in major, minor, and trace elements in prograde skarn silicates.

An electron probe microanalyzer (EPMA) at the University of Geneva has been used to determine major element geochemistry. All spot analyses were made at 15kV and 20 nA, with a beam diameter of 1µm. All map analyses were made at 15kV and 100nA, with a 2µm pixel size. Individual pixels from EPMA chemical maps were quantified using XMapTools, calibrated with point analyses within the map area (Lanari et al., 2014; 2018). Trace element data will be collected using laser ablation inductively coupled mass spectrometry at ETH Zürich using a RESOlution laser ablation system coupled to a ThermoFisher Element XR sector-field mass spectrometer.

3 Results

Results of pyroxene EPMA analyses show chemical distinctions across the longitudinal span of the ore field (~15 km) changing from more Fe-rich compositions in the southern-most mine at Marzian (Jo40Hd35Di11), to more Mn-rich compositions in the northernmost deposit at Mogilata (Jo97Hd2Di1) (Fig. 2). Grain size variations in the chemistry of pyroxene crystals are also consistent across the district, in which banded pyroxene starts with fine grained (<1cm), Fe-rich crystals with lower Mg/Fe, which grow systematically into larger (up to 5 cm), johannsenitic pyroxene with higher Mg/Fe (Fig. 3).

Epidote geochemistry in samples from the Petrovitsa deposit show two distinct groups, with both an Al-rich and Fe-rich groups. This distinction is associated with epidote derived from host-rock alteration (clinozoisite,) or later vein formation (ferriepidote). Until now, only epidote from the Petrovitsa deposit has been analyzed in this study.

4 Discussion

Regional patterns of pyroxene compositions indicate the most Fe- and Mg-rich pyroxene compositions from the southern deposits of the Madan ore field (Marzian, Figure 2). However, the variation between johannsenitic (Mn-rich) and hedenbergitic (Fe-rich) pyroxene is not the ideal indicator of proximity to a fluid source, as a wide range of pyroxene compositions exists within individual skarn bodies. The Fe/Mg ratio of the pyroxene crystals may be a more useful tool, as this can be used to differentiate pyroxenes generations in individual deposits (Fig. 3).

“Early” pyroxene crystallizes as fine grain needles with higher concentration of Fe and Mg, but low Fe/Mg ratios. During the crystallization of the pyroxene skarn, larger crystals form radially outward from the early pyroxene (i.e., Marzian), which become higher in Mn.
clusters (this study; Bovay, 2016). Fe³⁺ - Al³⁺ substitution in carbonate host rocks (Bovay 2016). aluminous hosts rocks and Ca-Si skarn formation in suggesting potentially syngenetic epidotization of compositional variations of pyroxene present at an ratio provides insight on the chemical banding and geochemistry of skarn- and skarn- related minerals. The district-scale patterns in major element zonation patterns at the local scale that reinforce the observed major element zonation patterns. Epidote can be grouped into two distinct geochemical clusters (this study; Bovay, 2016). Fe³⁺ - Al³⁺ substitution accounts for this difference, which can be attributed to the host rock in which epidote alteration occurs. Samples from Petrovitsa (altered pegmatite; gneiss) indicate that early, Al-rich clinozoisite, replaces the primary feldspars, versus later epidote, which appears commonly as a vein infill mineral, with a higher Fe/Al ratio. Additionally, previous work on epidote samples from Gyurdyurska which are in equilibrium with prograde or retrograde skarn minerals, have higher Mn concentrations, while retaining the low-Al signature, suggesting potentially syngenetic epidotization of aluminous hosts rocks and Ca-Si skarn formation in carbonate host rocks (Bovay 2016).

5 Early Conclusions and Future Outlook

The district-scale patterns in major element geochemistry of skarn- and skarn-related minerals indicate an increase of Mn and changing Fe/Mg ratios with northward position in the ore field. This helps to quantitatively support work from Vassileva (2004), suggesting more proximal skarn mineralogy and chemistry in the southern extent of the ore field.

Understanding the deposit-scale variations in Fe-Mn-Mg space is critical to decipher the metallogeny of the ore field. Major element geochemical patterns at the outcrop, hand sample, and thin section scales, suggest cyclic skarn growth events in which chemically evolving fluid pulses, along with temperature changes, control concentric chemical banding in skarn silicates.

Similarly, alteration of the host aluminous rocks in the form of epidote presents a promising chemical tracer for processes that may not be recorded by the pyroxene skarns in Madan. The distinction in major element chemistry suggests that the fluids which precipitate the later, Fe-Mn rich epidote, may contain trace element signatures indicative of the fluid source and evolution during transport.

The future aim is to complement the major element geochemistry with trace element compositions (via LA-ICP-MS) from the skarn-related silicates. Local and regional patterns in the silicate chemistry will be linked together to better develop the ore formation model for the Madan ore field. The ultimate goal of this project will be to identify chemical vectors in the skarn minerals to help point towards deeper parts of the mineralized system.

References


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Abstract. Grossular-andradites (grandites) of the Karavansalija Mineralized Centre (KMC) in the Rogozna Mountains, SW Serbia, were studied using relative and absolute dating methods. The KMC Cu-Au skarn deposit is a result of multiphase hydrothermal activity caused by discrete magmatic pulses. Shallow magmatic injection of trachyandesites into Cretaceous limestone led to the formation of an extensive prograde exoskarn field followed by retrograde hydrothermal phase that results in a main greenish mass of disseminated “atoll” garnets. Later crowded porphyry stocks and dykes interacted strongly with the skarns reactivating the hydrothermal system. This process led to the formation of endoskarn veins with garnets but also to an enrichment of valuable ore minerals, especially during the retro-grade stage when gold bearing minerals precipitated. All grandites reveal changing chemistry in narrow and/or wide growth zones and variable (<1 to >30 ppm) uranium content. LA-HR-ICP-MS dating yields lower intercept ages of 28.0 ± 1.4 Ma - 26.98 ± 0.75 Ma for the “atoll” garnets and a cross-cutting vein in them and 27.56 ± 0.20 Ma for vein garnets in the crowded porphyry dyke. Consequently, the grandite dating outlines the progress of mineralizing hydrothermal events but is complicated by alteration and overgrowth during the overprinting hydrothermal processes.

1 Introduction

The relative and absolute timing of ore deposits combined with tracing of the dated minerals is crucial for understanding the processes of ore sourcing and deposition and possibly for the general estimation of the economic potential (Rohrlach and Loucks 2005; Chiaradia 2009; Richards 2011; Carrichi et al. 2014; Von Quadt et al. 2018). While the relative timing is based on cross-cutting relationships of rocks, ore veins, and minerals, as well as inclusions in them, absolute dating requires the application of isotopic methods to datable minerals. The Cu-Au porphyry systems are most commonly dated not only because of their economic significance but also due to the possibility to cover the whole range of temperatures during the generation of the deposits (porphyry, skarn and epithermal) from the magmatic to the hydrothermal stages and exhumation (e.g. Chiaradia et al. 2013).

Skarn ore deposits might be part of porphyry systems (Sillitoe 2011) but could also result from a variety of metasomatic processes involving fluids of magmatic, metamorphic, meteotropic, and/or marine origin (Meinert et al. 2005). The availability of geochronological data on skarn hydrothermal deposits is rare, due to scarcity of dateable primary skarn minerals. Potential minerals for U-Pb geochronological studies of skarns are the calcium garnets of the andradite-grossular series (grandites). A real revival of the method is connected with the application of the LA-ICP-MS technique (Seman et al. 2017; Waßnorn et al. 2018). This is fast and can be applied directly to thin/thick sections or to separated and mounted grains. An important advantage is the possibility to avoid inclusions (if visible), choosing the position of the LA-craters. However, the application of the conventional ID-TIMS U-Pb techniques may provide even more precise age data (Seman et al. 2017; Salnikova et al. 2018) in a case of appropriate grandites.

In present study we are testing the U-Pb garnet dating techniques on the skarns of Karavansalija Mineralized Centre (KMC) in the Rogozna Mountains, SW Serbia (Borojević-Šoštarić et al. 2013 and references therein). Precise CA-ID-TIMS U-Pb zircon dating (Hoerler 2017) revealed 1.7 Ma of magma evolution, skarn formation and about 140 Ka timespan of economic ore mineralization. These results provide a perfect opportunity for comparison with our new geochronological garnet data.

2 Geological setting

The Karavansalija Mineralized Center in the Rogozna Mountains is related to a magmatic suite that is part of the NW-SE oriented Oligo-Miocene Serbo-Macedonian-Magmatic and Metallogenic Belt (SMMMB), which can be traced from Serbia to Macedonia, Bulgaria and Greece (Fig. 1). The belt is represented by Pb–Zn–Ag (± Sb ± Cu ± Au ± W) veined hydrothermal and/or skarn replacement mineralization. A few of the emplaced base metal deposits are located within the Rogozna Mts. and in its surrounding areas are the well-known occurrences of Trepa, Crnac, Belo Brdo and Leskova Glava (Borojević-Šoštarić et al. 2013; Fig. 1).

Two main magmatic episodes are distinguished in the Cenozoic magmatic complex of Rogozna Mts.: i) an older succession (Ar/Ar ages of about 30 Ma) composed mostly of andesite-dacite ± quartz-latite volcanic rocks, in the eastern part of the complex, and ii) a younger succession (29 to 24 Ma) comprising quartz-latite and related pyroclastics (Borojević-Šoštarić et al. 2013). Borojević-Šoštarić et al. (2012) found numerous
disequilibrium textures, which indicate that the younger rocks formed by crystallization of hybridized magmas. Thus, they concluded a genetic link to the adjacent Pb-Zn-Ag Crnac deposit (~ 5 km north of KMC).

3 Relative timing and the U-Pb CA-ID-TIMS zircon age constraints

The KMC Cu-Au skarn deposit is a result of multiphase hydrothermal activity caused by discrete magmatic pulses. Zircon LA-ICP-MS and ID-TIMS dating together with zircon trace element and Hf isotope measurements suggest that the magmatism started at around 29.3 Ma with andesitic to trachy-andesitic extrusives and shallow intrusive volcanics. Shallow magmatic injection of more evolved trachy-andesites into Cretaceous limestone at ca. 29.0 Ma led to the formation of an extensive prograde exoskarn field. The fluids in excess show 550°C and 55 wt.% NaCl equivalent, indicating a magmatic fluid source. A retrograde hydrothermal phase in the exoskarns led to incomplete reaction of garnet to hydrous phases like chlorite and epidote. After a period of quiescence of about 1.2 Ma, an increased heat and fluid pressure led to the expulsion of fluids from a "crowded" (crystal-rich) porphyritic stock (CP) at ca. 27.76 Ma. They strongly interacted with the skarns establishing/reactivating the hydrothermal system, which led to the formation of endoskarn veins with garnets but also to an enrichment of valuable ore minerals (arsenic pyrite, chalcopyrite, sphalerite and galena). During the retrograde stage the gold bearing minerals precipitated. Soon after an unmineralized second pulse of porphyry dykes cut the previous "crowded" porphyries and skarns at ca. 27.62 Ma, thus bracketing the maximum timespan of economic ore mineralization to about 140 Ka (Hoerler 2017).

Figure 1. Alpine tectonic units of the Balkan Peninsula (modified after Schefer et al., 2011) with the position of the Oligo-Miocene Serbo-Macedonian-Magmatic and Metallogenic Belt (SMMMB; red dash-line) and the Rogozna Ms. with KMC (purple rectangle). Numbers correspond to important ore deposits of SMMMB: 1 - Veliki Majdan; 2 - Rudnik; 3 - Golija; 4 - Kopaonik & Željin; 5 Karavansalija & Crnac; 6 - Trepa; 7 - Lece; 8 - Kisieljak; 9 - Surdulica; 10 - Kratovo – Zletovo; 11 - Buchim – Damjan – Borov Dol ore district; 12 – Ilovica; 13 – Jekario; 14 – Vathi; 15 – Kassandra (Olympias, Pavres Petres, Madem Lakkos, Skouries); 16 – Spahievo; 17 – Lozen; 18 – Madzharovo; 19 – Pcheloyad & Zvezdel; 20 – Sappes; 21 - Perama & Maronia.
4 Garnet sampling

The first group (i) of garnet samples for dating are from the exoskarns related to the early trachyandesitic shallow intrusion. They form a main greenish mass of disseminated “atoll” garnets with chlorite and epidote, which are cross-cut by later Garnet-Quartz-Calcite veins with arsenopyrite. The second group of garnet samples (ii) are from the endoskarn veins in the CP, where they form aggregates and well-shaped muddy orange-greenish crystals.

5 Analytical techniques

EPMA analyses were performed at ETH-Zurich using a JEOL JXA-8200 SuperProbe Electron Probe Microanalyzer. U-Pb isotope and trace element composition of the garnets were defined at ETH Zurich and the Geological Institute of the Bulgarian Academy of Sciences, using a Resonetics Resolution 155 laser ablation system coupled to a ThermoScientific Element HR ICP-MS and UP193FX New Wave LA system and Elan DRCe quadrupole ICP-MS, respectively. Mali (Seaman et al., 2017) and Dashkesan (Stifeeva et al., 2018) garnets were used as primary external standards for dating, and NIST 612 and NIST 610 for trace element analysis. The results were calculated using Iolite combined with VizualAge to obtain ages and ratios corrected for instrumental drift and down-hole fractionation. Iolite or SILLS programs and the SiO₂ content of the garnets (as internal standard or from mineral stoichiometry) are used for calculation of their trace element composition.

6 Results

EPMA analyses of the garnets reveal andradite-grossular (Andₐ₀.₃₉Grossₐ₀.₆₄) to end-member andradite composition (Andₐ₀.₉₉Grossₐ₀.₀₂) with changing chemistry in narrow and/or wide growth zones (Fig. 2). Typical trace elements are Ti and Mn (0.1-2.6% TiO₂ and 0.1-0.8% MnO). Uranium content is also highly variable (<1 to >30 ppm) with generally higher quantity in grossular-andradites and lower in andradite-grossular and end-member andradite. Chondrite-normalized rare earth (RE) patterns show enrichment in the light to intermediate RE and depletion of the heavy RE (opposite to the patterns of the Fe-series garnets). Other elements in elevated concentrations (compared to C1 chondrite and the trachyandesitic subvolcanics) are Y, W, Nb, P, V, Cr, Ga, Ge, As.

U-Pb garnet age dating with the LA-quadrupole ICP-MS was possible only in the case of U>5-7 ppm and resulted in ages with ±10% uncertainty. The LA-HR-ICP-MS dating yields lower intercept ages of 28.0 ± 1.4 Ma for the type (i) “atoll” garnets in the exoskarns (Fig. 3), 26.98 ± 0.75 Ma – the vein garnets in the exoskarns, and 27.56 ± 0.20 Ma (Fig. 4) for vein garnets in the crowded porphyry dyke (endoskarns).

7 Discussion and conclusions

ID-TIMS dating of selected grandite grains revealed high common lead contribution and resulted in poorly defined and generally younger ages for all garnet types and samples analyzed.
HR-ICP-MS ages (≥1-2% uncertainties) is similar to the one of LA-ICP-MS zircon dating but clearly less precise than the CA-ID-TIMS zircon ages. In the case of KMC absolute timing of the skarn garnets outlines the progress of mineralizing events but is complicated by the hydrothermal alteration, overgrowths and possible Pb-loss during the overprinting process.

As revealed by the relative timing skarification is a multi-stage process. From our garnet U/Pb age it appears that the retrogressive hydrothermal overprint in the exoskarns, formed at 26.98 ± 0.75 Ma, although less precise, is rather contemporary with the progressive and regressive stages of endoskarn than with the main event of skarification in the limestones. We may therefore conclude that the main mineralizing event is related to the crowded porphyry intrusions that postdate the formation of the extensive exoskarns. However, some porphyry dykes cross-cut the mineralized veins and post-date both, the two types of skarns and the Au-Cu-base metal mineralization.

Further potential of skarn garnets in mineral exploration are given through characteristic trace element signatures which is a focus of our ongoing studies.

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References


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Formation of the Xintianling scheelite skarn deposit, Nanling Range, South China: insights from petrology, mineral chemistry and C-H-O-S-Pb isotopes

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Abstract. The Xintianling scheelite skarn deposit is situated in the southern Hunan province, Nanling Range, South China. It hosts 0.33 Mt tons of WO3 and is genetically related to a magnetite-series S-type granitic intrusion, which has high magnetite/ilmenite ratios, high magnetic susceptibility and high zircon Ce4+/Ce3+ ratios, distinctly different from the ilmenite-series granites associated with quartz-wolframite-vein type deposits in the Nanling Range. This scheelite skarn deposit was formed at ~162 Ma and is characterized by a mineral assemblage of an oxidized skarn system. It can be divided into five stages: grossular + andradite + diopside (stage I), hornblende + actinolite + Fe-rich andradite + magnetite + scheelite (stage II), scheelite-bearing vein (stage III), molybdenite-quartz vein (stage IV), and calcite + pyrite + sphalerite + galena vein (stage V). Stage II is the dominant scheelite mineralization stage. C-H-O-S-Pb isotopes indicate that the ore-forming fluids are mainly magmatic water mixed with lesser meteoric water and the ore-forming materials are of crustal in origin and derived by mixing of magmatic and sedimentary materials.

1 Introduction

China hosts more than half of the world tungsten resources. The two most important tungsten mineralization belts are Jiangnan Orogeny Belt and Nanling Range, where lots of large tungsten deposits are developed such as Zhuxi (scheelite skarn), Dahutang (veinlet-disseminated scheelite), Shizhuyuan (scheelite skarn and greisen), Piaotang (quartz-wolframite vein), Xintianling (scheelite skarn), Yaogangxian (scheelite skarn and quartz-wolframite vein) and etc.

The Xintianling scheelite skarn deposit is situated in the southern Hunan Province, central part of the Nanling Range, South China. This deposit was discovered in 1957 and detailed prospecting was finished in 1981. It contains 80.9 Mt ore at 0.36% WO3, 21.8 Mt at 0.022% Mo and 9.5 Mt at 0.033% Bi. Few studies have been conducted to investigate the genesis of the Xintianling deposit (Bi et al. 1998; Cai et al. 2008; Yin and Wang 1994). The petrogenesis of the parental granites, the formation and genesis of the scheelite skarn are still unclear.

2 Petrology of the granitic rocks

The scheelite skarn is spatially related to the Xintianling granite intrusion. The granite intrusion is composed of a central facies of medium-grained biotite granite and a marginal facies of fine-grained biotite granite, cut by granite porphyry dykes (Figure 1). The two granite facies have zircon U-Pb ages of 165.0 ± 3.1 Ma and 164.0 ± 0.6 Ma, respectively, while the granite porphyry dykes have a zircon U-Pb age of 147.5 ± 0.5 Ma. The two facies of biotite granites are metaluminous to slightly peraluminous, and of high-K calc-alkaline compositions. They were formed by fractional crystallization of apatite, monazite, K-feldspar and plagioclase from the same magma system. They have consistent initial 87Sr/86Sr ratios of 0.7116 to 0.7198, εNd(t) values −7.1 to −9.5 and zircon εHf(t) values of −4.1 to −11.4, indicative of partial melting of the Cathaysian crustal basement (1.6-1.7 Ga). Granite porphyry dykes cut through the biotite granites and the skarn ore bodies, and have affinities to A-type granite. The dykes have similar initial 87Sr/86Sr ratios (0.7123 to 0.7153), slightly higher εNd(t) value (~6.2) and slightly younger Nd and Hf isotopic model ages (1.45 Ga and 1.53 Ga, respectively), suggesting generation by partial melting of Mesoproterozoic metamorphic basement in the lower crust, similar to the earlier granites, but probably involving injection of some mafic mantle-derived magma.

Figure 1. Geology map of the Xintianling scheelite skarn deposit, Nanling Range, South China

The Xintianling biotite granites have an assemblage of magnetite + allanite + titanite, and high magnetite/ilmenite ratio (>4:1), high magnetic susceptibility with an average value of 827×10−6 emu/g...
and Ce⁴⁺/Ce³⁺ ratios in zircon (Figure 2). These features indicate a high oxidation state of the Xintianling granites (magnetite-series), which distinctly differs from most W-bearing granites associated with quartz-woframite vein type deposits in the Nanling Range which are of ilmenite-series affinity. The oxidized nature of the Xintianling biotite granites also implies the absence of mineralization potential of tin.

**Figure 2.** Magnetic susceptibility of the granitic rocks in the Xintianling scheelite skarn deposit and other tungsten deposits in the Nanling Range, South China

### 3 Mineral chemistry of the scheelite skarn

The orebodies commonly occur in the contact zone between the granite stock and the limestone of the Shidengzi Formation (Yin and Wang 1994). The Xintianling deposit consists of approximately 80 skarn orebodies. Among them, 23 endoskarn, 25 proximal skarn and 32 distal skarn orebodies occur in the granite, at the contact zone and in the limestone, respectively. Endoskarn and proximal skarn are the predominant scheelite ore types, with stratoid, lens- and vein-like shapes. The orebodies are 100~1600 m in length and 1~67 m in thickness, striking nearly north-south and dipping to west at variable angles of 10~80°. Skarn minerals consist of andradite, grossular, diopside, wollastonite, vesuvianite, actinolite, hornblende, epidote, titanite, orthoclase, oligoclase, fluorite, muscovite, and chlorite. The main ore minerals are scheelite and molybdenite, with small amounts of bismuthinite, pyrite, galena, marmatite, azurite, pyrrhotite and limonite. Re-Os dating on molybdenites from skarn and quartz vein yielded an isochron age of 161.8 ± 2.2 Ma. This age is consistent with the zircon U-Pb ages of the host biotite granites within analytical uncertainties, indicating the direct genetic relationship between granitic magmatism and hydrothermal scheelite mineralization.

Several distinct stages of skarnization and mineralization are inferred from paragenetic relationships based on observations of field and thin sections. They can be divided into five broad stages in chronological order: grossular + andradite + diopside (stage I), hornblende + actinolite + Fe-rich andradite + magnetite + scheelite (stage II), scheelite-bearing vein (stage III), molybdenite-quartz vein (stage IV), and calcite + pyrite + sphalerite + galena vein stage (stage V). Scheelite mineralization occurred dominantly as disseminated in stage II and less in veins of stage III. Disseminated scheelite is closely associated with a hornblende + actinolite + magnetite assemblage. In terms of mineral assemblage, three kinds of scheelite-bearing veins can be identified: quartz + scheelite, epidote + fluorite + sphalerite + scheelite and tourmaline + chlorite + scheelite veins.

**Figure 3.** Chemical compositions of garnet from the Xintianling scheelite skarn deposit, Nanling Range, South China

**Figure 4.** Chemical compositions of pyroxene from the Xintianling scheelite skarn deposit, Nanling Range, South China

Mineral assemblages in stage I indicate oxidized skarn. From stage I to stage II, compositions of garnet change from And₃₁₋₆₀Gr₈₃₋₆₀Sp₃₋₁₀ (And I) to And₅₈₋₈₁Gr₁₀₋₃₇Sp₁₋₁₀ (And II) (Figure 3), indicating an increasing trend of Fe-end member and oxygen fugacity. After
replacement by hornblende and actinolite. And II was usually formed around And I. The occurrence of late stage molybdenite mineralization (stage IV) and a calcite + pyrite + sphalerite + galena assemblage (stage V) suggests an oxygen fugacity decrease in post-scheelite mineralization. A small amount of spessartine (Sp72-85Alm6-17Gr7-12) associated with sulfides is observed as spessartine-calcite vein in stage I, corroborating further low oxygen fugacity in the late stage. The formation of spessartine is possibly related to the involvement of Mn from the wall rocks. The characteristics of garnet compositions and mineral assemblages in the different stages indicate that scheelite mineralization developed under high oxygen fugacity condition. The compositions of pyroxene are Di46-69Hd20-52Jo2-11 (Figure 4). Hornblende and actinolite exhibit narrow Fe-rich and F-poor actinolite rims. Chlorite formed by replacing hornblende and actinolite is dominantly brunsvigite with Fe²⁺/(Fe²⁺+Mg+Mn) ratios of 0.26 to 0.4, whereas chlorite in the late stage scheelite veins is mostly rigidolite with Fe²⁺/(Fe²⁺+Mg+Mn) ratios ranging from 0.65 to 0.8. Tourmaline is mainly feruvite surrounded by a narrow rim of uvite.

The skarn minerals in the different stages contain extremely low W and no Sn. Mo content in scheelite is less than 0.3 wt% and lower than those in oxidized scheelite skarn of other mines. Scheelite has higher Ce contents (1~2 wt%). Re contents of molybdenite range from 44 ppm to 110 ppm and are higher than those in molybdenite of other scheelite skarn and wolframite-quartz type deposits associated with S-type granite in the Nanling Range, illustrating that Re content in molybdenite is probably influenced by oxygen fugacity of magma.

4 C-H-O-S-Pb isotopes

Figure 5. Carbon isotope of limestone and calcite veins in the granite and skarn from the Xintianling scheelite skarn deposit, Nanling Range, South China

The δ³⁴S values of pyrite and chalcoprite from the altered granite are -1.5 and +0.7. Disseminated molybdenite in the proximal skarn and molybdenite flakes from the quartz veins have δ³⁴S values of -1~+1.2. Pyrite and sphalerite from the pyrite-quartz vein and massive pyrite ores in the proximal skarn have δ³⁴S values of -0.1~+4.6 and +0.32~+3.9, respectively. Pyrite and sphalerite from the massive sulfide ores in the limestone and distal skarn have δ³⁴S values of +6.3~+8.78 and +7.68~+8.49. The δ³⁴S values from the distal skarn are +6.1 and +9.04. Sulfur isotopes of sulfides from the Xintianling deposit have two clusters with peaks around 0 and +7 (Figure 7), which indicate the sulfur in the proximal skarn was mainly from the granitic magma and the input of sulfur from the sedimentary wall rocks in the formation of the distal skarn and massive ore in the limestone.

Figure 6. H-O isotopes of quartz from quartz veins in the granite and skarn in the Xintianling scheelite skarn deposit, Nanling Range, South China

The δ¹⁸O values of pyrite and chalcoprite from the altered granite are -15.0 and +0.7. Disseminated molybdenite in the proximal skarn and molybdenite flakes from the quartz veins have δ¹⁸O values of -1~+1.2. Pyrite and sphalerite from the pyrite-quartz vein and massive pyrite ores in the proximal skarn have δ¹⁸O values of -0.1~+4.6 and +0.32~+3.9, respectively. Pyrite and sphalerite from the massive sulfide ores in the limestone and distal skarn have δ¹⁸O values of +6.3~+8.78 and +7.68~+8.49. The δ¹⁸O values from the distal skarn are +6.1 and +9.04. Sulfur isotopes of sulfides from the Xintianling deposit have two clusters with peaks around 0 and +7 (Figure 7), which indicate the sulfur in the proximal skarn was mainly from the granitic magma and the input of sulfur from the sedimentary wall rocks in the formation of the distal skarn and massive ore in the limestone.
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Figure 7. Sulfur isotope of the sulfides from the Xintianling scheelite skarn deposit, Nanling Range, South China

The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the biotite granites are 18.808–19.377, 15.691–15.758 and 38.922–40.358, whereas the corresponding ratios of granite porphyry dykes are 18.745–19.445, 15.705–15.769 and 39.212–39.839. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the sulfides are 18.455–19.595, 15.667–15.828 and 38.748–39.266, whereas those of limestones are 19.330–20.993, 15.689–15.792 and 38.853–38.909. Pb isotope of all the measured samples fall closed to the evolution line of upper crust, which indicate that the ore-forming materials are of crustal in origin.

Figure 8. Lead isotope of granites, sulfides and limestone from the Xintianling scheelite skarn deposit, Nanling Range, South China

5 Conclusions

Biotite granites related to the scheelite skarn mineralization in the Xintianling deposit, Nanling Range, South China are oxidized S-type. They have high magnetite/ilmenite ratios, high magnetic susceptibility and high zircon Ce$^{4+}$/Ce$^{3+}$ ratios.

The formation process of the skarn system can be divided into five stages: grossular + andradite + diopside (stage I), hornblende + actinolite + Fe-rich andradite + magnetite + scheelite (stage II), scheelite-bearing vein (stage III), molybdenite-quartz vein (stage IV), and calcite + pyrite + sphalerite + galena vein (stage V). Scheelite mineralization mainly developed in stage II and was formed at ~162 Ma and

C-H-O-S-Pb isotopes indicate that the ore-forming fluids are mainly magmatic water mixed with lesser meteoric water and the ore-forming material are of crustal in origin and derived by mixing of magmatic and sedimentary materials

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Genesis of massive magnetite associated with Jamaican-type adakite

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Abstract. A massive magnetite deposit with associated Cu, Co and Au mineralization, situated in the Mavis Bank district is the most important deposit of its kind in Jamaica. However, the deposit has not been the subject of any significant geochemical or petrogenetic studies. One early study described the deposit as a “hydrothermal replacement of limestone”. In this study, the geochemistry of magnetite was used as an important petrogenetic tool to classify the deposit type as well as to determine the genesis of the mineralization.

The Mavis Bank deposit is located within an inverted Eocene rift system. Bulk rock major and trace elements indicate that the host rock ranges from calc-alkaline basaltic-andesite to rhyodacite and belongs to the Jamaican Type Adakite (JTA) suite. The trace element composition of the magnetite was determined using LA-ICP-MS and the results were used to plot several discriminant diagrams including Ni/(Cr+Mn) vs Ti+V, Ca+Al+Mn vs Ti+V, Ti vs V and Ti vs Ni/Cr. The results indicate that the magnetite is of hydrothermal origin with geochemical signatures akin to skarns. In addition, oxygen isotope analysis of magnetite revealed δ18O values of 6.6‰ and 7.1‰ VSMOW which are values typically associated with skarns and may suggest a limestone signature.

1 Introduction

The Mavis Bank District hosts the largest known deposit of iron in Jamaica with an estimated reserve of 1.2 million tonnes (Zans 1955). Although comparatively small, the deposit has been of interest to several exploration companies since the 1950’s. Iron mineralization occurs chiefly as massive magnetite veins (with hematite) in contact with calcic iron skarns and intermediate lavas. Copper and associated cobalt and gold occur as low grade disseminations within skarns and massive magnetite bodies. Despite the varying ore morphology, there appears to be a co-genetic relationship between minerals (Blaise and Fenton 1976; Fenton 1982). The zones of mineralization occur preferentially at contacts and are believed to be of epigenetic or hydrothermal origin (Zans 1955).

Recent interest in the Mavis Bank Prospect has prompted a re-examination of its potential to produce economic quantities of iron and minor copper. Unfortunately, the deposit has been subject to limited geochemical research and as such, is not well understood; no research has been conducted to identify the source of the iron, the conditions under which the iron formed, nor the mechanisms by which the metal was concentrated. Data from this research will lead to a greater understanding of the magmatic and hydrothermal history of the region and add to the repository of information that is important in unravelling Jamaica’s geological history.

Research has shown that both the trace element composition of magnetite obtained from in situ analytical methods such as laser ablation ICP-MS, and the stable isotope signature of magnetite are reliable petrogenetic tools (Nystrom et al. 2008; Nadoll et al. 2014). This is based on the premise that the geochemistry of magnetite is influenced by environmental conditions such as temperature and oxygen fugacity at the time of formation. The geochemistry of magnetite can therefore be used to decipher the genesis of the deposit and to classify deposit types (Nadoll et al. 2014; Beaudoin and Dupuis 2009, Dupuis and Beaudoin 2011; Dare et al. 2014). The stable isotope composition of magnetite can also distinguish between magnetite formed within different temperature ranges typical of magmatic or hydrothermal environments.

This study utilizes several discrimination diagrams and other comparative plots proposed by authors such as Dare et al. (2014) and Dupuis and Beaudoin (2011) to decipher the ore genesis and deposit type of the Mavis Bank Prospect. The oxygen isotope composition of magnetite was also utilized in this process. These data, along with the petrology and mineralogy of the study region has been used to create a preliminary genetic model for the Mavis Bank massive magnetite deposit.

2 Regional and local geology

The district of Mavis Bank lies within a fault bounded Eocene rift system called the Wagwater Trough. This region is structurally and stratigraphically complex and consists of intercalated terrigenous coarse-grained strata, evaporites, limestone, marine shales, calc-alkaline and dacitic lavas, and porphyritic dykes (Robinson 1994).

The Wagwater Trough is bounded to the west by the Wagwater Fault (a NW-SE trending high angle fault) and to the east by the Yallahs-Blue Mountain Fault (Benford et al. 2012; Blaise and Fenton 1976; Mann and Burke 1990). Structural inversion has been critical in the unearthing of the stratigraphy of the basin that would be otherwise unexposed. Following the development of the rift zone and subsequent deposition of sediments, the extensional geometry reversed to contraction and uplift (Draper 1987, 2008; Mann and Burke 1990).
3 Petrology and mineralogy

The basal unit within the study area is a hard, dark grey recrystallized limestone which has been metasomatized in some areas to a calcic iron skarn. The degree of mineralization decreases with distance from the main mineralized zones. The limestone is also characterized by the presence of calc-silicate minerals, disseminated copper and pyrite. The limestone is overlain by fossiliferous, calcareous shales that have also undergone metasomatism and iron mineralization.

The sedimentary succession within the trough was intruded by aphanitic to porphyritic lavas of intermediate composition called the Newcastle Volcanics; these lavas crop out throughout the majority of the study area. The Newcastle Volcanics are characterized by magnetite and specular hematite mineralization with minor copper. Intense propylitic alteration is common within the main mineralized zones. Iron occurs chiefly as discontinuous massive magnetite veins in contact with limestone (skarn) and lavas. Magnetite is martitized in some areas and the veins are characterized by cubic pyrite and late calcite stringers.

4 Tectonic setting

The tectonic environment that produced the iron mineralization within the Wagwater Trough is genetically related to the Newcastle Volcanics which crop out over the majority of the study area. A plot of Th vs Co, which is used as a proxy for the K$_2$O vs SiO$_2$ plot, indicates that the lavas range from basaltic andesites to dacite-rhyolites and were produced in a calc-alkaline setting (Fig. 1).

The major and trace element geochemistry of the Newcastle Volcanics suggest that the lavas belong to a group of arc rocks, Jamaican type adakites (JTA). When plotted on the (La/Yb)$_{cn}$ vs Yb$_{cn}$ diagram (Fig. 2), the Newcastle Volcanics fall within the adakite field. This coincides with research first conducted by Hastie et al. (2010) which concluded that the Newcastle Volcanics were formed from 15-30 % partial melting of a garnet amphibolite source, the Caribbean oceanic plateau, which under thrusted Jamaica during the early Paleogene.

5 Source of mineralizing fluids

Trace element geochemistry of magnetite from massive magnetite veins and skarn within the study area was obtained using laser ablation induced coupled mass spectrometry (LA-ICP-MS).
The results of this analysis show that magnetite from these two sources has low trace element concentrations. In addition, the samples show a low concentration of elements such as Ti, Cr, Mn and Ni which are immobile in hydrothermal fluids but highly mobile in magmatic fluids. This suggests that both types of iron mineralization originate from fluids of similar temperature. A plot of Ti vs Ni/Cr (Fig. 3) shows that magnetite from both mineralization types are from hydrothermal fluids (< 300°C).

6 Deposit type

The trace element geochemistry of magnetite can be correlated to various mineral deposit types, which generally form under distinct geochemical conditions (Beaudoin and Dupuis 2009; Dupuis and Beaudoin 2011). Magnetite from the massive magnetite veins and skarns have very high concentrations of Ca, Al and Si which are highly mobile in low temperature environments and typically found in high concentrations in deposits such as skarns.

The Ca + Al + Mn vs Ti + V discriminant diagram after (Dupuis and Beaudoin 2011) is useful in distinguishing Kiruna, IOCG, porphyry Cu, skarn, Fe-Ti-V and BIF deposits. When plotted on this diagram, the magnetite from massive magnetite veins plotted within the skarn field (Fig. 4). A similar result was obtained when the samples were plotted on the Ni/(Cr+Mn) vs Ti+V discriminant diagram.

7 Discussion

The geochemistry of the magnetite veins is similar to that of skarns with which it is in contact and suggests that they are genetically related. The formation of distinct veins of massive magnetite suggests an overprinting of an initial skarn deposit by iron rich fluid. An iron rich source is therefore required to supply this magnetite.

By nature of its petrogenesis and adakitic composition, the Newcastle Volcanics could not have been the source of iron in the study area. The source of iron is therefore most likely from plutons of mantle derived basaltic lavas which also outcrop in the Wagwater Trough.

7.1 Preliminary deposit model

It is being proposed that the mineralization within the trough occurred in two phases. In the first phase of mineralization, silica rich lava formed from the partial melting of the under thrusted Caribbean oceanic plate and intrudes the sediments of the Wagwater Trough at shallow depths. Initial skarn formation occurred at the contact between porphyritic lavas and limestone. At some point, meteoric water entered the system and was heated along the geothermal gradient.

In the second phase of mineralization, hydrothermal fluids scavenged large amounts of iron from iron-rich mantle derive basaltic plutons. Iron rich fluids travel preferentially along the contact between skarn and silic-rich lava and overprinted the existing skarn, completely replacing calcium minerals with magnetite. As the fluids moved outwards, skarn formation became less intense and resulted in the formation of normal skarns. The Newcastle Volcanics and shales were also mineralized by this iron rich fluid. Further research will include isotopic analysis and dating to test this model.

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Abstract. In this study, the possibility of U-Th-He dating of pyrite is explained and then substantiated by isotope geochemistry. The first U-Th-He age obtained for 9 pyrite samples from the VMS type Uzelga deposit, Urals (377±8 Ma; MSWD 1.2) is in good agreement with independent biostratigraphic age estimations (380-390 Ma). This leads to the conclusion that pyrite can be used as a U-Th-He mineral geochronometer. Based on the results of step-heating experiments and U-Th-He age estimations it is shown that chalcopyrite, bornite and pyrrhotite are unlikely to be used in geochronology. The relative ease of U-Th-He dating in comparison with other geochronological methods makes this approach interesting for further application.

1 Introduction

Historically, isotope systems using radiogenic helium were found to be unsuitable in terms of geochronology. Retention of this element in crystalline structures is too low for use as a geochronometer, but use as a thermochronometer is well known. However, recent studies have shown that containment of helium in metals is possible even over geological timescales. High retentivity of He was found in gold and native minerals of platinum (Shukolyukov et al. 2012). Afterwards high migration parameters of helium were observed in non-native mineral sperrylite, PtAs₂ (Yakubovich et al. 2015). Sperrylite is chemically and crystallographically similar to some of the sulphides. Thus by analogous reasoning, we suggest that high migration parameters of helium can be expected in sulphides as well.

The purpose of this study is to test the possibility of U-Th-He dating of some of the sulphides including pyrite (FeS₂), chalcopyrite (CuFeS₂), pyrrhotite (Fe₇S₈) and bornite (Cu₅FeS₄) from a number of deposits in the Ural region of Russia.

The Gai, Uzelga, and Molodezhnoe deposits are classic, well-studied volcanogenic massive sulphide deposits (VMS), located in the South Urals (Magnetogorsk paleovolcanic arc). Gai is considered the world’s largest VMS deposit. Formation of this mineralization is closely related to andesite-dacite-rhyolite Early-Middle Devonian submarine volcanism and hydrothermal alteration of rocks (Herrington et al. 2005; Vikentyev et al. 2017).

2 Identifying the source of helium

We propose that the main sources of helium in the studied minerals are from inclusions of U-Th-containing minerals. There is evidence (Melekestseva et al. 2014) of U concentrations up to 11 ppm in sulphides of “black smokers” (which are the predecessors of modern VMS deposits). Nevertheless, the possibility of captured helium during crystallisation still remains. Helium concentrations found in chalcopyrite of modern “black smokers” are 1.1×10⁻¹⁰ – 1.3×10⁻⁸ cm³/g (Luders and Niedermann 2010). In our samples from the volcanogenic massive sulphide deposits, these concentrations are higher by orders of magnitude: up to 1.22×10⁻⁴ cm³/g in pyrite, 3.65×10⁻⁵ cm³/g in chalcopyrite and 2.93×10⁻⁴ cm³/g in pyrrhotite. This allows us to conclude that helium in the analyzed sulphides is mostly radiogenic and that trapped helium may be considered insignificant.

It should be noted that concentrations of helium may vary (sometimes 10 times or more) from sample to sample. This fact probably indicates unevenness of distribution of U and Th inclusions in mineral grains of the studied sulphides (cf., Ayupova et al. 2018). It can be used as an argument for submicroinclusions of radioactive minerals as the source of U and Th instead of isomorphic admixture in the crystalline structure.

Electron microprobe analysis made in the SPBU resource center “Geomodel” confirmed this hypothesis. We observed inclusions of uraninite and monazite in a number of grains, which record high helium concentrations (Fig. 1).

3 Methods

Experimental studies were performed in the isotope geology laboratory of IPGG RAS (St. Petersburg, Russia) with a MSU-G-01-M mass-spectrometer (made by CJSC “Spektron-Analit”). This instrument can detect ⁴He in quantities as small as 2.3×10⁻¹² cm³.
extraction is performed by electric heating of the sample in a rhenium cuvette up to 1400°C. Details of the helium measurement technique and the design of the instrument are described in Shukolyukov et al. (2012).

Analysis of each sample can be made by two different methods: a more precise destructive way, when we simply drop the mineral grain inside the cuvette; or non-destructively, when the grain is kept inside a vacuum-sealed quartz tube and placed into or out of the extractor using a tantalum cylinder. This second possibility allowed us to use the same grain we measured helium content in, to measure U and Th concentrations in, thus getting data necessary for U-Th-He isotope dating. Concentrations of radioactive isotopes were measured in dissolved grains by an isotope dilution method on an ICP-MS NexION 300D (Perkin Elmer) in IGS RAS and on an ELEMENT XR in IPGG RAS.

We also immersed samples in acids (HCl for pyrite and chalcopyrite, H₂SO₄ for pyrrhotite) for 24–48 hours to get rid of superficial impurities that might affect helium extraction. However, samples measured after acid etching showed no difference in extraction kinetics, compared to regular ones.

4 Identifying migration parameters

Migration parameters of different minerals were determined by destructive step-heating of samples (each step lasting 2–6 minutes, up to 20 stages from 440°C to 1400°C). During the experiments, we acquired quantities of helium, extracted at each stage. Using this data, we produce kinetics graphs (Fig. 2 and 4), allowing us to characterize extraction, and compose Arrhenius plots (Fig. 3 and 5). Activation energy [kcal/mol] then was determined by the slope of the line; while the y-intercept corresponds to the natural the frequency factor k₀ [s⁻¹] as described in Yakubovich et al. (2019).

For most minerals the desorption kinetics remained rather simple (Fig. 2), single-staged; pyrrhotite shows complex two-staged desorption with peaks at ≈900°C and ≈1300°C (Fig. 4).

In spite of the inclusions in some of the pyrite samples, none of them have shown multi-staged helium desorption. Considering average track depth of the α-particles as 10 μm (SRIM; Ziegler et al. 2010) and size of such inclusions (1-5 μm), this can be evidence of the prior implantation of ⁴He from radioactive minerals (monazite, zircon) into the sulphide matrix and its subsequent extraction from a single mineral, rather than from all of them in a grain, providing different migration parameters.

Summarizing the results of conducted step-heating experiments (Yakubovich et al. 2019), we can see greatest potential for usage of pyrite for rock ages determination, as it showed the highest activation energies (>80 kcal/mol). Chalcopyrite and bornite may have some possibilities to be used as geothermochronometers, as their Eₐ looks comparable to apatite (20-40 kcal/mol). Complex release of He from pyrrhotite makes it unlikely to be used in geochronology.
5 U-Th-He dating attempts

To test the possibility of U-Th-He dating of pyrite we conducted measurements of U, Th and He in FeS$_2$ grains from the Uzelga deposit with conodont-based age of mineralization (380-390 Ma; Artyushkova and Maslov 2008; Chernyshev et al. 2008). Also we determined U-Th-He ages of pyrrhotite and chalcopyrite from the Uzelga and Gai deposits.

As presented in Table 1, all pyrite measurements except sample 437 lie within the expected Devonian age of the Uzelga deposit within the 2-sigma error range. Six of the studied grains lie within the expected age within 1-sigma age error. Sample 437 has the lowest concentration of $^4$He (6.6×10$^{-6}$ cm$^3$/g). Thus it might be some influence of trapped or implanted $^4$He that led to the increase of the age. Overdispersion for a number of grains may be due to the relative long alpha-stopping distances that may affect the U-Th-He ages especially in case of the inhomogeneous distribution of parent nuclides (Farley et al. 1996; Vermeesch 2010). pooled – combined multi-grain estimation as if several grains were measured together as one sample (method proposed by Vermeesch 2008). All data are blank corrected. All uncertainties are in 1-sigma range.

![Figure 4. The character of helium migration kinetics from pyrrhotite of the Uzelga deposit. Representative example.](image)

![Figure 5. Arrhenius plot, acquired from the same pyrrhotite sample of the Uzelga deposit (Fig. 4) $E_a$ – activation energy, $k_0$ –frequency factor.](image)

![Figure 6. U-Th-He isochron for pyrite from Uzelga deposit calculated via method described in Vermeesch (2008) (constructed in Isoplot software; Ludwig 1999).](image)

The data confirms the results of step-heating experiments and predicts that pyrite may be used as a...
Pyrhotite samples showed systematically younger ages that indicates loss of radiogenic helium during their geological history. Younger ages are also common for chalcopyrite. Only one of four studied grains from the Gai deposit gave a Devonian age closely corresponding to the biostratigraphic age of the deposit. This agrees with results of step-heating experiments that predicted relatively low retention of helium in these sulphides. Thus it is unlikely that pyrrhotite or chalcopyrite may be used as geochronometers.

6 Conclusion

The results of step-heating experiments show the possibility of U-Th-He dating of pyrite. The first U-Th-He ages obtained for pyrite samples from Uzelga deposit (377±8 Ma) are in a good agreement with independent biostratigraphic age estimations (380-390 Ma). This leads to the conclusion that pyrite can be used as a U-Th-He mineral geochronometer. The relative ease of U-Th-He dating in comparison with other geochronological methods makes this approach interesting for further application.

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The state of copper, silver, and indium in sphalerite studied by X-ray absorption spectroscopy of synthetic minerals

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Abstract. We use X-ray absorption spectroscopy of synthetic crystals to investigate the substitution mechanisms in sphalerite containing In together with the group 11 metals. All the admixtures (Ag, Cu, In) are homogeneously distributed within the sphalerite matrix. In all studied samples In3+ replaces Zn in the structure of sphalerite. The In-ligand distance increases by 0.17 Å and 0.1 Å for the 1st and 2nd coordination shells, respectively, in comparison with pure sphalerite. The In-S distance in the 3rd coordination shell is close to the one of pure sphalerite. Our data suggest that both Ag and Cu in the presence of In exist in the solid solution state, where the metals are tetrahedrally coordinated with S atoms. Results of the present study demonstrate that in sphalerite, containing the group 11 metals (Cu, Ag, Au) together with In, an isomorphous substitution mechanism by the charge compensation scheme 2Zn2+ ↔ Me++Me3+ is implemented.

1 Introduction

Sphalerite ((Zn, Fe)S) is a host mineral for a wide range of minor and trace elements including Ag and In (Cook et al. 2009; 2012). Both Ag and In (critical metal) are in high demands in industry. Main source of In are base metal hydrothermal deposits, where In exists in the form of admixture in sphalerite ZnS. Ag-rich sphalerite is a common mineral in some low-temperature ores. The maximum concentration of Ag strongly correlates with the amount of In in the ore (Murakami and Ishihara 2013). In most samples of natural sphalerites In concentrations show a positive correlation with Cu which implies the coupled substitution mechanism 2Zn2+ ↔ Cu++In3+ (Cook et al. 2012). Based on similar chemical properties of Ag and Cu it can be suggested that the formation of solid solution in Ag-In-bearing sphalerite corresponds to 2Zn2+ ↔ Ag++In3+. These substitution schemes, however, can be verified only by means of spectroscopic methods.

2 Synthesis of doped sphalerite

The crystal growth experiments were performed using (i) the gas transport method, (ii) the salt flux technique (KCl/NaCl eutectic mixture: Chareev 2016; Chareev et al. 2016), and (iii) the dry synthesis method (Kullerud 1971). The synthesis method was chosen according to Chareev et al. (2017).

In the gas transport method NH4Cl and I2 were used as the transport agents. The initial phases (~ 0.5 g of ZnS – sphalerite), and several milligrams of Ag2S, Cu2S, and In2S3 were powdered and loaded into a silica glass ampoule (8 mm ID, 11 mm OD, ~110 mm length). Iodine was used as a transport agent (samples 4152 (ZnS+1mol.%Ag2S) and 4169 (ZnS+0.125mol.%Ag2S+0.125mol.%In2S3)). Sample 3757 (ZnS+0.01mol.%In2S3) was synthesized using NH4Cl as a transport agent. Ampoules filled with starting reagents were evacuated, sealed, and placed into a horizontal tube furnace with a steady-state temperature gradient. The furnace was heated to the synthesis temperature over a period of 2-3 hours, and then kept at this temperature for 20 days. The temperature gradient in the furnace was 50-100 °C, the temperature at the hot end of the ampoules was 850 °C. At the end of the experiment the ampoules were quenched in cold water.

Sample 4197 (ZnS+6mol.%Ag2S+8mol.%In2S3) was prepared by means of dry synthesis method in silica glass ampoule filled with powdered sulphides. The synthesis was performed at 550 °C during 28 days. After two weeks the ampoule was quenched, the sample was finely grounded to provide higher homogeneity, sealed in the ampoule, and heated for the second time during the last two weeks. The standards were prepared by the same method.

Samples 4065 (ZnS+0.6mol.%Cu2S), 4086 (ZnS+0.02mol.%Cu2S+0.6mol.%FeS), 4108 (ZnS+0.08mol.%Cu2S+0.04mol.%In2S3), and 4186 (ZnS+0.05mol.%Cu2S+0.05mol.%In2S3) were prepared using the salt flux method in steady-state temperature
3 Analytical methods

Synthesized phases were examined by means of X-ray diffraction (XRD) using Rigaku D/Max 2200 X-ray diffractometer (Cu Ka, 40 kV, 20 mA, 0.02° step). The morphology of the crystals was checked by means of scanning electron microscopy (SEM/EDS) using the JSM-5610LV microscope equipped with INCA-450 energy dispersive spectrometer. Chemical composition was determined via electron probe microanalysis (EPMA), and laser ablation inductively coupled mass spectrometry (LA-ICP-MS). EPMA analyses were performed using JEOL JXA-8200 WD/ED combined electron probe microanalyzer equipped with 5 wavelength dispersive X-ray spectrometers. LA-ICP-MS analyses were performed using the New Wave 213 laser coupled with the Thermo X Series2 quadrupole ICP-MS. X-ray absorption experiment was performed at the Rossendorf Beamline BM20 of the ESRF (Grenoble, France). IFEFFIT software package (Ravel and Newville 2005) was used for the experimental spectra treatment.

4 Results

4.1 XANES spectroscopy

Figure 1 shows the X-ray absorption near edge structure (XANES) spectra of In, Ag, and Cu K-edges of the sphalerite samples and standards.

In K-edge
Positions of the absorption edge (e.j.) and the first intense peak (WL) in all the sphalerite samples are different from those of InO2 and In2S3. Thus, the state of In in sphalerite is different from both oxide and sulphide. In contrast to In2O3 and In2S3, the spectra of In-bearing sphalerites are similar to CuInS2 (in case of In-Cu-bearing sphalerites : samples 3757, 4108, 4186) and AgInS2 (in case of Ag-In-bearing sphalerites : samples 4169 and 4197). This means that In in sphalerite has the "formal" oxidation state of 3+, and imply that the nearest-to-In atomic geometry in the samples is similar to roquesite CuInS2 and laforetite AgInS2.

Ag K-edge
The shape of Ag K-edge XANES spectra and results of linear combination fits show that Ag in the sample 4152 occurs as metal Ag0 (80%) and oxidized Ag1+ (20%) form. In the sample 4169 Ag also occurs in the form of metal Ag0 (64%) and in the Ag1+ state (34%). In the sample 4197 Ag1+ predominates and the shape of the spectrum is different from the standards - AgInS2 and Ag2S, which suggests that Ag presents in the solid solution state. In this sample series the WL positions regularly increase in the energy: WLAgInS2<WL4197<WL4169<WL4152<WLAg. This order of the WL position can be explained by increase of the metal (Ag0) concentration.

Cu K-edge
XANES spectra of all samples differ considerably from Cu0 standard. The spectra of the samples 4186, 4108, and 4086 are close to the spectrum of CuInS2 standard. Therefore, Cu has the "formal" oxidation state of 1+. The absence of the pre-edge feature in the spectra of CuInS2 and Cu-In-bearing sphalerites confirms 1+ oxidation state of Cu, which is consistent with the oxidation state 3+ for In. The spectra of the sample 4065 (Cu-bearing sphalerite) recorded at room temperature is different from CuInS2 but similar to the spectra of Cu1+ sulphides (not shown in Fig. 1). The spectrum recorded in situ at 650 °C, and the spectrum after heating correspond to CuO standard due to the oxidation of the sample.

4.2 EXAFS spectroscopy

Figure 2 shows the Extended X-ray absorption fine structure (EXAFS) spectra of In, Ag, and Cu K-edges of the sphalerite samples and Ag metal.

In K-edge
The best fit of the experimental spectra of Ag-In and Cu-In-bearing sphalerites were achieved when In substitutes for Zn in the sphalerite lattice. Analysis of the experimental spectra yields no difference in the local atomic environment of In regardless of the chemical composition of minerals. Local environments of In in the samples 4197 and 4169 are similar and don’t depend on
Ag concentration (for the 1st shell $N_{\text{Ag}}=4$, $R_{\text{Ag-S}}=2.48\pm0.01$ Å). Interatomic distance In-S increased with respect to the crystal structure of pure sphalerite (2.31 Å). In the sample 4197 the 2nd coordination shell consists of 12 Zn atoms ($R_{\text{Ag-Zn}}=3.93\pm0.01$ Å) and the 3rd coordination shell consists of 12 S atoms ($R_{\text{In-S}}=4.48\pm0.01$ Å). In the sample 3757, which doesn’t contain Ag and Cu, In has tetrahedral coordination of S atoms in the first coordination shell ($R_{\text{In-S}}=2.45\pm0.01$ Å), 12 Zn atoms in the 2nd shell ($R_{\text{In-Zn}}=3.91\pm0.01$ Å), and 12 S atoms in the 3rd coordination shell ($R_{\text{In-S}}=4.48\pm0.02$ Å). All the interatomic distances increased in comparison with pure sphalerite. In the 2nd coordination shell no presence of In was observed. These results imply the possibility of the formation of In-bearing solid solution in sphalerite without the In-In clustering.

**Ag K-edge**

The best fit of the experimental spectra of the sample 4197 (Ag-In sphalerite) was achieved when Ag and In substitute for Zn in the sphalerite lattice. In this sample Ag is tetrahedrally coordinated with sulfur atoms at a distance of 2.49±0.02 Å. The pronounced increase by ~0.18 Å of the Ag-S distance in Ag solid solution with respect to the Zn-S distance in pure sphalerite can be explained by large difference in the ionic radii of these metals (0.6 Å for Zn vs 1.0 Å for Ag, Shannon, 1976). The 2nd coordination shell expands notably ($N_{\text{Zn}}=12$, $R_{\text{Ag-Zn}}=3.91\pm0.01$ Å, in pure sphalerite $R_{\text{Zn-Zn}}=3.83$ Å), whereas interatomic distances in the 3rd shell ($N_{\text{Zn}}=12$, $R_{\text{Ag-S}}=4.19\pm0.01$ Å) are significantly lower in comparison with pure sphalerite ($R_{\text{Zn-S}}=4.49$ Å). In the sample 4152 the majority of Ag occurs in the form of Ag$^0$ ($N_{\text{Ag}}=8.3\pm1.5$, $R_{\text{Ag-Ag}}=2.86\pm0.01$ Å, parameters of local atomic environment of Ag in the form of metal are: $N_{\text{Ag}}=12$, $R_{\text{Ag-Ag}}=2.88$ Å). In the sphalerite sample 4169 the local environment of Ag is the combination of metal Ag$^0$ and the solid solution Ag$^+$.  

**Cu K-edge**

Cu K-edge EXAFS spectrum of the sample 4186 is best described by the solid solution model with $N_{\text{S}}=4$. In this sample the Cu-S distance $R_{\text{Cu-S}}=2.30\pm0.01$ Å (2.31 Å for pure sphalerite) was observed for the 1st coordination shell. In the 2nd coordination shell Cu has 12 Zn atoms ($R_{\text{Cu-Zn}}=3.85\pm0.04$ Å), and in the 3rd shell Cu is coordinated by 12 S atoms ($R_{\text{Cu-S}}=4.43\pm0.04$ Å). The local atomic environment of Cu in sphalerite is close to pure sphalerite, because Cu and Zn have similar ionic radii. Spectra fitting of the samples 4065, 4086 and 4108 are not finalized. However, we found that despite the variation of the coordination number of Cu from $N_{\text{Cu}}=2$ to $N_{\text{Cu}}=3$ the interatomic distances are equal to 2.26±0.01 Å. We suppose that the difficulties in the fitting of EXAFS spectra of these samples are induced by the disordering of the sphalerite crystal structure, caused by the replacement of Zn with Cu, Cu-clustering, or admixture of a Cu sulphide.

**5 Conclusions**

We synthesized crystals of In, Ag, and Cu-bearing sphalerite ZnS with dopants concentration of 0.01–1 mol%. Results of EPMA and LA-ICP-MS chemical analyses showed that all these elements are homogeneously distributed within the sphalerite matrix. X-ray absorption spectroscopy (XAS) was applied in order to determine the local atomic environment and the valence state of the admixtures in the synthesized crystal samples. In accordance with XANES spectroscopy these elements are present in sphalerite in $+3$ (In), $+1$ (Ag, Cu), and 0 (Ag) “formal” oxidation states.

![Figure 2. Fourier transforms (FT) of the $k^2$-weighed EXAFS spectra (colored lines – experiment, red dotted lines – fit results. Dopants are indicated near each spectrum.)](image-url)
Our data demonstrate that In, Cu, and Ag, can present in sphalerite in the solid solution state which is stabilized by the charge compensation scheme $2\text{Zn}^{2+} \leftrightarrow \text{Me}^{++} + \text{Me}^{3+}$. Formation of the solid solution of the group 11 metals (Cu, Ag, Au) together with other elements in 3+ oxidation state (Fe$^{3+}$, As$^{3+}$ and so on) is also possible but needs further experimental investigation.

Acknowledgements

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References


Scapolite as a sulfur and chlorine reservoir in metamorphic terranes

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Abstract. Scapolite is an accessory mineral in high grade metamorphic terranes, and abundant in medium-grade evaporitic calc-silicate rocks. It varies in composition through a ternary solid solution with end-members of marialite (Na₄Al₃Si₉O₂₄Cl), meionite (Ca₄Al₆Si₆O₂₄CO₃) and silvialite (Ca,Na)₄Al₆Si₆O₂₄(SO₄,CO₃), which are rich in chlorine (Cl), carbon dioxide (CO₂) and sulfur (S), respectively. If released, the S and Cl components may act as transport agents for metals and in the case of S, as the anion in sulfide minerals in ore deposits. Results of electron microprobe analysis on a selected sample set from a range of metamorphic grades shows that scapolite contains up to 1.29wt% S and 3.68wt% Cl. In addition, textural features in thin sections shows that albisation of scapolite occurs via coupled dissolution-reprecipitation (CDR) in regional-scale hydrothermal systems. This process which frees scapolite ligands for metal complexation, may play a role in formation of Iron Oxide Copper and Gold (IOCG) deposits. Deciphering the response of scapolite to albisation and metamorphic devolatilization may help to understand the formation of highly reactive mineralised brines.

1 Introduction

Scapolite is a common accessory phase in metamorphic rocks, although it can form over a wide range of pressure-temperature (P-T) conditions in evaporitic calc-silicate bulk compositions where it can be the dominant porphyroblastic phase. It is consequently found in greenschist, amphibolite (Kwak, 1977) and granulite facies metamorphic rocks (Hammerl et al., 2017; Porter and Austrheim, 2017). Although scapolite forms predominantly as a result of metamorphic processes, it may also form during metasomatism especially in skarns (Mi and Pan, 2018), or as a primary mineral phase in igneous environments, however this is uncommon (Smith et al., 2008).

The scapolite mineral group is an aluminosilicate with three endmembers, marialite (Na₄Al₃Si₉O₂₄Cl), meionite (Ca₄Al₆Si₆O₂₄CO₃) and silvialite ([Ca,Na]₄Al₆Si₆O₂₄(SO₄,CO₃)). Each end-member has volatile components in its structure in the form of Cl, CO₂ and SO₄. The structure of scapolite has a framework of aluminosilicate tetrahedrons with large open spaces that are large enough to host large ionic groups of either NaCl or CaCO₃. Pure endmembers rarely occur in nature.

Sulfur and Cl are the predominant ligands for metal transport in fluids. Scapolite is one of the most common but least appreciated non-halide and non-sulfide minerals to contain significant amount of S and Cl (Bernal et al., 2017). Silicates minerals such as micas and amphiboles also contain trace concentrations of Cl (Finch and Tomkins, 2017), and apatite can contain both ligands, Cl up to 6wt% and commonly minor S (Chew et al., 2014; Harlov and Aranovich, 2018).

This paper presents preliminary results on the potential role of scapolite in IOCG mineral systems. Given that scapolite is widely distributed in metamorphic terranes hosting IOCG systems we propose that albisation of scapolite in such environments releases S and Cl, generating hypersaline brines, which in turn have high mineralization potential.

2 Sampling and methods

2.1 Samples

The sample set reported in this paper is composed of three scapolite samples M24748, M34815 and M40397. They were analyzed to determine their compositional range, which lay between the scapolite endmembers (marialite-meionite). In hand specimen they have different colors (purple, blue and white). The samples were mounted on 25x75mm glass slides. All samples are from metamorphic rocks. Sample M24748 was collected at the Limberg Quarry in Finland. None of the deposits in the region have been described as IOCG. It is a limestone metamorphosed to amphibolite facies and coexists with garnet-bearing mica gneiss. Sample M34815 is from the Flinders Range in the Arkaroola area in South Australia and has the texture of the typical spotted greenschist facies siltstones in that region with scapolite porphyroblasts. The region hosts a number of IOCG deposits. Sample M40397 is from the Aust-Agder metamorphic belt in eastern Norway which host iron ore deposits in skarn (IOCGs?) as well as Cu-Mo deposits. The sample is collected from a calc-silicate rock metamorphosed to amphibolite facies.
2.2 Methods

Spot analysis and sample mapping were conducted by scanning electron microscopy (SEM) using a JEOL 7001F FEG SEM equipped with Energy Dispersive X-Ray Spectroscopy (EDS). The beam energy was set between 15kV and 20 kV, with a beam size between 10nm and 20nm. The working distance was 10mm with a probe current of 20nA. Measurements were undertaken at Monash University at the Monash Centre of Electron Microscope (MCEM).

A JEOL Super Probe JXA-8230 Electron Probe Micro Analyser (EPMA) was used to determine the concentration of elements of interest in scapolite. Analyses were carried out at the Laboratory of Critical Elements AGH UST-KGHM, Kraków under the following operating conditions, accelerating voltage of 15 kV and a beam size between 10-20nm.

3 Results

3.1 Mineralogy & scapolite chemistry

The SEM analyses showed scapolite compositions were meionitic (CaCO3-rich; M24748), marialitic (NaCl-rich; M34815) and intermediary composition (M40397) between the two end members. EPMA results in table 1, indicate Me% (Shaw, 1960a,b) contents of 24.7% for the marialitic samples; 60.4% for the meionitic samples and 44.6% for the intermediary samples. Scapolite grains are associated with amphibole, K-feldspars, albite, micas, and quartz mostly as inclusions.

Concentrations of S as SO3 are 0.03 wt.%; 0.75 wt.% and 1.10 wt.% respectively for the marialitic (n=7), meionitic (n=5) and intermediary composition samples (n=23). It is important to note that, S K-edge XANES spectroscopy on scapolite shows that S species in scapolite include sulfate (S6+), sulfite (S4+) (Fleet et al., 2005) but also polysulfides (HSn-;Sn2-; highly reactive S species) (Hamisi et al., in prep.). The forms of S in scapolite is critical as it affects redox conditions of mineralized brines which interact with host rocks as shown in the discussion. Concentrations of Cl are 3.45 wt.% in the marialitic samples 1.17 wt.% in the meionitic samples 1.73 wt.% in the intermediary sample. Cl in scapolite grains appears to be zoned (Figure 1A) with highest Cl concentrations in the less porous core and lowest concentrations in the highly porous rim. High S concentrations occurs as scattered inclusions of meionitic scapolite.

EPMA mapping on sample M34815 shows highly albited areas in the more porous core of scapolite grains (Figure 1C). Such reaction textures indicate that the albitation process exploited preexisting porosity in the parent mineral and it is typical of pseudomorphic interface coupled dissolution-reprecipitation (ICDR), which generates porosity in the product phases (in this case albite, K-feldspar, micas, quartz) and also in the parent mineral (scapolite). If the connectivity of the porosity is high enough, the process continues as long as enough fluid is available to drive the reaction (Hövelmann et al., 2010). Sporadic euhedral crystals of an Al-rich phase (most likely kaolinite) are also present but appear to be a late phase. The interstitial space between large scapolite grains is filled with quartz, micas and amphibole. Albite forms following a preferential structural pattern (bottom left to top right on the thin section, Figure 1C, 1E).

Table 1. EPMA data. Concentrations are in weight percent (wt. %); C is calculated as C=1-S-F-Cl; Number of ions are normalized on the basis of T (Si+Al+Ti)=12; n is the number of points measurements; Me% is Me=Ca/(Ca+Na)x100 and Equivalent Anorthite component is presented as Eq.An.=100x(Al-3)/3.

<table>
<thead>
<tr>
<th>Sample No</th>
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<th>M34815</th>
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<td></td>
<td>Intermediary</td>
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High sulfur concentrations in sample M34815 occur as micrometer-scale inclusions 5 to 25 microns in size (Figure 2), but also along grain boundaries forming a diffuse pattern between grains and interstitial space as well as filling in microfractures orientated bottom right to top left.

**Figure 1.** EPMA maps of sample M34815. 1A. Ca, Al, Si map - Overview of a portion of the sample M34185; 1B. Ca, Na, Mg map – Micas are the red spots, the large red area in the low-center area is amphibole; 1C. Na map - Dull green ground mass in marnallite, bright green areas are elongated (SW-NE) albited scapolite; 1D. S, Cl, K maps – overview of distribution of S and Cl in scapolite; 1E. dotted lines are S rich lines in microstructures.

**Figure 2.** EPMA maps S, Cl and K of sample M34815. Quartz grains (in black) fringed by K-feldspars. S rich micro-inclusions in blue.

### 4 Discussions and conclusion

The observation that albisation follows the structural fabrics of grains (Figure 1C, 1E) indicates that the replacement of scapolite by albite occurs during or shortly after deformation because of fluid (salty fluids - from evaporitic origin and/or metamorphic devolatilization) / rock interaction through the reaction: 

\[
\text{scapolite + fluids (NaCl+H}_2\text{O) } \rightarrow \text{albite } \pm \text{K-feldspar } \pm \text{SiO}_2 + \text{hypersaline fluids charged in Cl and S.}
\]

The breakdown of scapolite into albite will discharge Cl and S and increase the ability of the fluid to scavenge metals from the surrounding host rocks. The variety of S species present in scapolite is important because like other multivalent elements the redox conditions and the coexistence of various species will depend on the changes in oxygen fugacity (fO2). Jugo et al. (2010) document the behavior of S species as function of fO2.

As S is released in the fluid phase during albisation of scapolite, the coexistence of sulfate, sulfite and polysulfides, may lead to the formation of very reactive and complex mineralizing fluids similar in composition (Torresi et al., 2012) of those in IOCG systems (Figure 3). The presence of highly reactive species increases the ability of the fluids to mobilize S from scapolite breakdown and can also reduce the amount of S sequestered in major sulfur-bearing mineral phase such as pyrite or pyrrhotite and widen the PT window at which pyrite and potentially other S rich mineral phase continue to produce S-rich fluids (Pokrovski and Dubessy, 2015).

**Figure 3.** Sulfur species present in hydrothermal fluids model with 10wt% salinity (NaCl + KCl – Hypersaline fluids in IOCG systems may be higher than 10%), greenschist facies conditions (T=450 °C; P=1 kbar ) and total S=2 wt% as a function of oxygen fugacity at pH ~ 5, After (Pokrovski and Dubessy, 2015). The vertical dashed lines show fO2 values for mineral buffers for this model (QFM=quartz-fayalite-magnetite, NNO=nickel-nickel oxide, PPM =pyrite-pyrrhotite-magnetite, and HM=hematite-magnetite).
Bernal et al. (2017) conducted studies on scapolite from the Norbotten IOCG district in northern Sweden, an IOCG district which shows evidence of regional (km scale) albitionization and scapolitization alteration. Findings suggest that the variation of S concentration in scapolite was a result of rock buffering the fluid chemistry. In addition, the relative variation in concentration of the triplet SO4-Cl-CO3 in scapolite and the temporal/spatial relationship to IOCG alteration system indicate that scapolites were either formed or recycled during mineralisation process. Our study provides evidence of the coexistence of reduced and oxidized S species in scapolite. Whether it serves as a sink or a source for S and Cl, scapolite interacting with IOCG mineralising brines will buffer the redox states of the fluids. Oxidation/reduction and transition of S2- to S6+ and vice versa requires gains/loss of eight electrons, which means even when occurring in small amount, the presence, in scapolite, of very reactive S species such as polysulfides will lead to the formation of very reactive and complex mineralising brines which has the potential to actively interact with the host rock, scavenge metals and form a deposit in the presence of a suitable trap, and appropriate temperature-pressure, $fO_2$ conditions for metals precipitation. We propose that regional-scale albitisation commonly observed in scapolite-bearing metamorphic terranes hosting IOCG deposits could be the result of large scale breakdown of scapolite, plagioclase and/or K-feldspar leading to formation of voluminous amount of S- and Cl-rich fluid capable of mobilizing metals from surrounding host rocks and form IOCG deposits. Ongoing investigation, using synchrotron analyses on scapolite, will shed light on the role of scapolite breakdown and crystallization in the redox conditions of hypersaline mineralizing brines in IOCG systems, as the presence of different S species may buffer the fluids differently.

Acknowledgements

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References


Carbonate replacement and thallium enrichment: ultra-high-resolution trace element mapping, and the origin of Proterozoic sediment-hosted Zn-Pb deposits

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William DA Rickard
John De Laeter Centre, Curtin University, Australia

Abstract. There is ongoing debate on the origin of many sediment-hosted Zn-Pb-Ag deposits: the syndepositional ‘sedex’ model versus the diagenetic replacement model. Unequivocal evidence for exhalative ore is lacking, often underpinned simply by the presence of laminated ore textures. An alternative carbonate replacement diagenetic-epigenetic genetic model for some deposits is also not universally accepted.

In this study on a supergiant sediment-hosted Zn-Pb-Ag deposit with contrasting interpretations as either a sedex or carbonate replacement system (McArthur River [HYC], north Australia), we investigate this issue using ground-breaking technology that allows us to quantitatively characterize ore material from the sub-metre to nanometre at ultra-high resolution. We show the wide spatial distribution of ore textures in a large context. Furthermore, we are able to, for the first time, show the spatial and mineralogical distribution of trace elements such as thallium that were previously impossible to measure at this scale.

Our data show that base metal sulfide mineralization occurs entirely as a product of carbonate replacement in both finely laminated and nodular carbonate samples. Thallium enrichment is associated exclusively with late stage diagenetic (but pre-ore) pyrite overgrowths. Finally, with fluid chemistry modelling, these findings strongly imply a deep subsurface diagenetic-epigenetic model and preclude a syngenetic ‘sedex’ genetic model.

1 Introduction

The supergiant McArthur River (Here’s Your Chance [HYC]) Zn-Pb-Ag is hosted in the Proterozoic McArthur–Isa superbasin of northern Australia, the world’s largest Zn-Pb province. HYC is widely regarded as one of the classic examples of a sedimentary exhalative (sedex) base metal deposit (Large et al. 1998, Ireland et al. 2004b). This model of ore formation influences exploration approaches as it infers a direct control of the sedimentary environment and synsedimentary tectonic framework on base metal deposition.

A review of sedimentary-hosted Zn-Pb deposits by (Leach et al. 2005) found the term ‘sedex’ to be fundamentally concerning because it imparts a specific exhalative genetic component, given most deposits lack unequivocal evidence for exhalative ore. The presence of laminated ore textures, often regarded as the primary evidence for exhalative processes, have been shown to result from carbonate replacement processes in the subsurface well after deposition of the host sediment in other similar deposits.

The evidence for a synsedimentary-exhalative origin of HYC (and other similar deposits in the region) is predicated mainly on the observation that the ores with fine-grained laminated textures are sedimentary in origin (Large et al. 1998), and that ore clasts that occur within intraformational breccias indicate mineralization occurred before individual fault movements (Ireland et al. 2004b). Trace element enrichments, e.g. thallium (Tl) in the ore zone and surrounding and overlying lithologies, are also reported to represent a synsedimentary origin for mineralization (Large et al. 2000). These features have also been interpreted by some workers to be strong evidence for subsurface diagenetic-epigenetic carbonate replacement origin for the mineral system.

Despite having been well studied over the decades, controversy remains over the genetic model of the HYC mineral system.

Here we present evidence for a carbonate replacement style mineral system for HYC by employing state-of-the-art analytical techniques, and, critically, by quantitatively examining the mineral system through a range of scales from the sub metre to the nanometre scale.

2 Methods summary

Polished slab samples 300–400 mm in length from all 8 ore lenses in the central, southern and northern zones of the HYC pit were studied using the methods detailed below.

2.1 Ultra-high-resolution Maia Mapper µXRF element mapping

The Maia Mapper is a new laboratory XRF mapping system for efficient elemental imaging of drill core sections for use in minerals research and industrial applications. It targets intermediate spatial scales, with imaging of up to ~80 M pixels, each 30 µm, over a 500 long × 150 mm high sample area, as part of the
analytical workflow of the CSIRO Advanced Resource Characterization Facility, which spans spatial scales from ore deposit to atomic scales. It brings together (i) the Maia detector and imaging system, which is part of the Australian Synchrotron XFM facility; (ii) the high brightness indium alloy anode MetalJet D2 liquid metal micro-focus X-ray source at 200 W power at 70 kV into an effective 20 µm source size; all integrated with stage raster scanning for automated imaging and analysis of drill core sections (Ryan et al. 2018). Imaging for Maia Mapper uses an extension of the GeoPIXE method for synchrotron XRF analysis and imaging.

2.2 Focussed ion beam time of flight secondary ionization mass spectrometry (FIB–TOF–SIMS)

The trace element content of pyrite was mapped at high spatial resolution using ‘focused ion beam time of flight secondary ionization mass spectrometry’ (FIB–TOF–SIMS). A focused gallium (Ga) ion beam is used to sputter material from the surface of the sample and that material is accelerated into a time of flight mass spectrometer attached to a Tescan LYRA3GM FIB–SEM microscope.

3 Results

3.1 Paragenesis of base metal sulfides and relationship to carbonate

In all nodular carbonate samples analyzed in this study, sphalerite (Zn sulfide) is spatially associated with the outer margins of carbonate (Figure 1, middle). Only very minor sphalerite was detected in laminated primary (syngenetic) pyrite-organic laminae. Detailed SEM analysis of the interfaces between sphalerite and carbonate shows localized Mn enrichment on the outer margins of dolomite surrounded by sphalerite, with stylolytic dissolution cavities in the carbonate hosting the majority of the sphalerite. Large samples of laminated ore show thin laminae of base metal sulfides and pyrite. Discreet residual carbonate laminae are detectible in all samples analyzed. Isolated calcium (Ca) laminae which represent preserved carbonate (dolomite) laminae occur in the in the ore. Sphalerite in these areas occurs within and around residual carbonate.

3.2 Thallium distribution

One of the primary barriers to detecting Tl in ore deposit studies is due to the X-Ray peak overlaps with Tl, Pb and S. Interrogation of the Maia Mapper data from large HYC pit samples shows zones of high-Tl and low-Pb in some areas that seem unique spatially but not distinct in any other element image, although Fe (pyrite) is high in these zones. The sample shown in Figure 1 (bottom) hosts one such area of high-Tl within the pyritic band in the middle. By selecting this band of pixels with high-Tl, we are able to highlight the high-Tl and low-Pb pixel associations to filter out any artefacts (overlaps). Figure 1 (bottom) shows Tl (red), which when compared with the photomicrograph of the sample above,

Figure 21. Top: Photomicrograph of polished slab of laminated pyritic-carbonate HYC Zn-Pb ore. Middle: Maia Map of same sample showing distribution of Fe (red), Zn (green) and Ca (blue). Bottom: distribution of Tl (red), Pb (green) and Zn (blue). White box indicates approximate area of detailed FIB-TOF–SIMS analysis shown in Figure 22.

Figure 22. A) SEM image of early framboidal pyrite with late zoned pyrite overgrowths in the Zn-Pb ore zone outlined in Figure 7. B) FIB-TOF-SIMS map of Tl in zoned pyrite outlined in the white box in A. The framboidal core, in this case, has rare localized enrichments in Tl, whereas the zoned overgrowths have higher Tl concentrations.
demonstrates that the highest concentrations (brightest colours) correlate with paragenetically-late pyrite bands that are spatially proximal to the sphalerite (Zn - blue) occurring around the rims of nodular carbonate. Thallium is present in early syngenetic laminated pyrite zones but in lower concentrations. However, galena (Pb - green), which occurs in association with certain carbonate nodule margins, is not spatially associated with Ti enrichment in the late pyritic bands.

Closer SEM analysis of the zones of Ti-enriched late pyrite shows the pyrites bear rounded (possibly frambooidal) cores with numerous generations of later euhedral overgrowths (Figure 2a). Sphalerite that is observed replacing carbonate (dolomite) throughout, is here observed to have entirely precipitated after the latest pyrite overgrowths. Detailed analysis of these overgrown frambooidal pyrites using FIB–TOF–SIMS shows that the distribution of Ti is concentrated in the diagenetic overgrowths (Figure 2b). The frambooidal cores are mostly entirely void of detectable Ti, although in rare cases there are localized enrichments (e.g. Figure 2b).

4 Discussion

4.1 Carbonate replacement by Zn-Pb sulfides at HYC

The argument by Leach et al. (2010) that sulfide layering, by itself, is not sufficient evidence for exhalative ore was recently disputed by Sangster (2018) who stated that sulfides mimicking synsedimentary textures is not proof of replacement processes either. This counter point emphasizes the circular pattern of opposing arguments that arise when dealing with interpretations based on subjective, sometimes nonquantifiable observations. Sangster (2018) also noted that though carbonate replacement is frequently mentioned in literature to be responsible for layered sulfide textures at HYC and elsewhere, the replaced carbonate phase is ‘seldom identified’. This highlights the difficulty in visually identifying certain residual mineral phases in altered laminated sedimentary rocks; it also reflects a problem that arises from scale. Most studies are based on thin sections that are chosen on subjective, visual observational criteria at the sampling stage. Thus, traditionally there is a significant step in scale of study, from the deposit scale to thin section scale, that can lead to subtle, but potentially key features (such as residual carbonate) being overlooked. Clearly this is dictated by a historic lack of technologies capable of quantitative petrographic analyses on large samples. New developments such as the Maia Mapper (Ryan et al. 2018) can not only accommodate this gap in scale, allowing data-led decision making when choosing thin sections, but also can allow trace quantitative element mapping (e.g. Ti) at unprecedented ultra-high resolution.

Our data (from large pit samples up to ~300 mm long) clearly demonstrate that residual laminated carbonate is locally preserved in laminated base metal sulfide ore from the central zone of HYC. Critically, when visually inspecting these samples, residual preserved sub-1 mm laminated carbonate is extremely difficult to identify. Upon closer inspection, the textures of base metal sulfide proximal to preserved carbonate in these laminated ores are consistent with carbonate dissolution. The textures in nodular carbonate-bearing ore are more readily identifiable visually but are far clearer when Maia Mapper data is examined (e.g. Figure 1).

Figure 23. A) Stability of predominant Ti, Fe and Zn minerals and aqueous species as a function of log$f_{O_2}$ and pH at 150°C: A) Ti; B) Fe; C) Zn. Boundaries of Ti, Fe and Zn species are shown as red solid, dashed and dash-dotted lines respectively. The boundaries of sulfur species are shown with blue dashed lines in all subplots, and activities of total sulfur and chloride are the same as Cooke et al (2000): $a_{\sum S} = 0.001 \text{ m}; a_{\sum Cl} = 5.8 \text{ m}.$

4.2 Thallium hosted in late diagenetic pyrite

Thallium enrichments have been known at HYC (Large
et al. 2000) and numerous other similar ore deposits worldwide for decades. Previous studies have demonstrated that Tl is present in individual pyrite crystals in the HYC ore zone. Large variations in Tl concentrations in various pyrites, ranging from 176–919 ppm, were reported from the HYC ore zone by Mukherjee and Large (2017). Whilst these analyses are useful, what is critically lacking is context at a scale greater than that of a single pyrite grain. Thus, little is hitherto known about the overall deportment of Tl in the ore zone or the metallogeny of Tl in the greater HYC mineral system. Therefore, the potential of Tl as a pathfinder element in exploration for sediment-hosted Zn deposits, and in other geochemical exploration, is currently unclear.

Our new ultra-high-resolution data show that Tl is highly concentrated in late pyrite overgrowths that occur before base metal sulfide mineralization (Figure 1, 2). Pre-ore pyrite was also noted by Broadbent et al. (1998), Eldridge et al. (1993), and Polito et al. (2006). Whilst this not only precludes syndepositional base metal mineralization, there are implications for the use of Tl enrichment as a pathfinder for sediment-hosted Zn-Pb mineralization.

4.3 Fluid modelling

Thallium deportment in late pyrite suggests both Fe and Tl were transported in the same hydrothermal fluids, particularly given the homogeneity observed in the distribution within the overgrowths. Fluid modelling, assuming a temperature of ~150°C and a salinity of 15% eq NaCl (Cooke et al. 2000), shows that TlCl is mobile across a range of pH values above a Log fO2 of ~45, (Figure 3). However, FeCl+ complexes are only mobile at the same temperatures below pH4. Cooke et al. (2000) noted the likely dominance of oxidized fluids in the Australian Proterozoic sediment hosted Zn deposits. Our data are consistent with this; therefore, we argue that it is likely that FeCl+ and TlCl complexes were transported in oxidized fluids with pH<4 (Figure 3a, b) before being reduced, thus allowing hydrothermally-derived pyrite overgrowths to precipitate. Zinc can be transported at similar temperatures as ZnCl2 complexes across a range of pH values (0 – ~9) in oxidized fluids. Sphalerite cannot precipitate at these temperatures at pH values <~5; therefore, pyrite and sphalerite are unlikely to have co-precipitated. Sphalerite may have been deposited if the ore-bearing fluids were buffered to pH values >5 following acidic dissolution of carbonate, allowing reduction of the residual Zn-bearing fluid and precipitation of sphalerite. This mechanism could explain the presence of base metal sulfides that surround latest-stage pyrite overgrowths.

5 Summary

- Ultra-high-resolution geochemical mapping of large samples from HYC show sphalerite is associated with carbonate dissolution. Nodular is almost entirely replaced by base metal sulfides.
- Thallium is hosted in late-stage pyrite overgrowths bands that precipitated (perhaps immediately) before base metal sulfides.
- Fluid modelling suggests precipitation of initial Th-bearing pyrite overgrowths by reduction of acidic (pH<4) oxidized fluids. Acidic dissolution of carbonate created additional porosity and a pH buffering effect, allowing precipitation of sphalerite at site of carbonate dissolution.
- These findings provide strong evidence for a diageneric-epigenetic carbonate replacement origin for the HYC mineral system; precluding a syngenetic model.

References


Geology and mineralization of the Marinoan cap dolostone-hosted Dongjiahe Mississippi Valley-type Zn-Pb deposit, South China

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Abstract. The Marinoan cap dolostones (ca. 635 Ma) are distributed on almost every continent and feature similar in sedimentary structures. This study characterized the geology and mineralization features of the dolostone-hosted Dongjiahe MVT Zn-Pb deposit, South China, in order to understand how the ores are controlled by the lithology which is helpful for prospecting undiscovered MVT ores in Marinoan cap dolostones. At Dongjiahe, conformable orebodies occur in both the basal and upper units of the cap dolostone. In the basal unit, Zn and Pb sulphides filled remaining voids after the deposition of fibrous dolomite and chalcedony in breccias. Therefore, brecciation and preservation of the open spaces are critical for the Zn-Pb mineralization. In the upper unit, Zn and Pb sulfides occur in bedding-parallel and oblique cracks which were probably generated by regional folding deformation, in terms of filling remaining voids after the deposition of chalcedony. Thus, generation of cracks related to regional deformation and preservation of open spaces are important for the ore formation.

1 Introduction

The Marinoan cap dolostones are sedimentary beds immediately overlying the Marinoan (~650-635 Ma) glacial deposits during deglacial transgressions (Hoffman et al. 1998; Shields 2005). They are distributed on almost every continent and are characterized by basic uniform structures and textures (Shields 2005; Jiang et al. 2006; Hoffman et al. 2011). As the rocks recorded the process of the earth's paleoclimate from cold to warm, they have been extensively studied in sense of paleoenvironment. However, the rocks have been poorly documented as potential ore hosting rocks of Mississippi Valley-type (MVT) Zn-Pb deposits.

This study focuses on the geology and mineralization features of the Marinoan cap dolostone-hosted Dongjiahe MVT Zn-Pb deposit (20 Mt ore at 2.6% Zn and 0.8% Pb), South China (Fig. 1). Given that the cap dolostones are globally distributed and feature similar in sedimentary structures, the exploration potential of the rocks for undiscovered MVT Zn-Pb resources is likely to be significant. This study may be helpful for the establishment of exploration protocol for undiscovered MVT ores in the cap dolostones.

2 Geological setting

The South China block was built up by the amalgamation between the Yangtze and Cathaysia blocks along the Jiangnan tectonic belt during the early Neoproterozoic (Fig. 1). From the late Neoproterozoic to Silurian, the entire South China region incurred sedimentation of marine facies carbonates and fine-grained siliciclastic rocks in a passive continental margin setting (Jiang et al. 2006). In this period, the Marinoan cap dolostone deposited at the base of the Doushantuo Formation with an age of ca. 635 Ma (Jiang et al. 2006) and immediately overlying the Nantuo Formation glacial deposits. During the early Mesozoic, reactivated intracontinental subduction between Yangtze and Cathaysia or flat subduction of the Pacific plate in the southeast to South China caused the Xuefeng Mountain intracontinental orogeny along the older Jiangnan belt (Fig. 1; Wang et al. 2005). Meanwhile, northwestward oblique compression generated the NE- and NNE-trending fold and thrust structures and subsidiary strike-slip faults in the western Xuefeng Mountain orogen (Fig. 1B, C). The Dongjiahe deposit lies in the NE-striking fold and thrust belt.

Figure 1. a. Tectonic framework map of China; b. Tectonic map showing that the Dongjiahe deposit area lies in the western Early Mesozoic Xuefeng Mountain orogen (modified from Chu et al. 2012); c. Cross-section A-A’ showing that the Dongjiahe deposit is located in the fold and thrust belt in the western Xuefeng Mountain
3 Deposit geology and mineralization

3.1 General features

In the Dongjiahe deposit area, Neoproterozoic and Cambrian strata formed the NE-striking Dongjiahe anticline. The core of the anticline is the Neoproterozoic Nanhua Group clastic rocks and glacial diamictite, and the two limbs are Ediacaran (called Sinian in China) and Cambrian dolostone and limestone (Fig. 2). The deposit area is characterized by NE-striking thrust faults and subsidiary NW-striking and ~W-E-striking strike-slip faults. Except for a few diabase dikes, no magmatic rocks are exposed.

The Marinoan cap dolostone at Dongjiahe is 3-5 m thick and can be subdivided into three units where the basal and upper units host Zn and Pb sulfide ores (Fig. 2), called the lower and upper mineralization layers respectively by mine geologists. The two mineralization layers have similar average ore grades (Zeng and Li 2007). It is estimated that the lower and upper mineralization layers contain about 30-40% and 60-70% Zn and Pb sulfide ores of the entire deposit, respectively. Orebodies in both mineralization layers are conformable and laterally discontinuous with variable thickness. Generally speaking, the host unit is thicker, and the orebodies within it are thicker. At the deposit scale, near to the axial of the Dongjiahe anticline, the thickness of orebodies is increased, which is particularly remarkable for the upper mineralization layer.

3.2 Cap dolostone and mineralization

The basal unit of the cap dolostone at Dongjiahe is 1-2 m thick with the common occurrence of sheet cracks, breccias, tepee, and dome structures (Fig. 3A). The undisturbed dolostone zone contains bedding parallel, laminated, and cemented sheet cracks. Disturbed dolostone zone is shown as breccias. The breccia clasts are angular, ranging from several centimeters to several tens of centimeters in size, and commonly supported by cements (Fig. 3B). Unmineralized sheet cracks and breccias were cemented by fibrous, isopachous dolomite and chalcedony, locally with pyrite (called type II pyrite in this paper), quartz, and bitumen. The dolomite and chalcedony are shown as isopachous syntaxial growths, i.e., mineral growth from the existing rock/mineral wall to the centre of the unfilled void (Fig. 3C). Comparable structures and cementation have been observed in Marinoan cap dolostones from other regions of South China and worldwide (Shields 2005; Jiang et al. 2006). At Dongjiahe, Zn-Pb mineralization in the basal cap dolostone mainly occurs in breccias, rarely in laterally stable sheet cracks. Sphalerite and galena as breccia cements filled remaining voids after the precipitation of fibrous dolomite, chalcedony, and type II pyrite (Fig. 3C, D). Dolomite is the earliest mineral and commonly displays elongate fibrous crystals oriented normal to the crack/void walls (Fig. 3D). Precipitation of the chalcedony is found as linings subsequent to the fibrous dolomite (Fig. 3D). Lesser amounts of type II pyrite is cogenetic with chalcedony, whereas greater amounts of type II pyrite formed after the deposition of chalcedony (Fig. 3E). The replacement of type II pyrite by sphalerite indicates that sphalerite is younger than the pyrite. Sphalerite was then cut by younger quartz veins (Fig. 3D). Bitumen has been found in the remaining voids after the deposition of quartz.

The middle unit of the cap dolostone is a 1-2 m thick, gray-colored, finely crystalline dolostone. Lesser amounts of disseminated and fine-grained type I pyrite occurs in the unit, but Zn and Pb sulfides are scarce.

The upper unit is a 1-2 m thick, gray to dark gray, finely crystalline dolostone, locally containing quartz detrital grains. This lithological unit is transitional with the overlying dark dolomitic and clay-rich slate and siltstone. Stratiform and nodular type I pyrite are
Figure 3. The Marinoan cap dolostone and Zn-Pb mineralization in the Dongjihe deposit. 

a. Breccias from the basal unit of the cap dolostone with tepee and dome structures, locally overprinted by sphalerite; 
b. An unmineralized breccia from the basal cap dolostone, composed of angular dolostone clasts and cements including early stage of isopachous fibrous dolomite and chalcedony and late stage quartz; 
c. A mineralized breccia from the basal cap dolostone where sphalerite as the breccia cement filled remaining voids after the deposition of early stage fibrous dolomite, chalcedony, and type II pyrite, and was cut by late stage quartz; 
d. Cross-polarized light photomicrograph of a thin section of a breccia from the basal cap dolostone, showing that mineral sequence in the breccia cement is, from early to late, fibrous dolomite, chalcedony, sphalerite, and quartz; 
e. A breccia from the basal cap dolostone with abundant type II pyrite and a few bitumen; 
f. Stratiform type I pyrite occurring in the upper unit of the cap dolostone; 
g. Folding-related cracks within a massive type I pyrite-rich zone in the upper cap dolostone, filled by chalcedony and quartz with remaining voids; 
h. Bedding-parallel and -oblique cracks in the upper cap dolostone, filled by chalcedony, sphalerite, and quartz; 
i. Cross-polarized light photomicrograph of a thin section from the upper cap dolostone showing that crack-filling sphalerite is younger than chalcedony. Arrows point to younger stage of mineral deposition.
abundant in the unit (Fig. 3F), such that they are exploitable for the production of sulfuric acid. Folding-related cracks within type I pyrite-rich zones have been filled by chalcedony and quartz (Fig. 3G). Therefore, formation of type I pyrite was prior to the regional folding deformation and the deposition of chalcedony, probably during early diagenesis in view of the stratiform nature. In the dolostone unit, sphalerite and galena mostly filled the bedding-parallel and bedding-oblique cracks (Fig. 3E). Their precipitation was younger than chalcedony but earlier than quartz (Fig. 3I). Subordinate sphalerite replaced the host dolostone and type I pyrite where sphalerite crystals commonly contain dark cores composed of fine-grained type I pyrite.

In summary, the style of mineralization at Dongjiahe is dominated by open-space fill of sphalerite and galena in voids in breccias from the basal cap dolostone and in cracks from the upper cap dolostone. Lesser amounts of sphalerite and galena replaced the host dolostone and diagenetic pyrite. From early to late, mineral occurrence includes pre-ore stage type I pyrite, fibrous dolomite, chalcedony, and type II pyrite, ore stage sphalerite and galena, and post-ore stage quartz and bitumen.

4 Implications for ore prospecting

The Marinoan cap dolostones are globally widespread and they feature similar in sedimentary structures. The Dongjiahe deposit provides an example for prospecting undiscovered MVT ores in the cap dolostones. As far as lithological controls are concerned (regardless of other factors such as tectonic setting, fluid activity, and faulting), we have summarized several useful aspects for ore prospecting. 1) MVT ores can occur in both the basal and upper portions of the cap dolostone. The cap dolostone is thicker, and ore reserves within these strata are potentially larger. 2) In the basal cap dolostone, Zn and Pb sulfides filled remaining voids after the deposition of early stage fibrous dolomite and chalcedony in breccias. Ore-barren breccias are commonly lacking in voids due to filling of early (pre-ore) stage minerals. Therefore, brecciation and preservation of open spaces in the breccias are critical for the Zn-Pb mineralization. 3) In the upper cap dolostone, Zn and Pb sulfides occur in bedding-parallel and -oblique cracks which were probably generated by regional folding deformation. Zinc and lead sulfides filled remaining voids after the deposition of early stage chalcedony in the cracks. Thus, the generation of cracks and preservation of open spaces in the cracks are important for the Zn-Pb mineralization. For the former factor, zones near to the axial of a regional anticline have merit in the production of the cracks and are thus in favour of ore formation.

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Explaining metal zonation at the Lisheen Zn-Pb deposit

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Abstract. Metal zonation is an important feature of low-temperature carbonate-hosted Zn-Pb deposits. Its origin, however, remains poorly understood. In this article, we use the Lisheen deposit in Ireland as a case study to show how thermodynamic modelling can explain these zonation patterns.

Based on input data derived from fluid inclusion studies, bulk ore geochemistry and accepted models of ore formation in the Irish Orefield we construct a reaction path model that successfully accounts for the major features of the mineralisation, most importantly the presence of Cu-Ni-As-rich core zones around hydrothermal feeder structures, surrounded by more distal Fe-Zn-Pb-rich mineralisation.

The outcomes of this study strongly support current metallogenetic models for Irish-type deposits and have implications for near-deposit exploration.

1 Introduction

Distinct mineral and metal zonation patterns have been described for several low-temperature carbonate-hosted deposits (Heyl et al. 1959; Cavender et al. 2016; Torremans et al. 2018). However, the genetic significance of these patterns is not discussed in recent reviews (Leach et al. 2005, Paradis et al. 2007). Furthermore, none of the existing thermodynamic studies on the formation of these deposits (Plumlee et al. 1994; Garven et al. 1999; Appold and Garven 2000; Corbella et al. 2004) considers deposit-scale zonation patterns and mineral parageneses in any detail. This is despite the fact that the combination of zonation patterns with thermodynamic modelling and paragenetic observations has already been successfully applied to other types of hydrothermal ore deposits, e.g. Carlin-type Au deposits (Hofstra et al. 1991).

With this contribution, we address this gap, using reaction path modelling to understand metal zonation and paragenetic relationships at the Lisheen deposit, the second largest zinc deposit in the Irish Orefield.

2 Geological setting

The Lisheen deposit is located in the Rathdowney trend, a distinct structural feature in the Irish Midlands Zn-Pb Orefield that also hosts the Galmoy deposit and Rapla prospect (Hitzman et al. 2002).

The mineralisation occurs as flat-lying pyrite-sphalerite-galena dominated lenses that closely follow the base of the Waulsortian Limestone (Fig.1), a mudbank complex consisting of a variety of units (Hitzman et al. 2002). The lenses are mostly underlain by argillaceous biocalcarenites of the Ballysteen formation. Much of the Waulsortian Limestone in the mine area is completely dolomitised (Hitzman et al., 2002).

The ore lenses are strongly controlled by the location of breached relay ramps between the major normal fault segments of the Lisheen Fault System (LFS) and generally extend northwards from these ramps (Torremans et al. 2018; Fig. 1). Furthermore, they show a distinct metal zonation, with elevated Cu, Ni (and As) close to the LFS and high Zn, Fe (and Pb) values throughout the deposit (Torremans et al. 2018). Torremans et al. (2018) suggest that this metal zonation reflects the flow geometry of the deep ore-forming fluid, with Cu, Ni and As precipitating closest to the “feeder” zones, and the other metals being dispersed further. However, no thermodynamic modelling has ever been conducted to test this hypothesis.
3 Methodology

3.1 Reaction path model

To simulate ore precipitation, we used a binary mixing model based on the current understanding of oreformation in the Irish Orefield (Wilkinson and Hitzman 2015). In this model, an ascending metal-rich basement brine (Fluid A) mixes with a shallow reservoir of sulphur-enriched reduced seawater (Fluid B) (Table 1). Base metal ratios in Fluid A were chosen to reflect the overall composition of the Lisheen deposit. Along the reaction path, Fluid B is successively added to Fluid A in the presence of dolomite until no more minerals are precipitated.

The model was implemented using the "React" module of Geochemists’ Workbench. Mixing and host-rock reaction were simulated in flow-through mode, meaning that precipitated minerals were not allowed to react with the residual fluid after precipitation. Prior to mixing, the fluids were equilibrated for the given input parameters to ensure they are not supersaturated with respect to any solid phases. Fluid B was additionally equilibrated with dolomite and pyrite to reflect the overall composition of the Lisheen deposit. Along the reaction path, Fluid B is successively added to Fluid A in the presence of dolomite until no more minerals are precipitated.

3.2 Simulation of an ore lens

The results of the reaction path model (mass of precipitated minerals as a function of mixing ratio) were used further to simulate the formation of an actual ore lens. For these simulations we chose a simplified 2-dimensional geometry in which Fluid A propagates laterally outward from a central ellipsoidal feeder zone and mixes continuously with Fluid B along its path. This is an idealization of the current suggestion for the geometry of fluid flow at Lisheen (Torremans et al. 2018).

The resulting concentration profiles of Fluids A and B were assumed to be like those for outward diffusion of Fluid A into a reservoir of Fluid B from a continuous source. Thus, contours of constant concentration move gradually outward as the total volume of Fluid A (∇A) injected into the system increases over time, with the dimension of any given concentration contour directly proportional to ∇A. The injection process was approximated numerically by breaking the total volume up into small equally sized fluid batches passing through the expanding system. Adding up the minerals precipitated by each successive batch yields an approximation to the metal distribution in an ore lens.

4 Results and discussion

4.1 Ore mineralogy and paragenesis

The model predicts a relatively simple ore-mineral assemblage (Fig. 2) dominated by pyrite, sphalerite and galena, with trace amounts of tennantite, gersdorffite, arsenopyrite, and vaesite, in general agreement with field observations. The main difference to observed mineralogy is that vaesite does not occur in the deposit, while bornite and chalcopyrite, important constituents of some Cu-rich ores, are not predicted by the model.
4.2 Metal zonation

To visually compare the model results to the observed architecture of mineralisation at Lisheen, Fig. 3 shows element distribution maps for the simulated ore lens and the Main Zone orebody. Several similarities are immediately apparent:

1. Elevated Cu and Ni concentrations only occur around the feeder(s) in the southernmost parts of the ore lenses.
2. High As concentrations extend further north than those of Cu and Ni.
3. Fe and Zn concentrations are relatively uniform across the entire orebodies.

However, several differences are also apparent:

1. Ni and As concentrations are significantly higher in the northern part of the Main Zone than the northern part of the simulated ore lens. Particularly arsenic is much more widely dispersed in actual mineralisation.
2. Pb is more widely dispersed in the simulated ore than the Main Zone.

When considering these differences, it needs to be remembered that one of the major assumptions of the simulation is its simple geometry, with Fluid A emanating from a single feeder. While such a geometry is well suited to illustrate the salient features of our model, it cannot be a realistic representation of the deposit with its complex system of major and minor faults, many of which could have acted as feeder zones for the deep fluid (cf. Fig. 1). Therefore, the greater dispersion of Ni and As in the deposit is likely due to Fluid A entering the Main Zone at several points, not just one. While this provides a satisfactory explanation for the differences in Ni and As distributions, it does not account for the differences in Pb distribution.

The following tentative reasons may account for the observed Pb distribution:

1. Fluid composition could have changed over time. Experiments with different compositions for Fluid A showed that bornite will precipitate with tennantite at higher Cu/Fe and lower Cu/As ratios. Several potential causes are possible for these fluctuations such as changes in local and regional hydrology due to fault movements. For chalcopyrite, the mechanism of formation is not yet clear.

2. Thermodynamic data, particularly complex stability constants for Pb-Cl-complexes and solubility constants for galena could be slightly erroneous. This may lead to an underestimation of galena observations made at a fixed point, the model we used for the simulation of an actual ore lens would predict a local paragenetic sequence going from baryte to pyrite-sphalerite-galena to Ni-As-rich pyrite, gersdorffite and tennantite as the concentration of Fluid B decreases. This is consistent with the general observations reported by Hitzman et al. (2002) and Wilkinson et al. (2005a).
saturation in the fluid causing later precipitation in the model, and thus greater dispersion of Pb.

As discussed above, there is an indication that the Cu-Fe-As composition of Fluid A might have fluctuated as the deposit formed, resulting in the occasional formation of bornite. Therefore, it is not unreasonable to expect that similar variations of the Pb/Zn ratio also occurred.

The reliability of thermodynamic input data on the other hand is difficult to assess in this publication. However, we note that large uncertainties (> 15 rel.%) are often attached to experimentally determined values of equilibrium constants (e.g. Luknin et al. 2013). The observed behaviour may thus lie within the confidence range of the measured thermodynamic data.

In conclusion, both explanations may account for the observed features. Further work will be necessary to determine the exact cause of this discrepancy.

5 Conclusions

We used reaction path modelling to predict metal zonation and mineral paragenesis at the Lisheen deposit, Ireland. Our model successfully accounts for all major features of the deposit, particularly the occurrence of Cu-Ni-As-rich core zones representing hydrothermal feeder structures. Most differences between the observed and simulated mineralisation can be explained by complexities of the ore-forming system not incorporated into the model. Therefore, the model provides a reasonable approximation to the naturally occurring mineralising system, and is suitable to support further, more detailed investigations.

The results support current models of ore formation in the Irish Orefield. Furthermore, zonation from Cu-Ni-As-rich mineralisation to Zn-Fe-Pb dominant ores around hydrothermal feeder structures is also seen in other low-temperature carbonate-hosted deposits (Heyl et al. 1959; Cavender et al. 2016). This suggests that our results are of broader significance for economic geology and minerals exploration.

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The character and origin of barite in the giant Mehdiabad Zn-Pb-Ba Deposit

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Abstract. The Mehdiabad Zn-Pb-Ba deposit, which is the largest Mississippi Valley Type deposit in the world, is located in the Zagros orogen, Iran. A large volume of barite, of which the distribution is larger than the sulfide Zn-Pb orebody, has been recognized in this deposit and their origin and contribution to the Zn-Pb mineralization have been studied. These barites can be subdivided into three stages. The oxygen, sulfur and strontium isotopes of the barites indicate that they are diagenetic in origin, but precipitated in different environments, which include methane-devoid and cold methane seep environments. For their contribution to the Zn-Pb mineralization, the barites were a substrate for mineralization and a sulfur source for the sulfides.

1 Introduction

The Tethyan Domain is extraordinarily endowed with world-class Mississippi Valley-type (MVT) Pb-Zn deposits (Leach et al. 2005; Reynolds and Large 2010), especially in the Central to Eastern part that includes the Zagros orogen in Iran and the Himalayan orogen in China (e.g., Rajabi et al. 2012; Hou and Zhang 2015). The three largest MVT Pb-Zn deposits in the world are located in this region (Fig. 1) and include, the Mehdiabad Zn-Pb-Ba deposit (Pb+Zn: 20.70 Mt; Leach et al. 2005), the Jinding Pb-Zn deposit (Pb+Zn: 15 Mt; Xue et al. 2007) and the Huoshaoyun Pb-Zn deposit (Pb+Zn: 14 Mt; Dong et al. 2015). However, except for some new studies on the Jinding deposit (e.g., Leach et al. 2017), limited knowledge is known about them. In fact, it is critical to know the most important ore-controlled factors of these giant deposits which will help to understand the metallogenesis of the region.

The Mehdiabad Zn-Pb-Ba MVT deposit, is located in the Zagros Orogen of Iran and was first studied 55 years ago (Wright 1964). Till now, the sulfide ores in the deposit are still covered by Quaternary sediments and only drill cores are available for observation. This situation results in the limited understanding related to this deposit (e.g., Reicher et al. 2003; Reichert 2007; Maghfouri et al. 2018; Hashemi Marand et al. 2018). However, a large quantity of barite (up to 113 Mt) has been mined in an open pit in the Mehdiabad deposit recently and provides an opportunity to perform more work on this deposit. Based on previous studies (e.g., Reichert 2007) and field observations from the authors, barite in the Mehdiabad deposit shows strong evidence for replacement by Zn-Pb sulfides that is similar to the giant Red Dog Zn-Pb-Ag deposit (Kelley et al. 2004). Though the replacement textures have been mentioned by previous workers (e.g., Reichert 2007; Maghfouri et al. 2015), the important role of barite in controlling the Zn-Pb ore mineralization has not been recognized.

Consequently, the focus of this study is to understand the character and origin of barite in the Mehdiabad Zn-Pb-Ba deposit and its relationship with the sulfide mineralization. The results will provide insights into ore-controlled factors on sulfide mineralization in the Tethyan Domain.

2 Barite in the Mehdiabad deposit

The Mehdiabad Zn-Pb-Ba deposit is situated in the central part of Iran. Exposed host rocks consist of a thick Lower Cretaceous sedimentary sequence which includes, from the bottom to the top, the Sangestan Formation, the Taft Formation and the Abkuh Formation (Fig. 2). The sulfide Zn-Pb orebody is hosted by the Taft Formation dolostone. The distribution of the barite orebody is similar to but more extensive than the sulfide Zn-Pb orebody. Horizontally, the barite orebody is restricted by the syn-sedimentary Black Hill Fault to the West and is spread to the East with lesser thickness; in the vertical direction, it is mainly distributed in the Taft Formation, with replacement ceasing at the top of the lower Sangestan Formation, but spreading into the upper Abkuh Formation (Fig. 2).

The primary minerals in this deposit include, from greatest to least, barite, quartz, sphalerite, galena, siderite, pyrite and chalcopyrite. Based on cross-cutting
relationships among these minerals, they belong to four stages, which are defined primarily by barite type and the relationship between the sphalerite and barite.

Stage 1: Barite stage. Fine- to medium-grained barites (Fig. 3a and 3b) forming in Stage 1 are typically observed at the stratigraphic top of the deposit in the Abkuh and Taft Formations (Fig. 2). The distribution for this stage of barite may have been more extensive, but main-stage sulfide mineralization has obscured the original distribution. The barites were massive and formed mound in the outcrops. They are white and present as irregularly distributed flat, tabular-shaped crystals (up to 1mm long but generally smaller) (Fig. 4a) in the host carbonate rocks. Some residual barite nodules which form radial patterns with sheaves of barite crystals can be found in this stage.

Stage 2: Barite and siderite stage. Precipitation of Stage 1 white barite was followed by white barite and tan siderite during Stage 2 (Fig. 3c and 3d). The barite and siderite in this stage were mainly produced as veins in irregular bodies throughout the Abkuh and Taft Formations (Fig. 2). These veins cut the Stage 1 barite and the host carbonate rocks. The barite in this stage is coarser than the Stage 1 barite and present as large euhedral crystals (up to 2mm long or smaller) (Fig. 4b and 4c). The siderite is rich in Mn and usually oxidized to Fe-Mn oxides which made the stage 2 minerals appear black (Fig. 4a and 4b).

Stage 3: Quartz-sulfide and barite stage. Vein siderite, quartz, sulfide and barite, which clearly cut the host carbonate rocks and the Stage 2 barite+siderite vein, define Stage 3 (Fig. 3e). There is a transition precipitation of siderite, quartz and minor sulfides (sphalerite, galena, chalcopyrite and pyrite) (Fig. 4d), which is referred to as Stage 3a, before the barite in this stage precipitated (Fig. 4e), which we called Stage 3b. The barite in Stage 3b is much clearer than those in the previous stages. They precipitated as veins, massive bands, or cements of the breccias. They can be recognized in the middle of the quartz-sulfide vein forming in Stage 3a. The barite crystals in this stage are also coarse and the crystals are up to 2mm long. The distribution of minerals in Stage 3a can rich to the top of the Stage 1 barite, however, most barite in Stage 3b are distributed below the Stage 1 barite mound (Fig. 2).

Figure 2. A cross-section of the Mehdiabad Zn-Pb-Ba orebody (modified from Reichert 2007)

Stage 4: Main Zn-Pb sulfide stage. Elevated contents of sphalerite and galena (Fig. 3f and 3g) mark Stage 4 which is the main Zn-Pb mineralization stage in the Mehdiabad deposit. The sphalerite in this stage is lighter brown than those in the Stage 3a. Most sphalerite and galena occur with the barites; however, they did not co-precipitate with them. The phenomena that the sphalerite and galena precipitated by replacing (Fig. 4f) and filling the open space of the barite crystals, which are very similar to those in Red dog deposit (Kelley et al. 2004), gave strong evidence that the Zn-Pb sulfide minerals precipitated later than the barites. The Zn-Pb mineralization has the similar or a slightly larger distribution with the barite in Stage 3 (Fig. 2).

Figure 3. Outcrop and hand specimens showing the character of different stages of barite in the Mehdiabad Zn-Pb-Ba deposit

Figure 4. Photomicrographs showing textural variations of barite s in different stages in the Mehdiabad Zn-Pb-Ba deposit

3 Isotopic studies

21 barite samples were selected for sulfur and oxygen isotopic analysis. The results are presented in Figure 5. The barites show linear correlations between δ¹⁸O and δ³⁴S with varying slopes for different stages (Fig. 5). A plot of δ¹⁸O versus δ³⁴S values of Stage 1 barite has a steep positive slope of 5.0 and extends to high δ¹⁸O values. Stage 2 barite samples display a shallower slope of 1.5. For Stage 3 barites, four are included in the Stage 1 and 2 groups (Fig. 5). However, another four of them display the shallowest slope of 0.39 and extends to high δ³⁴S values. The data for the three stages of
barite all extend downward to the isotopic composition of marine sulfate for the Lower Cretaceous host carbonate rocks in Taft Formation (113–125 Ma) (Fig. 5; Claypool et al. 1980; Paytan et al. 2004).

Figure 5. O and S isotope composition of barite from the three stages in Mehdiabad deposit compared with the composition of seawater sulfate in Early Cretaceous at which time the host carbonate rocks precipitated (from Claypool et al. 1980; Paytan et al. 2004).

The same barite samples have also been analyzed for Sr isotopes and present a similar range for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with those of the host carbonate rocks in Taft and Abkuh Formation (Fig. 6).

Figure 6. Plots of Sr and S isotope values for barite samples in the three stages. The location of solid line rectangle for the marine sulfate at Albian time is from the data in McArthur et al. (2012) and Paytan et al. (2004). The location of solid rectangle for the carbonate rocks in the Taft Formation is from the analyzed Sr isotopic values and Paytan et al. (2004).

Nine sulfide samples (sphalerite and galena) from Stage 4 were selected for sulfur isotopes and the $\delta^{34}\text{S}$ values present a negative range from -17.3‰ to -7.9‰ (Fig. 7).

Figure 7. Sulfur isotope compositions of Stage 4 galena (Gn) and sphalerite (Sp) from the Mehdiabad deposit

4 Discussion

The O and S isotope systematics and the Sr isotope signatures of the barites in the Mehdiabad deposit indicate a clear diagenetic origin for them (e.g., Johnson et al. 2004; Johnson et al. 2009; Antler et al. 2015; Feng et al. 2016). According to the mineralogical character and the slopes of the $\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$ of barites in Stage 1 and 2, the authors consider them to be precipitated from pore waters within the sediment column during post deposition diagenetic processes (Torres et al. 1996b; Griffith and Paytan 2012) in a methane-devoid environment; however, the typical value of the $\delta^{18}\text{O}$ vs. $\delta^{34}\text{S}$ data for the barite samples in Stage 3 indicates that they must be precipitated in methane-in-excess environments (i.e., cold methane seeps) (Torres et al. 1996a; Aharon and Fu 2000).

The sulfide in Stage 4 could precipitate in the open spaces of the previous barite and they also could precipitate by replacing the previous barite. Further, the main Zn-Pb orebodies were almost hosted by the barite ore bodies. It is clear that the previous barite minerals have provided enough space for the later Zn-Pb sulfide precipitation via the physical porosities or chemical replacement. In addition, the sulfur isotopes of the sphalerite and galena are negative which suggest bacterial and thermochemical sulfate reduction (Leventhal 1990; Machel 2001) of the previous barite.

5 Conclusion

(1) Multiple events have been recognized in the Mehdiabad Zn-Pb-Ba deposit which includes at least three stages of barite formation and one stage of hydrothermal sulfide formation. The Zn-Pb mineralization overlapped on the preexisting barite and mainly formed through replacement.

(2) The O, S and Sr isotopic data suggest that the
barites were diagenetic origin but precipitated in a methane-devoid environment and cold methane seep environment, respectively.

(3) The barites provided space and a sulfur source for the Zn-Pb mineralization.

Acknowledgements

We are grateful to staff of the Mehdiabad Lead & Zinc Complex for their assistance with field work. We indebted to Dr. Zengqian Hou, Dr. David Leach and Dr. Craig Johnson for their insightful suggestions that significantly improved the focus of our work. Funding for this research was provided by the National Natural Science Foundation of China (Nos 41773043 and 41320104004), the National Key R&D Program of China (No. 2016YFC0600306), and the IGCP -662 program. The anonymous reviewer is appreciated for his or her helpful comments and useful suggestions which helped us to improve our abstract a lot.

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Sulphur and lead isotope characteristics of Hakkari Zn-Pb province, SE Turkey: implications for ore genesis

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Abstract. Hakkari Zn-Pb province is a newly discovered metallogenic province of the Neotethyan belt. The deposits of this province occur within Middle-Upper Triassic-Jurassic carbonates. Important deposits are Meskantepe, Karakaya and Üzümcü. More than one ore zone is observed parallel to each other along the province. The thickness of each ore zone varies from a cm scale to a few m (0.1 to 6 m). The primary ore was mostly in-situ oxidized and “non-sulphide” zinc deposits was developed. However, primary sulphidic ore lenses have been observed within non-sulphide ore zones. Non-sulphide ore zones consist of smithsonite, hemimorphite, zincite/hydrozincite, goethite, hematite, lepidocrocite, cerussite and anglesite. Primary ore include pyrite, marcasite, sphalerite and galena. This study details the sulphur and lead isotope characteristics of the province. The average δ\(^{34}\)S\(_{\text{CDT}}\) value of sphalerite, pyrite and galena (total 39 samples) of Hakkari province is 1.74‰ (from -3.43‰ to 8.78‰) indicating a large and relatively homogeneous sulphur source. Sulphur isotope data indicate that the source of sulphur most probably was marine sulphates and that TSR was effective in sulphur reduction processes.

The lead isotope ratios of galena (\(^{206}\)Pb/\(^{204}\)Pb between 18.325 and 18.756; \(^{207}\)Pb/\(^{204}\)Pb between 15.579 and 15.700; and \(^{208}\)Pb/\(^{204}\)Pb between 38.421 and 39.034) of the Hakkari Zn-Pb province are slightly heterogeneous, relatively radiogenic and fall close to upper crustal growth curves, like SEDEX deposits globally, rather than MVT deposits.

1 Geological background of the province

The Hakkari Zn-Pb province occurs in thick carbonate sequences (Permian, Triassic and Jurassic) of the Arabian Platform and was deposited in a passive margin environment (Fig. 1). Palaeozoic - Mesozoic clastics and carbonate rocks of an autochthonous sequence belonging to the Arabian Platform outcrop through the Zap River.

The geology of the Hakkari province is composed of Cambrian to Ordovician quartzites, Devonian clastics and carbonates, Carboniferous black shales, Permian thick bedded black limestones, Triassic shales and limestones and Jurassic and Cretaceous carbonates. The formations are concordant and typically represent a passive margin sequence, except for the Ordovician and Devonian boundary. An ophiolitic melange tectonically overlies the autochthonous carbonates from the north (Perinçek 1990). This melange is known as the Yüksekoova complex and represents deformed deep sea sediments of the Neotethyan Ocean.

Due to the N–S compressional regime, an E-W trending folding axis developed in the Hakkari region. The Alpine orogenesis was the latest mountain building event, from the Late Cretaceous to Miocene, and resulted in folding of the sedimentary sequences on the passive margin and in the closure of the Tethyan Ocean and its remnant basins (Şengör and Yılmaz 1981).

2 Sulphur isotopes

Stable sulphur isotope analysis was performed on 39 samples (19 sphalerite, 12 galena and 8 pyrite) from seven different Zn-Pb deposits/mineralization in the Hakkari province. While most of the galena samples were collected from non-sulphide ore zones (Fig. 2a), the sphalerite and pyrites were collected from primary sulfidic ore lenses (Fig. 2b) preserved in non-sulphide ore zones. Stable sulphur isotope values were obtained as follows: between -3.43 ‰ and 5.13 ‰ (mean 0.99 ‰) for galena, between -1.46 ‰ and 3.98 ‰ (mean 0.93 ‰) for sphalerite and between 2.4 ‰ and 8.78 ‰ (mean 4.77 ‰) for pyrite. The average δ\(^{34}\)S values of sulphide minerals is 1.74‰. Although δ\(^{34}\)S\(_{\text{CDT}}\) values in a narrow range close to zero may indicate a source of sulphur of magmatic origin (Kaplan and Hulston 1966), the
absence of magmatism in the geological environment where the mineralization is located eliminates this possibility. The sulphur isotope values of the Hakkari Zn-Pb province developed in passive margin carbonates can be compared with MVT deposits. However, as can be seen in figure 3, while the MVT sulphur isotope data exhibit a wide range, the Hakkari isotope data is in a very narrow range. The absence of framboidal pyrite and formation temperature higher than 200°C (Hanilçi et al. 2018) suggests the absence of bacterial sulphur reduction processes. The narrow range of δ34S values indicate a large and relatively homogeneous sulphur source. Sulphur isotope data indicate that sulphur in sulphides most probably was derived from marine sulphates by thermochemical reduction processes.

Figure 2: (a) Non-sulphide ore zone in Meskantepe deposit, and (b) preserved primary sulphidic ore in the Hakkari Zn-Pb province.

Figure 3. Comparison of δ34S data of the Hakkari Province Zn-Pb deposits with different geological environments (taken from Rollinson 1993) and carbonate-hosted Zn-Pb deposits of Central-Eastern Taurides (data from Hanilçi and Öztürk 2011, and Çevrim 1984).

3 Lead isotopes

The lead isotope studies were carried out on five galena samples from the Hakkari Zn-Pb Province. The lead isotope ratios of galena (206Pb/204Pb between 18.325 and 18.756; 207Pb/204Pb between 15.579 and 15.700; and 208Pb/204Pb between 38.421 and 39.034) are radiogenic and lie close to the average upper crustal curve of Zartman and Doe (1981). The lead isotope values of the Hakkari Province lie on the same trend as SEDEX-type deposits globally (Fig. 4a), rather than typical MVT deposits (Fig. 4b).

Figure 4. Comparison of 207Pb/204Pb versus 206Pb/204Pb plots of galena from the Hakkari Province Zn-Pb deposits with data of global (a) SEDEX and (b) MVT deposits. Average upper crustal curve (“upper crust”), and orogene evolution curve (“orogene”) are from the plumbotectonics model of Zartman and Doe (1981). Fields of MVT and SEDEX deposits drawn from Ayuso et al. (2016).

4 Conclusion

The Zn-Pb deposits in the Hakkari province were developed within Upper Triassic-Jurassic (?) aged, carbonate rocks rich in organic matter. The ore consists of three main zones parallel to each other. In supergene conditions, the primary ore was oxidized in-situ and transformed into non-sulphide zinc ore which contains mainly smithsonite, hemimorphite, zincite / hydrozincite and iron oxy-hydroxide minerals. The primary sulphide ore lenses preserved in the non-sulphide zones contain pyrite, marcasite, galena and sphalerite. Stable sulphur isotope (δ34S) compositions of sulphide minerals belonging to the Zn-Pb deposits in Hakkari province range between -3.45‰ and +8.78‰, with an average 1.74 ‰. Sulphur isotope data in a narrow range indicates that sulphur comes from a relatively homogeneous and large source. The absence of magmatism in the mineralization region eliminates the possibility of magmatic origin and and the absence of framboidal pyrite and strongly negative δ34S values makes bacterial sulphur reduction unlikely. The relatively homogeneous isotopic composition in a
narrow range suggests that the sulphur is sourced from sea water and reduced by the TSR.

Lead isotope data on Hakkari Zn-Pb province sulphides show that the lead is relatively radiogenic and probably derived from the upper crust and that it resembles SEDEX-type deposits rather than MVT-type deposits.

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Revised genesis for Scotland’s largest Pb-Zn deposit

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Abstract. The Leadhills-Wanlockhead (L-W) deposit has a documented mining history dating back to the 13th century and has produced >400,000 t of epigenetic vein-type Pb-Zn-Ag-Cu, making it one of Scotland’s most historic and productive metal mining districts. Here, we re-evaluate mineral paragenesis and combine novel dating with new stable isotope data to constrain ore-forming processes. Vein cross-cutting relationships and colloform banding revealed that hematite pre-dates Pb-S sulphur sourced from the underlying black shales (Samson and Banks 1988). (Anderson et al. 1989; Pattrick and Russell 1989; forming processes. Vein cross-cutting relationships and dating with new stable isotope data to constrain ore-forming processes. Vein cross-cutting relationships and colloform banding revealed that hematite pre-dates Pb-S sulphur sourced from the underlying black shales (Samson and Banks 1988). (Anderson et al. 1989; Pattrick and Russell 1989; (Porteous 1876). From the 16th century until 1958, the documented mining history dating back to 1239 (Porteous 1876). From the 16th century until 1958, the lead mining district has yielded over 400,000 tons of Pb, 10,000 of Zn, and minor Ag, Cu, and alluvial Au (Wilson 1921; Temple 1954; Leake et al. 1998).

Two models for ore genesis at L-W have been previously proposed: i) a Carboniferous, low to intermediate temperature hydrothermal deposit with a plutonic source of ore bearing solution (Temple 1954); ii) a large low temperature (~150°C), high salinity (~19 to 30 wt. % NaCl+CaCl) convective hydrothermal system associated with diagenetic pyrite in the Moffat Shales underlying the Pb-Zn deposit. Homogeneity suggests that S source, ore fluid temperature, and oxidation state were stable during the mineralisation process with sulphides precipitating at or near equilibrium ~190±40°C. Data is consistent with derivation from underlying Lower Palaeozoic shales and greywacke. Homogeneity suggests that S source, ore fluid temperature, and oxidation state were stable during the mineralisation process with sulphides precipitating at or near equilibrium ~190±40°C. Data is consistent with derivation from underlying Lower Palaeozoic shales and greywacke.

Here, we couple paragenetic and geochronological data with new δ44S sulphide data to test each model and shed new light on the ore-forming processes at L-W.

1 Introduction

The epigenetic-hydrothermal vein-type Pb-Zn deposits located within the villages of L-W has been one of the largest base metal resources in the UK and has a documented mining history dating back to 1239 (Porteous 1876). From the 16th century until 1958, the 16 km² mining district has yielded over 400,000 tons of Pb, 10,000 of Zn, and minor Ag, Cu, and alluvial Au (Wilson 1921; Temple 1954; Leake et al. 1998).

Two models for ore genesis at L-W have been previously proposed: i) a Carboniferous, low to intermediate temperature hydrothermal deposit with a plutonic source of ore bearing solution (Temple 1954); ii) a large low temperature (~150°C), high salinity (~19 to 30 wt. % NaCl+CaCl) convective hydrothermal system with mixed meteoric mineralising fluids and sulphide sulphur sourced from the underlying black shales (Anderson et al. 1989; Pattrick and Russell 1989; Samson and Banks 1988).

Previous work by Temple (1954) has identified quartz, pyrite, muscovite, albite, and gold as the earliest phase of mineralisation, occurring as joint filling in greywacke and Pb-Zn veining as vein breccias, or associated with slickenside vein walls. The main Pb-Zn mineralisation is reported to cut older shattered vein quartz and consists of two generations; early chalcopyrite, sphalerite, galena with ankerite, pyrite, calcite, and Ni-arsenide; later chalcopyrite, sphalerite, galena with pyrite, calcite, and barite (Temple 1954). Fe-oxides have not been included in the detailed paragenesis and are suggested to be replacement minerals (Temple 1954).

Aside from K-Ar dating of clay gouge mixtures which suggests an age for fault structures between 320 Ma and 265 Ma, no geochronological data exists for the L-W deposit (Ineson and Mitchell 1974). L-W is a problematic deposit since the ore phase does not contain datable cogenetic minerals and conventional methods may be skewed by common Pb interferences. Thus, developing new chronometers like the multi-aliquot hematite (U-Th)/21Ne method, comparable to Wu et al. (2019) in sample preparation and U and Th determination, and to Farley and Flowers (2012) and Farley and McKeon (2015) in 21Ne determination, may provide valuable data when considering ore genesis.

Anderson et al. (1989) produced the first δ44S data and suggested that sulphide sulphur is leached from diagenetic pyrite in the Moffat Shales underlying the Pb-Zn deposit.

2 Geological setting and samples

The vein-hosting Ordo-Silurian greywackes at L-W are part of the northern margin of the Southern Upland Terrane; an accretionary complex formed on the Laurentian margin synchronously with the subduction of lapatous oceanic crust beneath Laurentia during the Caledonian Orogeny (Stone 2012). The Southern Uplands Terrane consists of NE-SW striking, steeply dipping, folded, and low-grade metamorphosed greywackes with distinct detrital mineralogy defining formations (Leggett et al. 1979; Kemp and Merriman 2001). Formations are separated by high angle strike parallel faults with associated imbricate zones comprising interbedded black shales, siliceous mudstones and cherts (Leggett et al. 1979; Stone 2012).

~70 Pb-Zn-bearing veins have been worked since the 16th century (Brown 1925). Many are concentrated on normal faults and related fractures and trend NW-SW with minor NW-SE to NNE-SSW trends (Mackay 1959). Most workings were shallow but have been noted to depths of 530m (Brown 1925). Veins are predominantly
constrained to the NW of the district by the NE-SW trending Leadhills Fault and related imbricate zone. Galena, sphalerite, silver and chalcopyrite are the only noted mined vein minerals; silver as a byproduct of galena (Temple 1954). These minerals are present as fracture fill, bands, and infilled vugs with veins ranging from a few mm wide to ~1 m (Temple 1954).

By mid Palaeozoic, southern Scotland had amalgamated with the Pangaeao supercontinent at equatorial latitudes (Stone 2012). Carboniferous basins formed across Dumfries and Galloway and were subsequently inverted as a response to Variscan compression and were exposed as part of a land barrier between the Midland Valley and the Pennine Basin (Stone 2012). Transtensional reactivation of Caledonoid structures has been inferred to have resulted in Permo-Triassic basin formation across southern Scotland and northern England (Tyrrell 2012; Stone 2012).

The Thornhill Basin, a N-S fault-bounded ~17 km x 8 km x 0.3 km Permo-Carboniferous graben structure, unconformably overlies Lower Palaeozoic strata ~4 km to the south of L-W. Stratigraphically, the basin ranges from late Carboniferous limestones and Scottish Coal Measures into Permian basalts, red breccias, and aeolian sandstones with an erosional unconformity separating the Carboniferous from Permian strata (BGS 2005). Coal was not mined due to deep penetrative weathering of strata during the Permian period with oxidation of Carboniferous strata suggested to be a result of percolating groundwaters charged with oxidizing ions from the weathering of Permian basaltic lavas (McMillan and Brand 1995). Permo-Carboniferous basins in the area are thought to have covered a more extensive area prior to Quaternary glaciation and subsequent deglaciation (Leake et al. 1998).

In the absence of access to deep mine workings, a new selection of samples bearing hematite, ferroan dolomite, and Pb-Zn-Cu-Fe-sulphide mineralisation were collected from mine heaps at New Glencrieff (NS865133), Whyte’s Cleuch (NS868137), Glengonnar mine dump, and near the Lady Anne Hopetoun Shaft (NS87751404).

Fe mineralisation was identified in two forms; botryoidal, grey metallic, platy hematite (Fig. 1) and ferroan dolomite. Sulphide mineralisation is manifest as galena, sphalerite, chalcopyrite and pyrite. Cubic, metallic galena was the only mined lead ore at L-W and is concentrated in veins and breccias. Sphalerite was the only mined zinc ore at L-W and occurs in massive banded form containing inclusions of pyrite and chalcopyrite (Temple 1954). Metallic, brass yellow to iridescent chalcopyrite was present in samples. Metallic, pale brass yellow cubic and disseminated pyrite is present in many samples.

δ34S sulphide analysis was carried out on 46 samples from 11 veins and were either collected from mine dumps or gifted from museum collections.

3 Methodology and results

Vein cross-cutting relationships and colloform banding textures were used to create a paragenetic sequence (Fig. 1; Table 1). Hematite and Fe-dolomite veins cut and fill voids in basement lithology and are subsequently cut by or are in the core of colloform banding adjacent to sulphide mineralisation. Colloform banding has been used to infer core to outer surface growth structure with the younger side being towards the outer convex surface (Barrie et al. 2009). Pyrite is present within ferroan-dolomite and is cogenetic to and cuts Pb-Zn-Cu-FeS2 mineralisation. Quartz and calcite are ubiquitous gangue minerals.

<table>
<thead>
<tr>
<th>Mineralisation</th>
<th>Fe-oxide Phase</th>
<th>Ore Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphalerite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Parts per million concentrations of U and Th in hematite causes the formation of nucleogenic 21Ne by α capture and neutron release on 16O. By measuring 238U, 232Th, and 21Ne (in excess of atmospheric Ne) an age can be determined using production rates of nucleogenic 21Ne (Cox et al. 2015). The age determined is suggested to be representative of hematite formation (Farley and Flowers 2012; Farley and McKeon 2015).

(U-Th)/21Ne determinations were carried out at SUERC on several grains from a single sample then
homogenized to <38µm and >99% and separated into multiple aliquots for analysis (see Wu et al. 2019 for details). Mean U, Th and \(^{21}\text{Ne}\) concentrations and standard errors on the mean are then used in final age calculations. \(^{21}\text{Ne}\) was extracted by heating aliquots of hematite in a Mo crucible furnace for 20 minutes at 1350 °C with a single reheat for each aliquot at up to 1600 °C to ensure complete degassing. Gas purification and Ne determination procedures can be found in detail in section 3.5 of Vermeesh et al. (2015). Results documented in Table 2.

Table 2. Ne and U concentrations and errors used in age calculation

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>(^{21}\text{Ne})*</th>
<th>U</th>
<th>(^{238}\text{Th})</th>
<th>Age</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>WH-4</td>
<td>1.59</td>
<td>0.5</td>
<td>2</td>
<td>8.72</td>
<td>6</td>
</tr>
<tr>
<td>WH-6</td>
<td>1.58</td>
<td>0.5</td>
<td>2</td>
<td>8.72</td>
<td>6</td>
</tr>
</tbody>
</table>

*atoms/g (10^8); d in %; ^atoms/mg (10^13); "atoms/mg (10^11); age and age error in Ma

Conventional S isotope analyses (Robinson and Kusakabe 1975) of PbS, ZnS, CuFeS\(_2\), and FeS\(_2\) were carried out using a VG SIRA II gas mass spectrometer. Reproducibility of internal and international laboratory standards (CPI, NBS 123, and IAEA-S-3) was better than ±0.3‰. \(^{34}\text{S}\) results are as follows: Galena; -11.6 to -7.9‰ and average of -9.7±0.8‰ (n=40); sphalerite; 7 to -5‰ and average of -6.2±0.5‰ (n=16); chalcopyrite; -8.4 to -6.5 and an average of -7.1±0.6‰ (n=8); one pyrite gave -4.9‰ (n=1).

As galena and sphalerite have been suggested to be cogenetic, S isotope equilibrium can be inferred. By taking an average of \(^{34}\text{S}\) galena (-9.7‰) and sphalerite (-6.2‰), a temperature range for isotopic equilibrium of 188°C ± 10% or ± 40°C was calculated (errors recommended from Ohmoto and Rye 1979).

4 Discussion

The mixing of oxidized and reduced fluids at a basin/basement interface combined with decreasing fluid to rock ratio can result in precipitation of hematite as an initial oxidized fluid becomes more reduced (Reed 1997). This is often followed by the precipitation of sulphides under a more reducing solution (Reed 1997). The mixing of these fluids would result in temperature decrease and precipitation of ore minerals (Barnes 1986). Such processes of ore precipitation are consistent with L-W geology and ore paragenesis in this study.

\(^{21}\text{Ne}\) determinations are reproducible to 0.5% with U and Th determinations reproducible to 6% which is comparable to hematite (U-Th)\(^{21}\text{Ne}\) results currently published (Farley and Flowers 2012; Farley and McKeon 2015).

A Middle to Late Triassic hydrothermal mineralising event in Western Europe, associated with the initial break-up of Pangaea, has been hypothesised by Mitchell and Halliday (1976), Halliday and Mitchell (1984), and Crowley et al. (2014). Normal faulting in the Thornhill basin, and surrounding areas, may have been due to a Triassic rifting phase within the Pangaeao supercontinent (Tyrrell 2012). Rifting may have caused fracturing in surrounding basins and within greywacke and shales providing conduits for surface water to pass through to depth allowing for scavenging of metals and S which agrees with evidence in this study and in Anderson et al. (1989). S-isotopes differ significantly from other region Caledonian granites (Lowry et al. 2005), ruling out magmatic fluids as a source of ore S. Furthermore, subsidence and fracturing of basins, along with the fracturing and reactivation of previous fracture zones in basement lithologies, can allow meteoric waters to penetrate to depths of >10 km in the crust (Menzies et al. 2014). Deeply circulating meteoric fluid can become increasingly saline through extensive fracture-controlled wall rock interaction and, due to an elevated geothermal gradient of ~30°C/km during rifting, increase in temperature (Reed 1997; Lachenbruch et al. 1985; Chapman 1985). Meteoric fluids would need to reach depths between 4 km and 8 km to reach suggested ore fluid temperatures of 170°C to 210°C. An elevated geothermal gradient during rifting may have provided enough heat to cause hydrothermal circulation of connate fluid in the Lower Palaeozoic basement rock, giving a second source of non-magmatic fluid and a modified meteoric signal suggested in Samson and Banks (1988).

Since the L-W veins are shallow, often brecciated, and predominantly concentrated on fault planes, continued extensional tectonics may have allowed for fracturing of the host rock causing pressure release from hydrothermal fluid. Pressure release can cause fluid boiling which can result in brecciation of the host rock, a loss of volatiles in the vapour phase, a decrease in the fluid to rock ratio, and a fluid less capable of metal transportation (Guilbert and Park 1986). Further analysis of results from a Samson and Banks (1988) fluid inclusion study has shown that as homogenization temperature decreased, the melting temperature of ice became more negative (salinity increased). Such a trend is consistent with boiling in shallow hydrothermal ore deposits (Wilkinson 2001; Canet et al. 2011).

5 Conclusions

In this study we have established that hematite precipitated before Pb-Zn mineralisation and that hematite (U-Th)\(^{21}\text{Ne}\) dating provides a Late Triassic age of earliest vein mineralisation. Metals and sulphur are suggested to be leached from the Lower Palaeozoic basement based on \(^{34}\text{S}\) values from this study coupled with historic values of pyrite in underlying basement lithology. S source, ore fluid temperature, and oxidation state remained remarkably stable during the mineralisation process based on \(^{34}\text{S}\) homogeneity with sulphides precipitating at or near equilibrium between 170°C to 210°C. Hydrothermal convection to depths of between 4 and 8 km is based on an isotopic equilibrium temperature, fluid inclusion temperature of <150°C, and a geothermal gradient of 30°C/km which is not uncommon during rifting which, in this case, may be
related to early rifting of Pangaea. Ore precipitation may be due to fluid mixing between basement and basin lithologies as well as boiling in a shallow crustal environment. Lastly, the hematite (U-Th)/He dating method holds potential for increasing our understanding of otherwise difficult to date ore bodies.

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Exploration for a new Cu-Ag Kupferschiefer-type deposit north of the Lubin-Sieroszowice copper district

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Abstract. The gradual resource depletion of shallow Cu-Ag reserves in the Lubin-Sieroszowice district and elsewhere in the world requires exploration for deeper-seated deposits. Recently Miedzi Copper Corp. (MCC) completed 18 drill holes at a greenfield site in the Nowa Sól region that resulted in discovery of Cu-Ag rich mineralization within the northwest-trending extension to the Lubin-Sieroszowice deposits, trending parallel to the eastern extend of the Rote Fäule area. The newly discovered Nowa Sól deposit currently has an inferred and indicated resource of 11 Mt Cu and 29 thousand t Ag contained metal, grading in the range 0.79-9.61% Cu and 3-353 ppm Ag at the depths of over 1700 m. It has the potential to be an economic resource subject to geological, technological and legal considerations.

1 Introduction

The Polish Geological Institute has conducted investigations of the Permian copper-bearing series in Poland since 1957 (Wyżykowski 1958), when the giant sediment-hosted stratabound Cu-Ag Kupferschiefer-type deposit was discovered by drilling the S-1 borehole (Fig. 1). Subsequently, new deposits were successively documented within the Lubin-Sieroszowice (L-S) copper district. These deposits are located within the Fore-Sudetic Monocline, at the contact with the Fore-Sudetic Block, that lack Permian and Mesozoic cover due to Laramide uplift. Mineralization occurs in Permian sediments within the contact zone between the Rottliegend and Zechstein strata. Ore series encounters the Weißschiefer sandstones (Ws), the Kupferschiefer shales (T1), and carbonates of the Basal Limestone (Ca0) and the Zechstein Limestone (Ca1). Locally, small amounts of sulphides occur at the base of the Lower Anhydrite (A1d) The ore zone typically cut across the strata, moving from the Lower Anhydrite to the lowermost part of the Weißschiefer sandstones (Fig. 2).

Ore mineralization is represented by penconcordant zones of finely disseminated sulphides, mainly tabular or blanket-shaped. Sulphides are commonly zoned both in plan and vertical sections, showing the following sequence: chalcocite, bornite, chalcopyrite, galena, sphalerite and pyrite. Chalcocite predominates over other Cu sulphides in proximity to oxidized rocks.

The L-S deposit covers an area of 860 km² and the geological resource in the L-S deposit amounts to 1 828.86 Mt ore containing 33.17 million t Cu and 99.24 thousand tons of silver at the depths from 600 m to 1380 m. These resources include a reserve base of size 1 689.33 Mt ore (30.93 Mt Cu, 88.04 thousand tons of Ag) within the area of 516 km², and potential resource of 139,53 Mt ore (2,24 Mt Cu and 11,08 thousand tons of Ag) in undeveloped deposits (in the area of 344 km²) estimated in areas adjacent to current mining activities. Mine production in 2017 was 31.185 Mt ore at an average grade of 1.5 % Cu and 48 ppm Ag, yielding 467 000 t Cu and 1490 t Ag. The thresholds used in current mining activities are as follows: maximum depth to footwall – 1500 m, sample cut-off grade – 0.5% Cu, minimum Cu eq grade in composite sample – 0.5% (Cu eq=%Cu+0.01 ppm Ag), minimum Cu eq productivity – 35 kg/m². Consequently, the extent of the Cu-Ag deposits and prospects reflect the definition of the 35 kg/m² contour of the Cu eq productivity (fig. 1).

During 50-years of operation, the immense resources of the L-S copper district have gradually diminished. Currently economic resources support an expected mine life of 50-60 years at a production rate of 30 Mt ore per year. To expand resources, time span and scale of copper production in Poland, exploration and definition of new, deep seated reserves is of great importance. The most prospective areas are in close proximity to the documented deposits. New prognostic assessment follows a systematic examination of the drill holes located beyond the current L-S deposits. The close relationship between the Rote Fäule and the orebodies indicate that determination of the range of the oxidized zone is an extremely important exploration guide for the Kupferschiefer-type deposits. It had been previously suggested that the L-S deposit may continue north-west along the redox front (Oszczepalski and Rydzewski 1991, 1997) and with further information, the range of prospective areas and estimate of potential becomes more precise (Oszczepalski and Speczik 2011; Oszczepalski and Chmielewski 2015; Speczik et al. 2015). Recently, both brownfields and greenfields directly adjacent to the documented deposits have been recognised as having the best potential (Oszczepalski et al. 2016, 2017). MCC has continued exploration northwards from the L-S deposit, discovering rich copper-silver mineralization (Zieliński and Speczik 2017; Zieliński et al. 2017).

This paper focuses on the exploration potential for the Kupferschiefer-type deposit in Nowa Sól region by comparison with the operated L-S deposits.
2 The Nowa Sól deposit

North of the documented L-S deposits first exploratory boreholes were drilled by Polish Geological Institute in 1970-1979 (e.g. Sława IG 1 and Grochowice M 9). Later tens of gas exploratory holes were drilled by PGNiG. Those holes were drilled in irregular grid but they made some clusters in regions of brachyanticlines (e.g. Grochowice-Kulów area: Fig. 1). Despite this, those holes allowed four favourable areas to be identified: Grochowice, Kulów, Sława i Jany (Oszczepalski et al. 1997, 2016, 2017; Oszczepalski and Speczik 2011; Oszczepalski and Chmielewski 2015; Speczik et al. 2015). There were no exploratory holes completed anywhere in the Nowa Sól region (subject of this abstract). In order to find extensions to economic mineralization close to existing L-S deposits and in immediate vicinity of the Zielona Góra Rote Fäule area, MCC developed greenfield exploration program for Nowa Sól. The project followed the granting of exploration concessions by the Minister of Environment in 2011. The drilling program initiated in 2013 is still continuing and has resulted in discovery and preliminary definition. At the Nowa Sól deposit, 11 holes have been drilled in two grids, 1,5x1,5 km and 3x3 km (Fig. 1). Equal importance was placed on the reprocessing of geophysical data using the innovative method of effective reflection coefficients to complement the drilling. This method accurately determines structural elements crucial for exploration, suggesting the presence of various tectonic phenomena related to mineralization (Speczik et al. 2012).

The Nowa Sól (NS) deposit is closely associated with the huge Zielona Góra Rote Fäule area, where the lowermost Zechstein sediments are represented by barren red-coloured oxidized rocks. This area is characterized by the pervasive destruction of organic matter and replacement of pyrite and copper sulphides by hematite. A characteristic transition zone occurs between oxidized and reduced sediments, both horizontally and vertically (Oszczepalski and Rydzewski 1991). This zone is characterized by incomplete
oxidation of the reduced sediments and the presence of dispersed hematite and goethite (Oszczepalski 1999; Bechtel et al. 2002). There are common relics of covellite, digenite, chalcocite, chalcopyrite and pyrite among extensive replacement of copper and iron sulphides by hematite (Oszczepalski 1999; Oszczepalski et al. 2002, 2017; Chmielewski 2014; Chmielewski et al 2015). Both the progressive upwards-moving oxidation front, the occurrence of a transition zone, and rimming of the Rote Fäule by high-grade orebodies imply the formation of the Cu-Ag deposits through interaction of the oxidizing and metalliferous solutions with the reduced Kupferschiefer series (e.g. Oszczepalski and Rydzewski 1991; Speczik 1995; Oszczepalski 1999).

Figure 3. Correlation of the selected profiles of the Kupferschiefer series across the Nowa Sól deposit.

The Nowa Sól deposit is stratiform gently cross-cutting the bedding. The redox boundary moves from the Lower Anhydrite in the west to lower parts of the Weissliegend sandstones in the east (Fig. 3). In the NS C17A profile, the entire ore series is oxidized, from the Lower Anhydrite to lower parts of the Weissliegend sandstones. In turn in profiles: J C1 and NS C3, the redox front crosses the Zechstein Limestone, in profiles NS C1 and NS C13 the lower part of the Kupferschiefer horizon, and finally in profiles: NS C2, C4 and C33 it occurs along the T1/Ws contact. In other holes located in the eastern part of the investigated region, only the lowermost part of the Weissliegend is oxidized. Oxidized rocks contain relict copper mineralization in the form of remnant digenite, covellite and chalcocite, partially replaced by hematite (Fig. 4A). Hematite pseudomorphs after frambooidal pyrite are abundant. Oxidized rocks are typically enriched in Au and PGE (Oszczepalski and Chmielewski 2015), native gold, electrum, silver amalgam and auripure were found.

Mineralization is hosted by grey or black sandstones, shales and carbonate rocks. Mineral assemblages, textures and structures of the ore facies are similar to those of the L-S deposit. In reduced sediments the ores are composed of fine-grained disseminations, aggregates, lenses and nests (Fig. 4B, C, D). Complex sulfide composites and replacements of carbonates are common and the mineral assemblage comprises principally Cu-S-type sulfides. Chalcocite prevails over digenite and covellite. In smaller quantities, mainly in the chalcocite-dominated zone, bornite and chalcopyrite are commonly encountered, accompanied by galena, sphalerite and pyrite. In the lower parts of the reduced horizon numerous copper sulphide pseudomorphs after pyrite framboids occur. Native gold, electrum, silver amalgam, cobaltite and nickeline are also reported.

Figure 4. Selected photomicrographs of ore minerals in the Nowa Sól deposit. A Chalcocite (Cc) corroded by hematite (Hem); NS C17B borehole, T1/Ws. B Digenite (Dg) intergrown with bornite (Bn), chalcocite (Cc), and covellite (Cv); NS C3 borehole, Ca1. C Chalcocite (cc) and digenite (Dg) disseminated in carbonates; NS C4 borehole, Ca1/T1. D Chalcocite (Cc) and digenite (Dg) filling the interstitial space between detrital grains; NS C16 borehole, Ws.

The thickness of mineralized horizon ranges from 0.28 to 4.16 m while Cu content from 0.79 to 9.61% and Ag from 3 to 353 ppm. With the present level of information, indicated resources calculated for Nowa Sól deposit with ore horizon at the depth from 1700 to 2100 m are over 7 Mt Cu and 17.8 thousand tons of Ag at an average thickness of 3.4 m and Cue grade equal to 4%, while inferred resources are over 4.5 Mt Cu and 11 thousand tons of Ag (Zieliński et al. 2017 and the author's unpublished reports). The most prospective ore horizon (Cueq>35 kg/m²) is found in the majority of holes except those where the redox boundary cuts across the Lower Anhydrite (C17A).
and the Zechstein Limestone (J C1). The richest copper-silver mineralization (with CuEq from 100 to 300 kg/m²) occurs in drilling profiles (NS C1, C2, C4, C11, C12 and C25) located along the redox boundary at the top of the Weissliegend sandstones.

3 Conclusions

Based on studies of the boreholes performed by Polish Geological Institute on the Fore-Sudetic Monoclino (Oszczepalski and Rydzewski 1997; Oszczepalski and Speczik 2011), summarized by Oszczepalski and Chmielewski (2015), Speczik et al. (2015), and Oszczepalski et al. (2016, 2017), a large-scale greenfields exploration work by MCC discovered deep copper and silver ore resources north-west of the Bytom Odrzański deposit (Zieliński and Speczik 2017; Zieliński et al. 2017). 18 drill holes carried out by MCC in Nowa Sól region allowed to define an area that is approximately 25 km long and 5 to 10 km wide, where mineralization exceeds a grade of 35 kg/m² CuEq. In its central part, the new deep-seated Nowa Sól deposit has been recognized with indicated and inferred resources estimated to contain more than 11 Mt Cu and 29 thousand tons Ag metal, present at depths between 1700 and 2100 m. In addition to Cu and Ag, other commodities, such as Au, Pt, Pd, Pb, Zn, Re, Se, Ni and Co may be considered as by-products. Geological interpretation is in progress and will be forwarded to Ministry of Environment later this year for approval. The drilling program will likely be continued in order to extend reserves and precisely delineate the deposit borders, with the goal of developing an underground mine.

Due to earlier existing legal barriers which limited profitable extraction to depths not exceeding 1500 m (a depth limit for economic viability categories in Poland), this area of greenfield type was not formerly considered as potential mining target. Although both the geological setting and the considerable depth (and associated problems of high overburden pressure, elevated temperature and gas hazards) pose issues, future advances may lead to effective, profitable, technologically attainable, and safe working in this deep environment (Zieliński and Speczik 2017). The principal challenges to deep mining include waste disposal, ventilation, air conditioning and underground ore processing methods, as well as the correct strategy that involves focusing on these parts of the deposit that are characterized by a higher quality of ore relative to shallow deposits. Overcoming geological, technical and technological limitations seems feasible, while the economic barriers require a very deep change of the investment’s policy in the mining industry. The real economic barrier for new mining investments in deep Cu-Ag deposits in Poland has been the introduction of a mining tax for copper and silver implemented in 2012.

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Physicochemical model for the formation of REE minerals associated with emeralds from the Colombian western emerald belt

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Abstract. Parisite has been reported in the Colombian Western emerald belt since the 18th century. Due to emeralds, many studies have been done in the area, showing the frequent association of this mineral with fluorite and emeralds. A physicochemical model is developed for the association of REE minerals revealing the fluorine activities under they were formed, key conditions to understand the evolution of the hydrothermal system (i.e. aF = -1.5 to -4.9).

1 Introduction

Emeralds have been an important and traditional Colombian mineral product, which had been extracted by aboriginal indigenous communities before colonial times (Singewald 1950). Nowadays, more than 150 localities scattered in two areas (Giuliani and Sheppard 1992), both hosted in a peculiar lithology, Cretaceous black shales series (Cheilletz and Giuliani 1996) and its genesis has been cause of debate for decades. Different authors have tried to organize a genetic classification for emerald mineralizations from around the world using different techniques (Gavrilenko and Dashevsky 1998; Dereppe et al. 2000; Barton and Young 2002). However, Colombian deposits are always categorized as a unique example in its own category. These unique mineralizations have had different interpretations of its genesis, ranging from magmatic-hydrothermal solutions (Oppenheim 1948) to the removal of major and trace elements from the shales, transporting the beryllium as a chloride-hydroxide complex (Cheilletz and Giuliani 1996).

The transportation of Be as fluoride complexes has been taken into account in this particular mineralization, although given the results of fluid chemistry a Na-Cl dominated fluid is thought to be responsible for the Be transport (Banks et al. 2000). It is commonly believed that fluoride concentrations in natural hydrothermal systems are limited, involving fluoride bearing minerals with low solubility like fluorite (Kelly and Turbneare 1970; Patterson et al. 1981; Jackson and Helgeson 1985; Robert et al. 1993; Ramboz 2005); as a result, the interpretations of hydrothermal systems usually involve a high rate of chloride and hydroxide complexes rather than fluoride. This paper attempts to explain the mechanisms of Be transport and beryl precipitation.

2 Geological setting

Colombian emeralds are located in the Eastern Cordillera, it consists of Precambrian and Paleozoic metamorphic and igneous rocks overlain by Paleozoic-Cenozoic sedimentary sequences, (Aspden et al. 1987; Vinasco et al. 2006; Horton et al. 2010). Within these lower Cretaceous sedimentary sequences, emerald mineralizations are found, restricted to the Muzo and Rosablanca formations, in the western margin of this cordillera (Fig.1) where REE minerals have been reported. These units have an age range of Valanginian and Hauterivian-Barremian, respectively determined (Reyes et al. 2006; Terraza and Montoya 2011). During this period of time, the Eastern Cordillera was an opening graben system separated into two sub-basins (i.e. Tablazo and Cocuy sub-basins) by the Santander-Floresta paleo-massif (Cáceres and Etayo 1969; Villamil 1998), which was an important barrier to sediment transport until the Aptian (Sarmiento-Rojas et al. 2006). Hence, the sediments in the Tablazo subbasin (i.e. Rosablanca and Muzo Formations) were mainly sourced from the Central Cordillera and the Santander-Floresta paleo-massif.

Figure 1. Simplified geological map and location of the Colombian western emerald belt.

3 Mineralogy

Based on textural analysis of the mineralization in the Western emerald belt on the Muzo, Quipama, Otanche and Peñas Blancas areas, three different stages were identified. The first two stages are mineralogically similar, characterized by the association of calcite, pyrophyllite, pyrite and anthracite, generated by hydrothermal processes, but separated by cross-cutting relationships between them, the second stage denoted by the presence of considerable quantities of sphalerite. The third stage is economically the most important, because emeralds are found associated with parisite,
4 Physicochemical model

For several years, the determination of the conditions of formation of deposits containing fluorocarbonate minerals was done mainly by field relationships, due to the lack of data on the thermodynamic properties of these minerals (Gysi and Williams-Jones 2015). As a result of different geological processes, that concentrate REE minerals, its physicochemical conditions of formations will be different (Chakhmouradian and Wall 2012). Therefore, the stability of these minerals, among other factors, could be measured as a function of the variation of chemical activity of fluorine. These activities are a trustful way to quantify the relative stability of a solid phase despite the use of aqueous solutions or gases to obtain the equilibrium reaction for a solid phase (Simon and Essene 1996).

Thermodynamic calculations were carried out for the system REE-F-CO$_3$ at a temperature of 250°C and a pressure of 1.2 Kbars. Thermodynamic constants of stable REE minerals in the system were taken from Williams-Joones and Wood (1992), Gysi and Williams-jones (2015), while the constants for the aqueous species were taken from Chai Kao et al. (1995). With this data it is possible to determine the chemical activities for the reactions in the deposit. Moreover, calculations of the activity coefficients for the reactions where done to establish the deviation from ideal cases, by the extended Debye-Hückel equation (Helgeson 1969; Helgeson et al. 1981; Oelkers and Helgeson 1990).

\[
\text{Log} \gamma_i = \frac{A z^2 \sqrt{U}}{1 + B k \sqrt{U}}
\]

Where $A$ and $B$ are the Debye-Hückel solvent parameters, $z$ is the ionic charge, the ion size parameter $a$ was taken to be 1.36Å and $U$ is the crystal lattice energy (in kJ/mol) for an ionic crystal.

The chemical potential equilibrium method was applied in the construction of the phase relation among the minerals described by Gysi and Williams-Jones (2015). Providing highlights on the details relevant to mineralogical applications.

Given any balanced reaction, the equilibrium constant ($\ln K$) can be calculated using the Gibbs free energy of the reaction. ($\Delta_r G^\circ$):

\[
\ln K = \frac{\Delta_r G^\circ}{RT}
\]

Where $R$ is the gas constant, $T$ is the temperature in Kelvin and the Gibbs free energy expressed as:

\[
\Delta_r G^\circ = \sum (\delta_i \Delta G_i^\circ)_{\text{res}} - \sum (\delta_i \Delta G_i^\circ)_{\text{rea}}
\]

Where “res” and “rea” represent the resultants and the reactants of the reaction and $\delta_{i,j}$ represent the stoichiometric number of a resultant or reactant (Xu et al. 2014).

Presuming that the solid phases are pure, then ($\ln K$) will depend on this temperature. As a result the chemical activity for the reaction could be expressed as:

\[
\text{Log} a_i = \frac{\Delta_r G^\circ}{RT} = -2.303
\]

This expression is a result of taking into account a correction for the influence of confining pressure on the equilibrium constant proposed by Afifi et al. (1988) and Simon and Essene (1996).

The activity calculations are done assuming a univariante system with the method previously described. As an example, given the balanced expression:

\[
\text{Par} \leftrightarrow \text{Ca}^{2+} + \text{REE}^{3+} + 2\text{CO}_3^{2-} + \text{F}^- + \text{Bas}
\]

Where “Par” and “Bas” correspond to paraisite and bastnäsite compositions (i.e. $\text{Ca(REE)}_2(\text{CO}_3)_2\text{F}_2$ and $(\text{REE})\text{CO}_3\text{F}$ respectively). The activity of fluorine ($\text{F}^-$) could be calculated as follows at a temperature of 523.15°K:

\[
\Delta r G_{\text{F}^-} = 523.15 K = \left[\Delta_r G_{\text{F}^-} = 523.15 K(\text{Ca}^{2+}) + \Delta_r G_{\text{F}^-} = 523.15 K(\text{REE}^{3+}) + \Delta_r G_{\text{F}^-} = 523.15 K(\text{F}^-) + \Delta_r G_{\text{F}^-} = 523.15 K(\text{Bas})\right] - \Delta_r G_{\text{F}^-} = 523.15 K(\text{Par})
\]

The Gibbs free energies of formation of bastnaesite, paraisite $\text{Ca}^{2+}, (\text{REE})^{3+}, \text{CO}_3^{2-}$ and $\text{F}^-$ are -1709.7, -4571.5, -1151.6, -527.8, 572.8 kJ/mol. This equals to -96.37 kJ/mol. Thus, the equilibrium constant:

\[
\ln K = \frac{\Delta r G_{\text{F}^-} = 523.15 K}{RT} = 20.22
\]

And

\[
\text{Log} \text{aF}^- = \frac{\ln K}{-2.303} = -8.7
\]

5 Results and discussion

Applying the method described above, the phase relation between paraisite, bastnäsite and fluorite can be constructed as an activity-activity diagram (Fig. 2). This is built taking into account the calculations of Gysi and Williams-Jones (2015). Since all the variables cannot be fixed in one diagram (i.e. $a_F$, $a\text{CO}_3$, T, P, time), we used fluid inclusion data from previous works (Ottaway 1991; Romero and Schultz 1995; Banks et al. 2000; Giuliani et al. 2000; Terraza and Montoya 2011; Garcia 2017) to fix the diagram to a temperature of 250°C and 1.2 Kbar and the geochemical data obtained from fluorites, paraisites and bastnaesites to establish the chemical activity conditions under which the mineralization was formed.

These results shown a great variation of the fluorine activities, since emeralds are found to be in paragenetic association with these minerals it is reasonable to believe that they share the same conditions of formation.
6 Conclusions

Emeralds from the western emerald belt are formed with fluorite, parsite, and bastnaesite, offering a very interesting perspective to the better understanding of the deposit formation. Showing a high fluorine activity during the genesis of these minerals (i.e. aF = -1.5 to -4.9). This variation on the fluorine activity can be an important variable on emerald precipitation. This could lead to the use F anomalies can be used in regional metallogeny as an exploration guide to find new deposits in the area.

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Metal sources and fluid characteristics of the Khoemacau sedimentary-hosted Cu-Ag mineralization in the Ghanzi-Chobe Belt of NW Botswana

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Abstract. The metal sources and fluid characteristics of Khoemacau sedimentary hosted Cu-Ag mineralisation in the Ghanzi-Chobe Belt portion of the Kalahari Cu Belt of NW Botswana were assessed using Pb isotopic compositions of both sulphides and whole rocks, as well as fluid inclusion microthermomethy. Pb isotope compositions of sulphides span a wide range with $^{206}\text{Pb}/^{204}\text{Pb}$ of 17.204-67.717, $^{207}\text{Pb}/^{204}\text{Pb}$ of 15.576-19.025 and $^{208}\text{Pb}/^{204}\text{Pb}$ of 37.026-45.911. The Pb isotope compositions of whole rocks spatially associated with the Cu-Ag mineralisation also span a wide range ($^{206}\text{Pb}/^{204}\text{Pb}$, 17.961-25.069; $^{207}\text{Pb}/^{204}\text{Pb}$, 15.636-16.185; $^{208}\text{Pb}/^{204}\text{Pb}$, 37.667-45.916). The heterogeneity of the Pb isotope compositions of sulphides from Khoemacau Cu-Ag deposit indicates multiple sources of Pb, and by inference Cu and Ag. The ore forming fluids as deduced from the first melting temperatures ($T_e = 52.5$ to $-25^\circ\text{C}$) are categorized as $\text{H}_2\text{O}-\text{NaCl-CaCl}_2$ fluids. These fluids are two-phase aqueous liquid-vapour fluids with unequal liquid-vapour ratios. These fluids are characterized by a wide range of salinities (4.0 – 23.5 wt. % NaCl + CaCl$_2$ equiv.) and homogenization temperatures ($T_h$) (93.9 – 396$^\circ\text{C}$). Whereas multiple fluids input including basinal brines, metamorphic waters and meteoric waters were involved in the mineralisation process, fluid mixing, boiling and cooling are the possible ore-precipitation mechanisms.

1 Introduction

The Ghanzi-Chobe Belt (GCB) forms the northeastern wing of the Kalahari Copper Belt (KCB) in Botswana (Fig. 1). The KCB situated between the Congo craton to the north and the Kalahari craton to the south has many similarities with the world class European Kupferschiefer and Central African Copperbelt (CAC) sedimentary-hosted Cu-Ag deposits (Hitzman et al. 2010). The GCB hosts several copper deposits/ mineral occurrences amongst them the Khoemacau Cu-Ag mineralisation. The Khoemacau Cu-Ag mineralisation contains numerous mineralised zones including from south to north: the Chalcocite Zone (CC), New Discovery (ND), North Limb (NL), South Limb Definition (SLD), North East Fold (NEF), Mango, Zone 5, Zone 5 North, Boseto, Zeta NE and Zone 6.

The Khoemacau Cu-Ag mineralisation is hosted by the Ghanzi Group consisting of continental red beds (Ngwako Pan Formation), chemically reduced marine sedimentary rocks (D’Kar Formation) and oxidized clastic with minor carbonate units (Mamuno Formation) (Modie 1996). Underlying the Ghanzi Group is a volcanic sequence of metarhyolites and metabasalts referred to as the Kgwebe Formation. These rocks were folded and metamorphosed to greenschist facies during the Damaran Orogeny (Schwartz et al. 1996). Unfoliated dolerite dykes of the Karoo age crosscut the Ghanzi-Chobe belt (Schwartz et al. 1995).

Previous studies (Morgan et al. 2013; Hall 2013; Walsh et al. 2014; Shephard et al. 2014) have well constrained the sources of sulphur (bacteriogenic seawater sulphate reduction), but the source of metals and fluids remains poorly constrained. Various lithologies that are usually older than the hydrothermal mineralisation can be the source of ore metals in sedimentary-hosted Cu deposits. For example, Borg and Maiden (1987) and Gorman et al. (2013) regarded the underlying basalts of the Kgwebe Formation as the main metal source for the strata-bound copper deposits in the KCB, however, Schwartz et al. (1995) has demonstrated that the Kgwebe Formation basalt cannot be the likely source of metals. Meanwhile, other studies in the CAC (e.g. Hitzman 2000; Hitzman et al. 2005, 2010) argued that the metals have been derived from the siliciclastic iron-rich red bed sequence at the bottom of the basin. Calleux et al. (2005) has indicated that some of the Cu in the CAC might have been derived from the erosion of the basement rocks in the region. Therefore, in this study we present Pb isotopic compositions of both sulphides and whole rocks from the Khoemacau Cu-Ag mineralisation in order to identify the likely source(s) of metals. Furthermore, the characteristics of mineralizing fluids are examined through fluid inclusion investigation.
2 Results

2.1 Pb isotopic compositions

Sulphides from the Khoemacau Cu-Ag deposits are radiogenic and show heterogeneous Pb isotopic compositions that span a wide range (Table 1). $^{206}$Pb/$^{204}$Pb ratios are from 17.204 to 67.717, $^{207}$Pb/$^{204}$Pb from 15.576 to 19.025 and $^{208}$Pb/$^{204}$Pb from 37.026 to 45.911. Chalcopyrite from NEF is more radiogenic than the one from ND. Galena and sphalerite have similar Pb isotopic compositions (Fig. 2), suggesting a similar Pb source. Pyrite from CC is highly radiogenic and yielded $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb and $^{208}$Pb/$^{204}$Pb ratios of 67.717, 19.025 and 37.204, respectively. This pyrite is possibly of sedimentary origin.

Pb isotopic compositions of whole rocks are highly heterogeneous and display a wide range of Pb isotope ratios (Table 1). The Pb isotopic compositions of the rhyolites of the Kgwebe Formation are more radiogenic and show a large scatter both in the uranogenic and thorogenic plots (Fig. 2). On the other hand, the clastic rocks of the Ngwako Pan and D’Kar formations can be discriminated into two radiogenic rock sub types; least radiogenic and highly radiogenic rocks (Fig 2). The younger dolerite dyke displays a relatively non-radiogenic character in comparison to the rhyolites of the Kgwebe Formation and the highly radiogenic rocks of the Ngwako Pan and D’Kar formations.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>$^{206}$Pb/$^{204}$Pb</th>
<th>$^{207}$Pb/$^{204}$Pb</th>
<th>$^{208}$Pb/$^{204}$Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhyolite</td>
<td>23.979</td>
<td>15.349</td>
<td>38.743</td>
</tr>
<tr>
<td>(Kgwebe</td>
<td>25.269</td>
<td>15.636</td>
<td>37.667</td>
</tr>
<tr>
<td>Formation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolerite</td>
<td>17.680</td>
<td>15.579</td>
<td>37.026</td>
</tr>
<tr>
<td>(Ngwako</td>
<td>22.774</td>
<td>15.636</td>
<td>37.667</td>
</tr>
<tr>
<td>Pan Form.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clastic rocks (D’Kar Form.)</td>
<td>19.595</td>
<td>15.718</td>
<td>38.929</td>
</tr>
<tr>
<td></td>
<td>21.667</td>
<td>15.902</td>
<td>41.185</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>17.680</td>
<td>15.579</td>
<td>37.026</td>
</tr>
<tr>
<td></td>
<td>22.724</td>
<td>15.579</td>
<td>37.663</td>
</tr>
<tr>
<td>Galena</td>
<td>17.206</td>
<td>15.579</td>
<td>37.667</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>29.902</td>
<td>16.325</td>
<td>45.911</td>
</tr>
<tr>
<td>Pyrite</td>
<td>29.902</td>
<td>16.325</td>
<td>45.911</td>
</tr>
</tbody>
</table>

In the uranogenic and thorogenic plots (Fig. 2), most of the Pb isotope ratios of sulphides fall and cluster between the upper crust and the orogene evolution curves of Zartman and Doe (1981) and overlap the compositions of the least radiogenic clastic rocks of the Ngwako Pan and D’Kar formations, as well as that of the younger dolerite dyke. On the other hand, the compositions of the more radiogenic clastic rocks of the Ngwako Pan and D’Kar formations overlap that of the rhyolites of the Kgwebe Formation indicating a similar Pb source. Of note is the high Pb isotopic compositions of chalcopyrite from NEF suggesting a very radiogenic source (Fig. 2).

2.2 Fluid inclusions

The criteria such as shape similarity, size diversity, constant liquid to vapour ratios and the occurrence along growth zones (see Roedder 1984; Goldstein and Reynolds 1994; Van den Kerkhof and Hein 2001) were employed to study fluid inclusions in quartz and calcite crystals from Cu-Ag-bearing veins. All the fluid inclusions studied are two-phase aqueous liquid-vapour with unequal liquid-vapour ratios. In the liquid-rich inclusions the gas bubble makes up approximately 10% to 20% of the entire volume. In the vapour-rich inclusions the vapour bubble makes about 90 % to 95 % of the entire volume.

Microthermometric results obtained only from the liquid-rich inclusions are presented in Fig. 3. Measurements of final ice melting and homogenization temperatures (Th) (LV → V) in the vapour-rich inclusions were hindered by the large size of the vapour bubble. Fluid inclusion data from previous studies (e.g. Morgan et al. 2013; Shephard et al. 2014) are included to complement our data and get a clear picture of the entire property. In all investigated samples, the first
melting was observed to occur between -52.5 and -25.0°C, thus indicating the presence of NaCl and CaCl₂ in the fluids. The fluids parameters differ according their mineral assemblages.

At NEF, three populations of fluid inclusions are observed. The first population from quartz, calcite and chalcopyrite assemblage is characterized by high T_h (LV → L) of 268 to 396°C and moderate salinities (13.0 to 16.1 wt. % NaCl + CaCl₂ equiv.) The second population from quartz, calcite and chalcopyrite assemblage exhibits moderate T_h (LV → L) of 140 to 156°C and moderate salinities (11.8 to 14.0 wt. % NaCl + CaCl₂ equiv.). These two populations of fluid inclusions were recorded within a single quartz crystal. The third population (data from Morgan et al. 2013) hosted in quartz, calcite, bornite and chalcopyrite assemblage is also characterized by low to high T_h (LV → L) of 93.9 to 296°C but moderate to high salinities (15.6 to 23.5 wt. % NaCl + CaCl₂ equiv.).

Fluid inclusions from the ND also display three populations. The first population hosted in quartz, chlorite, bornite, sphalerite and galena assemblage is characterized by high T_h (LV → L) of 279 to 357°C and high salinities (20.4 to 23.2 wt. % NaCl + CaCl₂ equiv.). The second population from quartz, calcite, bornite and chalcopyrite assemblage is characterized by moderate T_h (LV → L) of 158 to 196°C and moderate salinities (13.0 to 19.3 wt. % NaCl + CaCl₂ equiv.). The third population in calcite and galena assemblage exhibit moderate T_h (LV → L) of 172 to 219°C and moderate salinities (8.7 to 11.8 wt. % NaCl + CaCl₂ equiv.).

Fluid inclusions from CC are hosted in quartz, calcite, chalcocite, bornite, chalcopyrite and wittichenite assemblage. These inclusions are characterized by moderate T_h (LV → L) of 177 to 261°C and moderate salinities (7.9 to 15.9 wt. % NaCl + CaCl₂ equiv.). Fluid inclusion data from Zone 5 and Zone 6 were investigated by Morgan et al. (2013) and Shepard et al. (2014), respectively. These fluid inclusions were associated with quartz, calcite, pyrite and galena assemblage. Zone 5 is characterized by low to moderate T_h (LV → L) of 115 to 165°C and variable salinities between 4.0 and 18.9 wt. % NaCl + CaCl₂ equiv. At Zone 6 fluid inclusions exhibit moderate T_h (LV → L) of 147 to 179°C and moderate salinities (12.6 to 18.5 wt. % NaCl + CaCl₂ equiv.).

3 Discussion

3.1 Source(s) of metals

Our Pb isotope results at first glance rule out the rhyolitic basement rocks of the Kgwewe Formation as the possible source of metals (see Fig. 2). The heterogeneous Pb isotope composition of sulphides from the Khoemacau Cu-Ag deposits points to multiple sources of Pb and by inference Cu and Ag. In both the uranogenic and thorogenic plots (Fig. 2), most sulphides, the least radiogenic clastic rocks of the Ngwako Pan and D’Kar formations as well as the dolerite dyke fall and cluster between the upper crust and the orogene evolution curves of Zartman and Doe (1981), suggesting mixing of mantle and crustal-derived Pb components (see Bineli Betsi et al. 2018). However, the highly radiogenic clastic rocks of the Ngwako Pan and the D’Kar formations plot on the upper crust evolution curve of Zartman and Doe (1981), suggesting crustal-derived Pb components. The isotopic compositions of sulphides (except for pyrite) overlap the compositions of the least radiogenic clastic rocks of the Ngwako Pan Formation, D’Kar Formation and the dolerite dyke, thus indicating a similar Pb, and by inference Cu-Ag source(s). However, one chalcopyrite from NEF is highly radiogenic and its radiogenic character may be explained by the leaching of high radiogenic source rocks total different from the source rocks of the other sulphides. The above implies that Cu and Ag in the Khoemacau Cu-Ag mineralisation could have been leached from the clastic rocks of the Ngwako Pan Formation (red beds) as well as an unidentified source(s) during the hydrothermal event(s). On the other hand, the Pb isotopic composition of highly radiogenic pyrite significantly differs from the compositions of the whole rocks, suggesting sedimentary-derived pyrite (euhedral crystals). Variability of the Pb isotopic compositions of sulphides may reflect differences between metal source rock packages on the basin scale (see Wilkinson 2014).

3.2 Fluid characteristics

Microthermometric analysis of the fluid inclusions allows the physico-chemical characterization of the fluids involved in the mineralisation process (es). The salinities and temperatures of the fluids as observed in Fig. 3 suggest multiple fluid inputs. The coexistence of liquid-rich and vapour-rich inclusions observed in some of the samples is suggestive of boiling process attributed to drop of the fluid pressure below vapour saturation (see Bauer et al. 2019). An increase in salinity accompanied by a decrease in T_h observed in fluid inclusions from the CC is attributed to boiling process, which led to subsequent cooling of the ore fluid. It is also evident that fluid mixing process occurred in
the NEF, ND and CC as shown by the occurrence of both high temperature-high salinity and low temperature-moderate salinity fluids. Fluid mixing has been observed before by Morgan et al. (2013) in Zone 5. The mixing phenomena is also observed in fluid inclusions from Zone 6 (data from Shepard et al. 2014) that show a wide range of salinity (12.6 to 18.5 wt.% NaCl + CaCl₂ equiv.) and roughly similar Tₑ. In addition to the mixing process, post-entrainment modifications (e.g. necking-down) may have taken place as demonstrated by two clusters of fluid inclusions from NEF hosted within a single quartz crystal having different temperatures but same salinities. The decrease in temperature from 357°C to 279°C observed in ND reflects drastic cooling of the ore fluid triggered by water-rock interaction. The high homogenization temperatures recorded (up to 357°C) clearly indicate the presence of an abnormal geothermal gradient and possibly the involvement of metamorphic fluids in ND. On the other hand, low temperatures (115 to 260°C) and salinities ranging from 4.0 to 23.5 wt. % NaCl + CaCl₂ equiv. are typical of basinal brines (Leach et al. 2005) with possible involvement of meteoric fluids (as indicated by low salinity and low Tₑ of 93°C). As deduced from the first melting temperatures (Tₑ = -52.5 to -25°C), the fluids involved in the mineralisation process are categorized as a H₂O-NaCl-CaCl₂-rich fluids.

4 Conclusions

Based on the discussion elaborated above, the following conclusions can be drawn:

1. Pb isotope compositions of sulphides from the Khoemacau Cu-Ag mineralisation are heterogeneous reflecting the derivation of Cu and Ag from two or more sources.
2. Clastic rocks of the Ngwako Pan Formation are the major source(s) of Cu and Ag.
3. Multiple fluid inputs were involved in the mineralisation process, with fluid mixing, boiling and cooling regarded as the possible ore-precipitation mechanisms.
4. Basinal brines, meteoric water and metamorphic fluids are the predominant solutions involved in the mineralisation process.

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We thank Khoemacau Copper Mining for financial support to TK, and their staff for logistic support.

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Investigation of large-scale brine circulation as mechanism of ore formation in the Kalahari and Postmasburg Fe-Mn fields, South Africa

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Abstract. The Kalahari and Postmasburg ore fields are host to giant, economically significant and texturally diverse iron and manganese ores. While hydrothermal metasomatism has been well-demonstrated in the Kalahari district to have locally upgraded the sedimentary manganese orebodies, ore-genesis in the Postmasburg field has been attributed primarily to surficial lateritic processes. However, many ore occurrences in the latter show comparable alkali metasomatic signals to that seen in the Kalahari field. Initial results from our ongoing mineralogical, geochemical and isotopic study, document the regional similarities, the metasomatic nature of the alkali-rich assemblages (replacements, vug-fills, veins) and the remarkable enrichment of the mineralizing fluids in Na, K, Ba, Sr, Ca, Mg, Li, S, Pb, As and V. The widespread occurrence of barite, aegirine, banalsite, natrolite, witherite, phlogopite and other Ba- or Na-bearing silicates observed across Postmasburg ores and neighboring lithologies correlate well with alteration mineralogy described from the Kalahari field. Sulfur isotopes from barite suggest a model invoking fluids of at least partly evaporitic origin, being responsible for the observed alkali metasomatism in both fields. Hydrothermal brine migration is further buttressed by the enrichment in radiogenic 87Sr in barite, consistent with Ba in the involved fluid(s) being derived from basement.

1 Introduction

The Northern Cape of South Africa is a unique metallogenic province hosting various economically important Fe and Mn deposits which owe their origin to sedimentation and a succeeding series of prolonged epigenetic events. According to the prevailing models, central to the epigenetic history of the BIF-hosted iron ores and karstic/sedimentary manganese ores of the Postmasburg field (PMF) has been a range of palaeo-weathering processes which formed the main mechanism of ore-upgrade (Gutzmer and Beukes 1996b; Beukes et al. 2003). The sedimentary deposits of the Kalahari Manganese Field (KMF) which stretch as far as ~150 km to the north of Postmasburg (Fig. 1b) represent Earth’s largest known, land-based manganese resource (~13,500 Mt) and have been locally upgraded by hydrothermal metasomatic processes introducing an unparalleled array of alkali-rich gangue mineralogy (Beukes et al. 1995).

Our study was motivated by the recent discovery of similar alkali-rich assemblages contained in and flanking the Postmasburg Fe and Mn orebodies (Fairey 2013; Bursey 2018) owing to new exploration drill-cores. The recurring theme of complex alkali assemblages and high Ba-Na-K-Ca concentrations in both fields is consistent with the presence of highly saline alkaline fluids similar to those responsible for the upgrade in KMF (Lüders et al. 1999) and of which the origin, sources and pathways are poorly understood. Our focused research on the regional “alkali flooding” aims to understand its role as a shared mechanism in the formation, or at least hydrothermal upgrade, of the two ore fields and discern the origin, source(s), characteristics and timing of mineralization. Whilst establishing a possible link between the two ore districts is an over-arching aim for the project, the ores exhibit a wide textural diversity, demanding the need to forensically differentiate the local from regional influences in order to decipher the individual alteration histories.

2 Geological setting

Ore deposits in the Kalahari Manganese Field occur as three stratiform beds interbedded with the Hotazel iron-formation in the uppermost part of the Palaeoproterozoic Transvaal Supergroup (Beukes 1983). Ores in the NW part of the area have been hydrothermally enriched by fault-controlled, circulation of highly saline fluids which leached carbonates and/or silicates, precipitated manganese as coarse-grained oxides and silicates [hausmannite (Mn²⁺Mn⁴⁺₂O₄), bixbyite ((Mn,Fe)₂O₃), braunite (Mn²⁺Mn⁴⁺₆(SiO₄)O₈)] and produced a complex gangue mineralogy including silicates, borates and sulphates such as sugilite [KNa₂(Fe,Mn,Al)₂Li₂Si₁₂O₃₀], andradite, gaudefroyite [CaMn⁵⁺₂·₃(BO₃)₃(CO₃)(O,OH)₃] and barite (Beukes et al. 1995). This enrichment has been tentatively assigned to a late stage event of the Mesoproterozoic Namaqua-Natal orogeny (Dixon, 1989). A pervasive sodic metasomatism forming aegirine immediately above and below manganese ore beds has also been described by Tsikos and Moore (2005).

The Transvaal Supergroup in the PMF is mainly...
represented by the Asbestos Hills BIF which overlie the Campbellrand carbonates and is in turn separated by an angular unconformity from the overlying siliciclastic sediments of the Olifantshoek Supergroup (Fig. 1a, d). The stratigraphy in the region has been affected by three major deformational events, the Kalahari (~2.35-2.25 Ga), Kheis (~1.83-1.73 Ga) and Namaqua-Natal orogenies (~1.35-1.0 Ga) (Basson 2018). BIF-hosted iron ores are considered to be products of lateritic weathering, formed by the residual enrichment of iron-formation when the latter slumped into karstic sinkholes during a period of uplift and erosion between ~2.2 and 2.0 Ga (Beukes et al 2003). Similarly, pivotal to manganese ore formation was palaeo-weathering and residual concentration of manganese wad from the dolomites into cave systems while dissolution of different chert-rich and chert-free members of the carbonates led to the formation of siliceous and ferruginous ores respectively (Gutzmer and Beukes 1996b). Research on the footwall of so-called conglomeratic iron ore in the northern part of Postmasburg field has uncovered the occurrence of complex alkali assemblages being very similar to the ones found in the KMF and containing aegirine, serandite \([\text{Na}(\text{Mn}^{2+},\text{Ca})_2\text{Si}_3\text{O}_8(\text{OH})]\), barite, strontianite, sugilite and norrishite \([\text{KLiMn}^{3+2}\text{Si}_4\text{O}_{10}\text{O}_2(\text{OH})_2\text{H}_{2}\text{O}]\) (Moore et al 2011). Further south, parageneses bearing barite, witherite, noelbensonite \([\text{BaMn}^{3+2}\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}]\) and the rare As-rich Tokyoite \([\text{Ba}_2\text{Mn}^{3+2}\{\text{As},\text{V}\}\text{O}_4]\{\text{OH}\}\) were documented in Mn ores (Costin et al 2015).

### 3 Sampling and methods

Targeted samples were obtained by drill cores on the basis of anomalous enrichments in alkalis (mainly Ba, Sr and Na) occurring in Mn-, Fe-ore and neighboring lithologies. Postmasburg localities include Kapsteevel, Langverwacht, Leeufontein and Lohatla environs. Additional samples were acquired from underground mines (N’Chwaning I and II; Fig. 1c). Sulfur data were obtained by conventional sulfur analysis and \(^{34}\text{S}/^{32}\text{S}\) were determined using a VG SIRA II mass spectrometer (Coleman and Moore 1978). Strontium isotopes from barite were separated using ion exchange chromatography and measured on a VG-Sector 54 TIMS.

### 4 Petrography

Although the alteration assemblages of KMF are relatively well-studied, our research shows that important mineral paragenetic and textural information can be still attained by detailed optical and SEM microscopy. Initial focus was given on barite- and sugilite-bearing assemblages. Sugilite in aegirine-rich iron formation is seen associated with minerals of the pectolite \([\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})]\)-serandite solid solution, tephroite and possibly later formed K-feldspar and phlogopite spreading laterally along banding. Lipuithe \([\text{KNa}_2\text{Mn}^{3+2}\text{Si}_2\text{O}_5(\text{OH})_3][\text{PO}_4\text{O}_2(\text{OH})_2\text{H}_2\text{O}]\) and K-richerite occasionally intergrown with needles of norrishite indicate an even later stage (Figure 2a). The Pb-Mn silicate kentrolite is generally restricted to vein vicinity and likely replaces earlier-formed minerals such as...
as sugilite. Barite is omnipresent in the studied alkali-assemblages and occurs mostly as fine disseinations, fills in late open structures within Mn ore matrix, or aggregates of alteration mineralogy. Its strontium content is usually low (~1 wt. %), however in some crystals it reaches ~4 wt. %. Other identified Sr-rich phases commonly occurring in the vicinity of barite include strontian apatite, strontianite and granular occurrences of Sr-rich, HREE-bearing apatite in aegirine-matrix. Minute crystals (~25 μm) of a strontium- and vanadium-rich arsenate along with apatite are found as inclusions in barite co-existing with chemically zoned piemontite. Abundant, coarse and bladed barite is found crystallizing perpendicular to the contact between BIF and shale and co-exists with hematite, muscovite and fluorapatite.

Figure 2. Backscattered electron images. a) norrishite needles associated with lipuite, K-richterite and sugilite, crosscutting an aegirine-hematite iron formation in KMF b) Aegirine-hyalophane-barite assemblage filling the breccia matrix in-between BIF-clasts in PMF. c) Complex vein-filling in manganese ore displaying the rare mineral pyrobelonite along with hyalophane and banalsite (Langverwacht). d) Barite intergrown with paragonite in massive iron ore (Kapsteevel). Abbreviations: aeg=aegirine, brn=braunite, btt=barite, bh=banalsite, cal=calcite, hem=hematite, hyl=hyalophane, K-rit=K-richterite, lip=lipuite, ms=muscovite, nor=norrishite, pg=paragonite, pm=piemontite, pry=pyrobelonite, sug=sugilite.

Aegirine-bearing assemblages are also common in the PMF and form zoned vugs or fill the matrix of breccias in braunite-hematite ores (Figure 2b). The manganese matrix hosts complex and uncommon parageneses developing interstitially or in veins and veins. Carbonate-dominated assemblages contain calcite, kutnohorite, ankerite, siderite, barytocalcite – and the Sr-rich equivalent witherite – barite, banalsite (BaNa2Al2Si2O8), apatite, natrolite (Na2Al2Si2O8·2H2O), serandite, tamaite, celsian-hyalophane, phlogopite as well as numerous unidentified micas and Ba-silicates. Pb-bearing minerals are commonly present including the rare manganese vanadate pyrobelonite (Figure 2c) and the minute acicular macedonite (PbTiO3), the latter occurring as disseminations in paragonite. Quartzites overlying the Postmasburg ores can be enriched in barite, associated with muscovite, abundant rutile and apatite while vugs of barite are usually rimmed by unidentified LREE alumino-silicates. Barite in massive iron ore is finely disseminated in the matrix, fills cracks and veins and is associated with hematite, paragonite, muscovite, apatite, berthierite and rutile (Figure 2d). It also displays conspicuous replacement textures such as pseudomorphs after former carbonates and colloform layering along with hematite. Other possible relict textures from pristine iron-formation are hematite ooids filled with barite and paragonite.

5 Sulfur isotopes

Sulfur isotopic compositions hitherto determined for a large number of barite from both KMF and PMF, show enrichment of δ34S and a distinct homogeneity which is characteristic of marine-derived sulphate (δ34S = 25.6 ± 1.76 ‰ (1σ; n=50). The data also supports derivation chiefly from a single reservoir across the basin. The primary candidates for the observed δ34S are evaporite deposits, with any contribution from sulphides known to occur in the underlying strata or mixing with other S sources unlikely. Field and petrographic evidence support the occurrence of now-absent, extensive evaporites in the Campbellrand carbonates underlying the ores (Gandin 2005). If this assumption is true and since there is only negligible fractionation of S isotopes (1.65 ‰) during crystallization of sulphates then barite and other sulphates in the basin could reflect a slightly modified composition from that of Early Proterozoic (~2.5 Ga) seawater. The limited available data from literature display similar ranges for Precambrian seawater (Fig. 3).


6 Synthesis and conclusions

Textural observations allow for the alkali gangue mineralogy in the Kalahari and Postmasburg ore fields to be attributed to the interaction of metasomatic fluids with the ores. Intricate relationships between minerals in veins and vugs as well as replacement textures emphasize the successive alteration stages. Complex mineralogical parageneses including aegirine, serandite, pectolite, phlogopite, natrolite and banalsite observed in both regions, imply comparable metasomatic fluid compositions. Barite is directly associated with the


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References


Resolving the paragenesis of gold at the Avoca VMS deposit: implications for exploration in Caledonian terranes of southeast Ireland

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Abstract. The Avoca Cu-Zn-Pb-Ag VMS belt in southeast Ireland comprises a SW-NE Caledonian trend of Ordovician volcano-sedimentary rocks that host over 16 Mt of sulphides (0.6% Cu) distributed in six defined orebodies. The Kilmacoo Au Zone, on the northeast extremity of the Avoca belt comprises a resource of 300,000 tonnes at 1.5 g/t Au, containing discrete phases of electrum associated with late Caledonian structures. Although historically mined for Cu, notable resources of Zn, Pb and Ag remain at Avoca, occurring as syn-sedimentary (black shale) stratiform pyritic lenses that sit conformably within the host volcano-sedimentary stratigraphy. Sulphides have been modified by early Caledonian shearing, which has resulted in ductile attenuation of sulphides during greenschist facies metamorphism. This has resulted in recrystallization of early primary pyrite with the development of meta-blastic overgrowths and discrete porphyroblasts of pyrite. Gold contents in the Avoca VMS deposit are low overall, occurring as a refractory phase in pyrite (Avg. 0.29 ppm) and arsenopyrite (0.33 ppm). Metamorphic rims are distinctly depleted in Au, indicating barren fluids associated with prograde metamorphic processes (D1). This would suggest that the Kilmacoo Au Zone is not related to primary zonation within the Avoca VMS system, but related to a separate distinct paragenesis.

1 Geological context

Lower Palaeozoic volcanogenic massive sulphides in the Caledonian terrane of southeast Ireland offer an ideal setting for the study of complexly deformed mineral deposits, where geochemical zonation and mineral textures are discernible through the overprinting effects of orogenesis. The effects of syn-metamorphic deformation on sulphide assemblages are important for the concentration of ore resources, resulting in structural thickening and attenuation, as well as possible secondary mobilization and enrichment from later orogenic fluids. Sulphides in the Avoca District exhibit both cataclastic and fluid-assisted deformation textures, and recrystallization (coarsening) in response to variable lower to middle-greenschist facies metamorphism. This has also had an effect on mineral chemistry, with the re-equilibration of major elements in sphalerite and arsenopyrite, and the heterogeneous distribution of trace-elements across multiple phases of pyrite. Advancements in microanalytical techniques now allow for detailed trace-element mapping of sulphide phases (pyrite), which can reveal much of the complex interplay between fluids and mineral growth, resolving the mineral paragenesis for metamorphosed VMS deposits. This project has been developed to address outstanding questions surrounding the genesis of volcanogenic massive sulphides at the Avoca Cu-Zn deposit and possible genetic links for the adjacent Kilmacoo Au occurrence. These questions have relevance to local geology and mineral resources, but also to broader questions of fluid evolution in response to Caledonian geodynamics and correlation with equivalent hydrothermal systems across the Caledonian-Appalachian transect.

Figure 1. Simplified geological map of Ireland featuring lower Palaeozoic lithologies. Inset diagram shows the distribution of sulphide orebodies.

1.1 Regional geology

Volcanogenic massive sulphides of the Avoca Belt are hosted by Ordovician volcano-sedimentary rocks of the Duncannon Group (Figure 1). These rocks were generated on an active Peri-Gondwanan margin (Iapetus Ocean) of Ganderia, with volcanism initiated during a period of extension within a volcanic arc (Stillman and Williams, 1979; McConnell et al. 1991). The volcanic pile sits conformably to unconformably on a Cambro-Ordovician sequence of continentally-derived carbonaceous (graphitic) sediments (Ribband Group), which are exposed primarily in the Caledonian Highlands of southeast Ireland. Closure of the Iapetus Ocean resulted in the development of an accretionary wedge, with subsequent obduction and associated polyphase deformation accompanied by greenschist metamorphism.
1.2 Deposit geology

Massive sulphides at Avoca are found in both aphyric rhyodacite breccias and tuff as an epigenetic Cu-rich replacement facies and as a syngenetic exhalative massive sulphide facies in close association with black shale above the felsic volcanic pile. Orebodies have been delineated at West Avoca, Tigroney, Cronebane and Connary (Sheppard 1980; Williams et al. 1986; McArdle 1993) (Fig. 1). Massive sulphides form stratiform lenses that are coeval with their host volcaniclastic and sedimentary rocks. Their lenticular shape is in part attributed to exhalative processes. However, the aspect ratios of the ore bodies have also been affected by post-depositional poly-phase deformation. Progressive deformation has resulted in fluid-assisted remobilization and the structural attenuation of most massive sulphide bodies along the limbs of folds.

Epigenetic sulphide mineralization, comprising stringers of pyrite and chalcopyrite in siliceous veins, occurs in the footwall of the Avoca massive sulphides. Due to strong ductility contrasts between these sulphides and their host volcaniclastic rocks, stringer sulphide zones are commonly transposed parallel to the predominant S1 composite deformation fabric. Stringer sulphide mineralization is accompanied by large alteration haloes of chlorite, sericite, silica (quartz), sulphide and carbonate, which formed through circulation of hydrothermal fluids in the footwall during massive sulphide deposition.

Metal zoning within massive sulphides is not discernible due to the thin nature of the massive sulphide lenses at Avoca. For thicker orebodies, higher temperature and lower F/S2 and pH conditions over hydrothermal vents can commonly lead to the metasomatic transformation (zone-refining) of massive sulphides into a high-temperature assemblage dominated by pyrite, pyrrhotite, and chalcopyrite. Nevertheless, a classic hydrothermal architecture does persist at Avoca, where a Cu-rich stockwork is overlain by Pb-Zn bedded sulphides and flanked by iron formation to the northeast.

1.3 Kilmacoo gold occurrence

The gold-rich Kilmacoo zone at the northeast end of the Avoca Belt (Fig. 1) is hosted by intensely sheared and altered (silica-chlorite-sericite) sulphide-rich tuffs of the Duncannon Group. Gold is associated with higher contents of pyrite, sphalerite and galena and are accompanied by a peculiar banded quartz vein unit comprising fine white to grey semi-translucent quartz (Milner and McArdle 1992). Unlike the massive sulphides to the southwest, Au is elevated in mineralization at Kilmacoo occurring as fine-grained inclusions, veins and fracture fills of native gold and electrum. The gold mineralization has broadly been interpreted as an Avoca equivalent horizon affected by late shearing (Caledonian) and influx of orogenic fluids, resulting in the enhanced gold tenor (Milner and McArdle 1992).

2 Geochemical paragenesis

Sulphides consist of pyrite, sphalerite, galena, and chalcopyrite with lesser arsenopyrite and tetrahedrite (Fig. 2). In addition, trace phases such as anglesite, stannite, chalcocite, bornite, bismuthinite, molybdenite, electrum, and a range of sulfosalts and native metals (Bi, Au, Ag), occur both as discrete phases and sub-microscopic inclusions in major phases.

Previous studies on the mineralogy of sulphides at Avoca are sparse, and any metallurgical characterization of the ores has not been reported. Other VMS deposits hosted by Ordovician volcanic sequences have described pyrite and arsenopyrite as the principal repositories of Au in massive sulphides (McClenaghan et al. 2004; 2009), with discrete Au-bearing phases making up a small proportion of the overall mineralogical balance. Microscopic examination of sulphide minerals at Avoca was unable to establish the presence of any discrete Au-bearing phases i.e. native gold or electrum in massive sulphides or vein material. The scarcity of visible gold and electrum is not uncommon in VMS deposits and suggests gold may be present as a sub-microscopic refractory phase, or as sub-microscopic inclusions, undetectable by SEM.

Major sulphide minerals were analyzed by Laser Ablation ICP-MS in order to determine the trace element composition of the sulphide paragenetic sequence and illustrate chemical variations along their grain boundaries. Spot analyses were carried out using a spot
size of 25 μm, a fluence of 1.1 J/cm², 5 Hz repetition rate and a shot count of 180. Element mapping was carried out on selected mineral grains with maps generated through the ablation of overlapping 10 μm lines and processed as a continuous profile at a rate of 20 μm/sec, a laser fluence of 1.2 J/cm² and a 40 Hz repetition rate.

2.1 Pyrite

Pyrite at Avoca is arsenian in nature with As averaging 0.11% and ranging from as low as 15.7 ppm up to 2.15%; Arsenic exhibits a positive Spearman Rank correlation with Sb \((r'=0.43; 99\% \text{ confidence interval, } r'>0.1)\). Large anhedral masses commonly exhibit zonation of As from core to rim (Fig. 3). Element mapping of a single pyrite grain reveals rhythmic growth banding of arsenic in colloform pyrite indicating the presence of lattice bound As, as opposed to inclusions of As-bearing minerals. Variations in As within the interior of the pyrite grain are likely due to fluctuating hydrothermal fluid conditions during early deposition with variable recrystallization from metamorphism. Arsenic-rich pyrite on the rim of the colloform mass is attributed to euhedral metamorphic overgrowths, which correspond to porphyroblastic growth of arsenopyrite in massive sulphides. The core of many pyrite grains can appear porous or diseased, with regions variably replaced by galena, sphalerite, chalcopyrite and sulfosalts.

Contents of Au in pyrite average 0.29 ppm and range from the detection limit to 3.9 ppm. Interestingly, Au is invariant with respect to As, suggesting gold may in part be controlled by sub-microscopic inclusions in addition to a refractory phase; a positive correlation with Ag \((r'=0.67)\), Cu \((0.62)\), Pb \((0.51)\) and Sb \((0.44)\) would support the presence of sub-microscopic inclusions of electrum. Analyses of compositionally zoned pyrite have shown that late euhedral overgrowths exhibit depletions in Au contents relative to primary forms of pyrite. Figure 3 shows increased Au within the interior of colloform pyrite; a sharp decrease in Au within the centre of the colloform mass is due to the presence of tetrahedrite at the expense of pyrite. Spatially, Au covaries with As and to a lesser degree Ag, indicating substitution into the pyrite lattice during precipitation and consistent with chemically bonded (refractory) Au in the sulphide structure.

2.2 Arsenopyrite

Contents of Au in arsenopyrite \((n=120)\) are similar to pyrite, averaging 0.33 ppm, ranging from the detection limit to 2.94 ppm Au. Gold is generally invariant with respect to most hydrothermal tracer elements, exhibiting a weak positive correlation with Cu \((r'=0.44; 99\% \text{ confidence interval, } r'>0.21)\). Arsenopyrite is only found in the form of porphyroblasts with its growth possibly sourcing Au from pyrite during metamorphic recrystallization. Intergrowths of arsenopyrite and pyrite are common, indicating that Au contents in arsenopyrite could be due to encroachment by surrounding pyrite inclusions. Furthermore, contents of Sb average 2313 ppm overall but vary considerably between Pb-Zn sulphides from the Cronebane pit (up to 1123 ppm Sb) and a sphalerite rich sample from the Connary zone (8900 ppm Sb). Antimony contents in arsenopyrite are refractory in nature, exhibiting a negative correlation with Zn \((-0.52)\), Ag \((-0.49)\) and Pb \((-0.40)\) with inclusion of host sphalerite and galena minerals coming at the expense of Sb. Raw data for arsenopyrite spot analyses exhibit distinctive signal spikes for Pb and Ag indicating
the presence of discrete microscopic inclusions. Similarly, contents of Zn, which cover the detectable range of the instrument, including values in excess of 10% indicate inclusion of sphalerite.

3 Summary of findings

A mineralogical assessment of sulphides at the Avoca deposit indicates that Au contents in epigenetic stockwork (Cu-resource) and syngentic exhalative sulphides (Zn-Pb-resource) are low overall. Visible gold phases (electrum, native gold) were not identified in any of the sections examined. Laser ablation ICP-MS analyses of major sulphide minerals indicate that the low gold contents in the Avoca deposit overwhelmingly occurs as a refractory phase in pyrite (Avg. 0.29 ppm) and arsenopyrite (Avg. 0.33 ppm). Given the preponderance of pyrite in massive sulphides in the VMS mineralization, the mineralogical balance of Au is hosted by pyrite. Massive sulphides at Avoca exhibit mineralogical zonation consistent with a vertically zoned hydrothermal architecture. The large Cu-resource comprising epigenetic stockwork sulphides and Cu-rich massive sulphides are stratigraphically overlain by banded Zn-Pb sulphides. An exhalative origin is ascribed to this Py-Sp-Gn facies due to its association with black shale and strong layered appearance ascribed to this Py-Sp-Gn facies due to its association with black shale and strong layered appearance representing pseudo-bedding that has been modified by syn-metamorphic deformation (D1). Although massive sulphides at Avoca have been extensively modified by the effects of ductile remobilization during early shearing, primary Au signatures are largely unaffected by metasomatism. The core of primary colloform pyrite masses contain higher Au contents than late euhedral rims, which have grown and annealed in response to greenschist facies metamorphism. This suggests that prograde metasomatism was not a significant source of Au-bearing hydrothermal fluids in the region. The Zn-Pb sulphides at Kilmacoo appear to be an equivalent exhalative facies to massive sulphides outlined along strike at the Cronebane and Connary. The auriferous banded quartz unit at Kilmacoo is intercalated with the massive Zn-Pb sulphides and appears to have undergone the same syn-metamorphic deformation seen in the adjacent deposits. However, upon closer examination, the banded quartz units are seen to be cutting the early penetrative fabrics which postdate sulphide deposition and structurally modify their distribution. This indicates that Au has not been concentrated during the synthesis of VMS mineralization, but is instead related to post-D1 cross-cutting shear structures.

Addressing issues surrounding the extent of late-orogenic Au enhancement of syngentic massive sulphides has far-reaching implications for exploration strategies along the entire Avoca Trend. The disparate styles of mineralization between the Avoca Cu-Zn-Pb VMS deposit with refractory Au signatures and low overall concentrations versus the Kilmacoo Au occurrence with visible phases of native Au and electrum with significant grades highlights the differing ore processes, and timing of emplacement. Late sulphide-bearing shear structures post-dating the formation of penetrative cleavages are now targets for structurally hosted Au mineralization.

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References


Synvolcanic gold in the Archean – Recent contributions to genetic and exploration models, with examples from the Superior province, Canada

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Abstract. Archean synvolcanic gold deposits represent desirable, but often challenging exploration targets. Such deposits primarily include gold-rich VMS, pyritic gold ±polymetallic vein and disseminated-style systems, and synvolcanic intrusion-hosted deposits.

The formation of Archean synvolcanic gold deposits can be the result of: 1) inherently Au-enriched source rocks and fluids due to a specific geodynamic setting or heritage and/or to a magmatic input, and, alternatively or additionally 2) efficient transport (favorable ligands) and precipitation (e.g. boiling/phase separation and zone refining).

Synvolcanic gold deposits are preferentially associated with transitional to calc-alkaline magmatic successions and andesite-dacite-rhyodacite-rhyolite magmatic suites comprising thick felsic units. Deposits formed in pericratonic settings, or on older crust basement in the early stages of rifting, are commonly slightly better endowed in gold than those formed in settings with no or limited basement influence. Evidence for a magmatic input include the presence of complex mineral assemblages (sulphosalts, sulphides, native elements, and tellurides), and anomalous trace element signatures (e.g. enrichment in the “epithermal suite” of elements Au-As-Sb-Ag-Hg and/or in felsic magma-associated elements Bi-W-Te-In-Sn). Large white mica-siliceous alteration, intense aluminous (variably metamorphosed argillic to advanced argillic-style) alteration, and heterogeneous Au distribution are also indicators of a possible magmatic contribution of Au, Ag, and other metals, such as Te and Bi.

1 Introduction

The Superior province is characterized by an exceptional gold endowment (>420 Moz Au, or 13,000 metric t: Dubé and Mercier-Langevin, in prep.) that is the result of a number of key factors that cumulated into forming a diversity of styles of mineralization through time and space. This is particularly the case in the different oceanic crust segments (greenstone belts) that are variably preserved in the southern part of the province (e.g., Abitibi belt). Although the bulk of the gold mineralization in the Superior formed over a relatively short period towards the end of the main north-south shortening episode (orogenic gold deposits), significant gold mineralization is synvolcanic. The synvolcanic gold mineralization therefore predates the peak of orogenic gold mineralization by a few tens of million years. However, the overlap in space with large orogenic gold deposits and districts and major synvolcanic gold deposits (e.g., southern Abitibi greenstone belt) is most likely related to common underlying causes (e.g., common source or recycling: Dubé et al. 2007b; Mercier-Langevin et al. 2014a), which may have implications on the understanding of ore-forming processes in the Archean.

2 Archean synvolcanic gold deposits

2.1 Deposits types and styles

Archean synvolcanic gold deposits are a subtype of Precambrian gold deposits formed early in the geological evolution of their host succession, i.e., prior to the onset of major regional compressional deformation. Synvolcanic gold deposits and prospects are present in both the Abitibi and Wabigoon subprovinces (Fig. 1) and show a large spectrum of sizes and styles.

Figure 1. Simplified map of the Superior province showing the location of selected synvolcanic gold deposits.

Synvolcanic gold deposits can be hosted in volcanic ±sedimentary rocks and are associated with volcanism (Fig. 2), the most common types/styles being Au-rich volcanogenic massive sulphide (VMS) deposits, synvolcanic pyritic gold deposits, and auriferous ±polymetallic stockwork/disseminated sulphide systems (sometimes interpreted as epithermal-like deposits). They can also be hosted in intrusive rocks (Fig. 2) and associated with synvolcanic or pre-regional deformation intrusive bodies and generally consist of stockwork-disseminated-style sulphide zones (sometimes referred
to as porphyry-like or intrusion-related), and Au-Cu sulphide vein systems. A continuum between volcanic and intrusion-hosted deposits exists in many cases. In many of the synvolcanic gold deposits, gold is a byproduct, except for a restricted number of deposits where it represents the principal, and in some cases, only commodity. Many of these deposits have been classified as gold-rich and auriferous VMS deposits based on anomalously high gold grades (e.g., ≥3.5 g/t Au) or a gold to base metal ratio greater than 1 (cf. Poulsen and Hannington 1996; Mercier-Langevin et al. 2011a). The gold-rich VMS-type deposits share broadly similar geometries, although each deposit presents some unique characteristics, whereas the pyritic gold, volcanic-hosted auriferous polymetallic veins and the intrusion-hosted deposits are all distinct.

![Figure 2](image.png)

**2.2 Timing of gold introduction**

Synvolcanic gold deposits are formed during the volcanic-magmatic construction of their host sequence and in the vast majority of cases, the primary characteristics of such early styles of mineralization are obscured by overprinting deformation and metamorphism. Recent work has demonstrated that the syngenetic nature of many Archean gold deposits in the southern Superior province and research on active systems at sea made it clear that gold can be strongly enriched in volcanogenic submarine hydrothermal systems (Hannington et al. 2005, and references therein). However, establishing the precise timing of gold introduction in ancient systems can be difficult. Among the more robust indications of a synvolcanic timing for Au and associated alteration are: 1) overprint of structural fabrics and metamorphic minerals on the auriferous sulphides and associated alteration zones; 2) the presence of auriferous sulphide clast-bearing units associated with the ore in VMS environments; 3) spatial correlation between Au and the base metals at the scale of a deposit or lens; 4) spatial association of Au with synvolcanic/syngenetic alteration; 5) the presence of auriferous mineralization that is cut by synvolcanic (deformed) dykes; 6) stacking of auriferous sulphide zones in the volcanic sequence; and 7) gold-bearing late structural features devoid of Au when extending outside the limits of a sulphide orebody. The absence of isotopic (e.g., O, S, Pb) disturbance due to overprinting metasomatism associated with deformation and/or metamorphism is considered indirect evidence for syngenetic Au introduction, especially when supported by field evidence (Mercier-Langevin et al. 2015).

**2.3 Ore-forming processes**

Gold enrichment in synvolcanic gold deposits can be due to a series of specific features and processes active at different scales (Poulsen and Hannington 1996; Hannington et al. 1999; Huston 2000; Dubé et al. 2007a; Mercier-Langevin et al. 2011a, 2015).

Synvolcanic gold deposits can result from: 1) inherently enriched source rocks and deep-seated fluids, and/or 2) efficient transport (in aqueous fluid and/or vapour) and precipitation. These two conditions are not mutually exclusive, and different processes can be active at the same time and/or at the same site but at different scales (Fig. 3).

An inherently enriched source (magma or host sequence) and/or fluids, as suggested by the strong provinciality of synvolcanic gold deposits, and more particularly Au-rich VMS deposits (Fig. 1), can explain why some areas are so well endowed in synvolcanic gold. Enrichment in the source can be related to a specific geodynamic setting or heritage. It is commonly thought to be associated with a direct magmatic input of Au-bearing (and other metals) fluids into the ore-forming system (Fig. 3).

The geodynamic setting strongly influences not only the type of deposit (including synvolcanic examples) that is formed but also the metal budget. Mature submarine arc and arc – back-arc rift systems constructed on older crust appears to have influenced the overall Au budget of the deposits as indicated by their contaminated Pb-isotope signature and association with felsic rocks showing evidences of crustal contamination (e.g., inherited zircons, evolved Nd-isotope signature). A preferential association of synvolcanic gold deposits with rifted arc and back-arc type settings, packages containing thick felsic volcanic rock and transitional to calc-alkaline andesite-dacite-rhyodacite-rhyolite magmatic affinities is another common characteristic of the synvolcanic gold deposit-bearing belts and districts (Mercier-Langevin et al. 2015 and references therein). Early rifting in an arc – back-arc-style environment is considered important in the genesis of the Au-rich VMS deposits of the Blake River Group in the southern Abitibi belt, where 6 of 11 of the richest and
largest Au-rich VMS deposits are located (Mercier-Langevin et al. 2011a, b). The concept of a favorable heritage or predisposition of certain areas of the upper mantle and lower crust to preconcentrate Au has been proposed for Phanerozoic belts where ore-forming processes tap the same enriched lithospheric mantle source for a prolonged period of time with the recurrent generation of Au deposits. This is perhaps related to favorable geodynamic conditions that fertilize the upper mantle and lower crust and link them to the upper crust (Sillitoe, 2008; Hronsky et al. 2012). Such favorable predisposition in the lower crust and/or upper mantle has been proposed to explain the strong provinciality of Au-rich VMS and orogenic Au deposits in the southern Abitibi belt (Dubé et al. 2007a; Mercier-Langevin et al. 2012). This uniquely endowed portion of the greenstone belt contains more than 85% the Au in the entire belt (all deposit types) and more than 90% of the synvolcanic Au (Mercier-Langevin et al. 2011a, 2014a).

Figure 3. Graphic summary of the many different possible controls on Au enrichment in synvolcanic gold deposits and gold-rich volcanogenic massive sulphide deposits that operate on different spatial and temporal scales. From Mercier-Langevin et al. (2015).

A magmatic input of Au, either direct through degassing and/or fluid exsolution, or indirect through leaching of crystallized magma bodies at depth is a plausible mechanism to explain precious metal-enrichment in some synvolcanic gold deposits and districts as indicated by research on active systems and ancient deposits of the southern Superior. The evidence for a direct magmatic input of Au can be circumstantial, but the involvement of magmatic fluids can be readily inferred in many systems. The presence of extensive zones of aluminous alteration (metamorphosed advanced argillic alteration) has been interpreted as evidence for a magmatic input into the hydrothermal system (Dubé et al. 2007b; 2014; Mercier-Langevin et al. 2013, 2014b; Yergeau et al. 2015). Such aluminous alteration zones develop in response to H₂S vapour condensation or disproportionation of magmatically-derived SO₂ that produce very low-pH, acidic and oxidizing fluids that leach most elements in the rock except for Al and Si. Specific element suites, such as In, Te, and Bi in high-temperature Cu-rich ores and As, Sb, Hg, and Ag (the “epithermal suite”) and complex sulphosalts assemblages in low-temperature Zn-rich ore also have been linked to a direct magmatic contribution of metals into the ore-forming hydrothermal system (Hannington et al. 1999; Huston et al. 2011).

Whereas some districts contain deposits that are uniformly enriched in Au, some districts/camps contain VMS deposits that are much more enriched than others in the same district (e.g., Horne and Quemont, Noranda district). This implies that local processes were involved in precious metal enrichment (i.e. efficient transport and precipitation mechanisms), including boiling/phase separation, optimal zone refining history, the availability of favorable ligands for transport, and the presence of elements acting as sinks for precious metals (e.g., Bi at Lemoine: Mercier-Langevin et al., 2014b). These processes control how gold is transported and deposited, and where in the system it may occur.

2.4 Ongoing research

Numerous synvolcanic gold deposits of the southern Superior appear to be associated with calc-alkaline intermediate to felsic centers that have unusually heavy whole-rock oxygen isotopic signatures, and most of these centers have been dated (U-Pb on zircon). The recovered zircons are currently being analyzed at the Geological Survey of Canada, the University of Alberta, and the University of Toronto for O, Li, and Hf isotopes, trace elements, and thermometry to better constrain the nature and evolution of the ore-associated magmas and
get a better understanding of the genesis of synvolcanic gold deposits at the Archean.

3 Conclusion

The classic exploration models used in Archean terranes for decades are being revised in part because there is clearly a much broader spectrum of gold deposit styles than previously considered. These include syngeneous and syngmamtic (“syngenetic”) deformed and metamorphosed gold deposits that are distinct from the orogenic model. Such a reappraisal has an impact on exploration models since significant gold mineralization formed during the volcanic construction of the greenstone belts. Evidence of the causative processes in Archean systems commonly is not observable in the field; therefore, exploration must focus on the visual evidence of the enrichment process(es) (or diagnostic features) that can be mapped at a range of different scales.

Large areas of the Archean cratons have not yet been explored thoroughly despite a great potential for precious and base metals, and more mature areas will have to be re-examined taking into account the potential for more diverse types of deposits than previously recognized.

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Fluid constraints for Au deposition at the Monges iron deposit, Ossa-Morena Zone (Montemor-o-Novo, Portugal)

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Abstract. The Monges deposit was an important iron mine during late 19th and early 20th century. In recent decades the region of Montemor-o-Novo has attracted the interest of several exploration companies due to high-grade gold anomalies found through soil geochemistry work. Exploration drilling carried out in the WNW-ESE and conjugated N-S shear-zones (≈30 km) identified interesting gold grades, including in the vicinity of the Monges iron deposit. The fluid inclusion study presented here is focused on constraining the fluids related to iron and gold mineralization processes. Fluid constraints for the iron mineralization are difficult assess in the early stage (SEDEX environment) of the Ossa-Morena Zone geodynamic evolution. An overprinting of these early fluids is found, and most of the fluids present may be related to late metamorphism. Gold in Monges area shows affinity to a H$_2$O-CO$_2$-NaCl fluid system showing evidence of immiscibility and trace concentrations of CH$_4$. The geological settings hosting gold mineralization and its relationship with iron ore deposits that are spatially associated. Seven boreholes from the Monges area were sampled to characterize the fluids involved in the mineralization genesis; for this study samples from two boreholes were selected.

1 Introduction

The Ossa-Morena Zone (OMZ, Portugal) comprises a Fe-Zn metallogenic belt (Montemor-Ficalho) that hosts several Fe deposits with different recognized metallogenic origins, such as, 1) Fe-Skarn deposits related with Variscan igneous intrusions (Orada, Azenhas and Alvito deposits); and 2) massive iron ore deposits hosted in carbonate and calcsilicate rocks that are currently accepted to have formed in a SEDEX-VMS continuum which is the case of Montemor-o-Novo ancient mining complex (Salgueiro 2011, Salgueiro et al. 2011). Monges is part of the Montemor-o-Novo area composed of 10 iron ore mining sites and was the largest mine regarding its size and tonnage of iron ore exploited. The ore is mainly magnetite and the ore paragenesis is magnetite + pyrite + hematite + pyrrhotite (± chalcopyrite).

These mines ceased all exploitation in early 20th century, more recently, gold anomalies were found through soil geochemistry, attracting exploration companies to the area. These companies carried out prospecting that revealed new data and interesting gold grades along a WNW-ESE shear zone (Montemor-o-Novo shear) which inflects to a N-S direction in the southeastern part of the shear belt (Ribeiro et al. 1993). This work aims to characterize the gold mineralization and its relationship with iron ore deposits that are spatially associated. Seven boreholes from the Monges area were sampled to characterize the fluids involved in the mineralization genesis; for this study samples from two boreholes were selected.

2 Geological setting

The Serra do Monfurado, where the Monges area is located, is characterized by three main geological formations (Araújo 1995; Chichorro 2006).

i) Escoural Formation (Ediacarian to Lower Cambrian) – characterized by black-schists with sparse intercalation of felsic rocks.

ii) Monfurado Formation (Lower-Middle Cambrian) – a lower unit composed of felsic magmatic rocks (leptinites), and an upper unit of calc-silicate (skarn-like) rocks, marbles and dolomitic limestones;

iii) Carvalhal Formation (Middle-Upper Cambrian) – mainly characterized by banded and massive amphibolites with N-MORB and E-MORB signatures.

2.1 Iron-oxide mineralization

In the Monges mine magnetite occurs as a massive ore (stratiform) and as disseminated mineralization in chloritic-amphibolitic marbles and calcsilicate rocks (skarn-like) from the Monfurado Formation (Salgueiro 2011 and references therein). Remobilization and reprecipitation has resulted in late cross-cutting vein structures and a magnetite + barite primary assemblage is commonly found in waste rock disposals.

2.2 Gold mineralization

Gold mineralization from Montemor-o-Novo developed within a late-Variscan WNW-ESE shear-zone, along a 30km belt which inflects to N-S direction in its most SE
zone, close to the Boa-Fé village (Ribeiro et al. 1993, Chichorro 2006, Inverno 2011). Gold mineralization is usually hosted in shear-zones affecting the Carvalhal and Escural Formations, where higher gold grades are found.

The main identified gold-bearing mineral assemblages are arsenopyrite, loellingite and pyrite, although hedleyite, native bismuth and maldonite were also found associated with quartz and calcite (São Pedro 2019, in prep.). These mineral assemblages are typically accompanied by intense hydrothermal alteration, such as sericitization and intense chloritization (propylitic alteration).

3 Fluid inclusions study

For this study eleven doubly polished thick sections were prepared (=200 µm). Sampling was mainly focused in quartz (+ calcite) veins cross-cutting the host rocks. Over 300 individual fluid inclusions were studied using a LINKAM THMSG 600 microthermometry stage attached to a Nikon Eclipse 50Ipol with 100x long focus objective lens.

3.1 Fluid inclusion petrography

Fluid inclusions hosted in quartz, hornblende, tremolite and barite crystals were studied. Hornblende and tremolite were identified in late veins and in matrix alteration in felsic metavolcanic and calcsilicate (skarn-like) rocks from the Monfurado Formation. These minerals are interpreted to have formed during late metasomatic alteration of the host rocks in the shear zone.

Fluid inclusion petrography revealed two main FI types throughout all the studied samples, defined as Type I and Type II (Fig. 1 A-B).

![Figure 1](image)

Type I consists of two-phase fluid inclusions containing H2O liquid and vapor phases. These FI show predominantly negative crystal shapes when related to primary fluid inclusion assemblages (FIA) and irregular shapes in secondary FIA’s, although this is not a necessary distinguishing factor between the two FIA’s. Three phase NaCl oversaturated FIs were rarely identified in the studied samples, and are grouped in this type, containing H2O liquid-rich and vapor phases and a halite crystal at room temperature (≥25ºC) (Fig. 1-D). Type II fluid inclusions are characterized by two and three-phase FI’s and were subdivided as Type II.a and Type II.b respectively. Type II.a FIs are multiphase having a CO2-rich liquid phase plus an aqueous liquid phase. A CO2 vapor phase may sometimes be present at temperature of 25ºC. Type II.b consists of two phase inclusions with a CO2-liquid phase and a CO2 vapor phase.

Although these FI types are clearly predominant in the studied samples, it is important to note that CH4 liquid-rich fluid inclusions occur with Type II FI cluster assemblages. Several inclusions from Type I and Type II were identified as containing one or two solid phases in their composition, sometimes with an opaque daughter mineral (Fig. 1.C).

3.2 Microthermometry data

Figure 2 plots Salinity (wt. % NaCl Equiv.) versus Th, displaying the microthermometry results of all the FI’s studied, arranged by host mineral.

Type I FI’s eutectic temperatures (T_e) range between -10.2ºC and -49.4ºC, corresponding to fluids with several solutes in its composition, such as, NaCl, MgCl and CaCl2. Salinities were calculated from ice melting temperatures (Tmice), ranging from 0.88 and 23.18 wt. % NaCl Equiv. with a mean of 7.72. Homogenization temperatures (Th) were measured between 116ºC and 460ºC, with a Th average of 253ºC. There were decrepitation temperatures (Td) measured between 216ºC and 247ºC. Type I FI data includes the FI’s where one or two daughter mineral phases were found, with higher salinities - ranging from 32.9 to 34.7 wt. % NaCl Equiv. (calculated from halite melting temperature, TmHal) and Th values of 116ºC, where vapor homogenized into liquid and Th < TmHal.

![Figure 2](image)

$n = 265$
Type II FIs were studied exclusively in quartz crystals and subdivided into Type II.a and Type II.b due to their different compositions. Type II.a FIs revealed CO₂ melting temperatures (TmCO₂) ranging from -58.6°C and -56.8°C, with corresponding CO₂ homogenizations (ThCO₂) between +3.9°C and +24.6°C. Salinities range from 7.17 and 18.04 wt. % NaCl Equiv.

Type II.b shows liquid CO₂ as their dominant component, and TmCO₂ range from -57.5°C and -56.8°C. ThCO₂ were measured from 0°C and 5°C.

3.3 Raman spectroscopy

Raman spectroscopy was carried out on the main FI types aiming to identify the volatiles and solids observed in FIs during petrography and microthermometry studies.

Figure 3-A shows a barite typical Raman spectrum with its characteristic main Raman vibrations at 986 cm⁻¹ (ν1), 458 cm⁻¹ (ν2), 1141 cm⁻¹ (ν3), 615 cm⁻¹ (ν4), which allowed for the identification of the host mineral of some of the studied FIs.

The solids present in Type I FIs were studied by this technique allowing the identification of calcite as the main daughter mineral phase (1084 cm⁻¹) (Figure 3-B). The opaque daughter mineral found in some FI’s could not be identified due to its small size (≈ 1 µm).

Liquid CO₂ was identified in Type II (Type II.a and Type II.b) FIs by its characteristic Raman main vibrations of 1285 cm⁻¹ and 1388 cm⁻¹ (Fermi doublet). The obtained spectra allow for the calculation of the Fermi Diad distance (Δ), in order to determine the CO₂ density (g/cm³) for these types of FIs. Figure 3-C shows some of the obtained spectra for Type II.a and Type II.b FIs. Fermi Diad distance of Type II.a range from 104.25Δ and 107.22Δ with an average of 105.75 Δ corresponding to a CO₂ density of 1.2 g/cm³. Type II.b FIs showed Fermi Diad distances between 104.25 and 106.52Δ with an average of 105.00Δ, which corresponds to CO₂ densities of 0.92 g/cm³. The average values between these two subtypes of Type II FI’s reveal a 105.38Δ distance indicating a CO₂ density of 1.06 g/cm³. Although their scarcity, several CH₄-bearing fluid inclusions were identified and studied. Raman spectroscopy shows that these FI’s composition is near a pure CH₄ composition (Fig. 3-D).

4 Fluid flow contribution for mineralization

The gathered FI data reflects the fluid circulation in the Montemor-o-Novo shear zone affecting the Escoural, Monfurado and Carvalhal Formations, where gold-mineralization occurs. This puts aside the possibility that the studied fluids are related to the iron mineralization of the Monges deposit, which precedes the gold-related mineralizing events. Primary fluids were most certainly overprinted by late-metamorphic fluids as can be evidenced by the FI present in the amphibole group minerals. Therefore, the data gathered in this study concerns mainly the late episodes related to the gold ore genesis. This study provides evidence for a revised metallogenic model for gold emplacement for the Ossa-Morena Zone.

Previous studies classify the Montemor-o-Novo deposit as an orogenic gold related deposit (Ribeiro et al. 1993, Pereira et al. 2002, Inverno, 2011). The metallogenic models have been supported by regional structural studies and hydrothermal alteration geochemistry, although, no fluid inclusion studies were ever carried out. The work presented herein is the first FI study elucidating gold transport and deposition in the Montemor-o-Novo gold deposit.

The iron and gold mineralizations although being in the proximity of one another, clearly show different genetic and metallogenic evolutions.

4.1 New Research

The relatively low salinity fluids (< 10 wt. % NaCl Equiv.) and Tₑ temperatures between 150°C and 350°C are consistent with typical fluid properties identified for orogenic gold deposits worldwide (Bodnar et al. 2014).

The Tₑ (first ice melting temperatures) range indicates the presence of Mg²⁺ and Ca²⁺ in the fluids trapped in Type I FIs (Fig. 4). The presence of these ions justifies the crystallization of calcite daughter minerals in some of the studied FIs.
The higher $T_h$ values found in Type I FIs were recorded in metamorphic amphiboles (hornblende and tremolite) indicating that metamorphic fluids reached temperatures of 460°C, close to metamorphic peak conditions described for the region (Pereira et al. 2012). Type II CO$_2$-bearing fluid inclusions in assemblages with Type I FI’s indicated a H$_2$O-CO$_2$-NaCl system. The different H$_2$O and CO$_2$ concentrations suggest that immiscibility occurred, reflecting devolatilization of the amphibolite and black-schist units. Halite bearing fluid inclusions are rare (two FI’s registered) and are not representative of the mineralizing fluids (Robert et al. 1995; Boullier et al. 1998).

CH$_4$ concentrations in H$_2$O-CO$_2$-NaCl and CO$_2$-pure FIs is estimated to be ≈ 5 mol. % (Fig. 5). Nevertheless, liquid CH$_4$ bearing FIs were found in samples from quartz veins that cross-cut carbonate/calcisilicate host rocks and could be evidence of organic matter thermal degradation in these lithologies (Demir et al. 2017).

**Figure 5.** $T_{mCO2}$ versus $T_{hCO2}$ plot from CO$_2$-bearing fluid inclusions. Trend lines adapted from Bodnar et al. (2014).

### 5 Conclusions

Data suggests that gold mineralization originated from low to medium salinity fluids in a H$_2$O-CO$_2$-NaCl system, containing variable concentrations of CO$_2$ in their composition. This indicates that immiscibility occurred, possibly due to fluid pressure cycles promoted by cyclical reactivation of the host shear zones in ductile and brittle regimes (Ribeiro et al. 1993). Fluid temperatures ranged from 150°C to 350°C, although during peak metamorphism they could be higher than 460°C, as seen in FIs hosted by amphibole.

The data corroborates the orogenic gold model accepted for this deposit, although, identifying a clear source for the gold-bearing fluids is unresolved. The data presented here closely approaches a model where fluids may have had a high metamorphic devolatilization contribution generated by the Montemor-o-Novo WNW-ESE and N-S Boa-Fé shears.

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The presence of colloidal gold in epithermal mineralizing fluids

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Abstract. Transport of gold and silver as colloidal particles has been observed in c. 300 °C low salinity fluids from the Arapucandere intermediate sulphidation epithermal base-metal-Au deposit in NW Turkey. Large euhedral quartz crystals, grew after the deposition of sulfides. Overgrowths have a fibrous texture which grew perpendicular to the existing crystal faces and facilitated trapping of large elongate fluid inclusions between the quartz fibres. Episodic trapping of fluid inclusions occurred throughout the growth of quartz. Trapped within primary fluid inclusions are numerous particles of gold, the largest observed is c. 1 μm but most are smaller. BSE element mapping show these to contain Au, Ag, Cu + Hg. LA-ICP-MS ablation of fluid inclusions confirms Au and Ag is not present in solution, occurring as numerous particles. The concentration of gold in fluid inclusions is orders of magnitude greater than has been previously measured or thought likely in crustal fluids. The average Ag concentration is c. 32 ppm and Au is c. 41 ppm, but the maximum concentrations may reach several 100’s to 1000 ppm. Au-Ag particles could not have precipitated in the fluid inclusions, therefore have precipitated elsewhere and transported by the hydrothermal fluid.

1 Introduction

Concentrations of gold are usually very low and difficult to determine in fluid inclusions, which are micron sized aliquots of the mineralizing fluid trapped in minerals that precipitated during mineralization. The inability to measure gold concentrations was a fundamental problem in understanding key processes that transport and precipitate the metal. Recent technological advances now allow direct measurement of Au concentrations in the ore-forming fluids trapped in various minerals as fluid inclusions. This study provides evidence for the presence of colloidal Au-Ag particles in epithermal fluids through their observation, using scanning electron microscopy (SEM), in primary fluid inclusions trapped during the different stages of growth of large quartz crystals. SEM cathodoluminescence (SEM-CL) was used to define the multiple growth stages of the quartz which were linked to different generations of largely primary fluid inclusions, which record rapid changes in pressure and temperature. Microthermometry of the fluid inclusions constrained pressure, temperature and salinity of the hydrothermal fluids over the period of euhedral quartz growth. Combining the salinity of the fluid inclusions with laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) of individual fluid inclusions allowed the concentration of Au and Ag to be determined and in what form Au and Ag were present.

2 Geological setting

The Arapucandere deposit can be considered as an intermediate-sulfidation epithermal deposit hosted by Palaeozoic metamorphic rocks and Permo-Triassic clastic rocks related to the collisional and post-collisional tectonic regime in the Biga Peninsula. Mineralization at Arapucandere, which was a base-metal deposit, results from episodic lithostatic–hydrostatic pressure variations (Bozkaya and Banks 2015) within fault and fracture systems creating space for mineralization and providing a mechanism that induces massive ore deposition. Quartz is present as largely pre-ore coarse crystals and syn-to post ore finer-grained crystals. Different episodes of deposition for each type of quartz are evident indicating repeated influx of fluids. Sulfides, sphalerite, galena and chalcopyrite, cut the coarser grained quartz and also show evidence of multiple periods of deposition. Pyrite is an early phase, occurring within the quartz that is cut by other sulfides.

3 Fluid Inclusion analyses

Primary inclusions are located in zones where, predominantly L-V, fluid inclusions are trapped in significant numbers in linear arrays originating from existing crystal faces (Fig. 1). These are typically between 20 μm and 100 μm in size (Fig. 2). V-rich inclusions are much less common, but may occur with L-V inclusions in these linear trails. V-rich inclusions frequently occur in fractures that appear to be pseudo-secondary where trails originate from the outer surface of the quartz crystal, however they may also be of secondary origin. There are also examples of clear secondary fluid inclusions as seen in CL where a trail of inclusions starts in the later quartz growth and cuts the
outer face of the euhedral crystal and through numerous growth bands.

Th values are between 270 and 340 °C and the majority of the salinities are low c. < 2 wt.% NaCl equiv. but a small number of areas, where the inclusions appear to secondary, have salinities up to c. 8 wt.% NaCl equiv.

4 SEM observations

Due to their large size many fluid inclusions were opened during polishing of wafers which were used both for fluid inclusions and CL. In the CL images, bright mineral/solid inclusions were observed in open fluid inclusions. Two open inclusions of c. 50 µm size are shown in the back scattered electron (BSE) image Figure 3a.

In both inclusions and in almost all open inclusions imaged by BSE, several sub-micron gold particles can be seen (Fig. 3b) with the largest being c. 1 µm in size, but they are commonly smaller than this. These are attached to the walls of the inclusion or on calcite or baryte crystals. Gold particles can be distinguished as they are always rounded and are the brightest objects, for example (Fig. 3c) where the two brightest inclusions are attached to a more rectangular, less bright, baryte. With the largest gold inclusions, it was possible to use BSE element mapping to obtain compositional data that showed there was silver, copper and occasionally mercury in addition to gold (Fig. 3c). Other small crystals are present in the inclusions and energy dispersive spectroscopy (EDS) identified these as pyrite, baryte, galena, sphalerite and calcite (spectra are presented in supplementary data). Element mapping of the fluid inclusions content (Fig. 4) shows the presence of small
individual mineral crystals and also that the inner surfaces are coated in calcite and sulphides/sulphates.

The actual number of gold particles and other minerals in the fluid inclusions is unclear as an unknown number would have been lost when the inclusions were opened during polishing. At greater magnification (Fig. 5) the BSE image of part of the inner surface of the inclusions in figure 4 shows numerous sub-micron gold particles, some as small as 100 nm can be observed in the BSE image. These are attached to the surface of semi-crystalline calcite that coats the inner surface of the fluid inclusions.

5 LA-ICP-MS analyses

The reproducibility of analyses for Au and Ag is well over 100% due to these elements being present as particles in the fluid inclusions and not dissolved in solution. The particulate signal for Au and Ag can be seen from the ablation signal where Au and Ag are seen as spikes, contrasting with the smooth asymmetric signal for Na and K that are present in solution. Part of the variability in concentration is due to the inevitability that the sequential measurement of isotopes, using quadrupole mass spectrometers, will result in an unknown number of particles passing through the ICP-MS without being measured, hence the reduction in the precision of the analyses and concentrations that are too low. In addition, if the particles were precipitated before entrapment, the number trapped in the fluid inclusions will vary immensely between different fluid inclusions.

The range in Au and Ag analyses can be seen in Figure 6, where Ag-Au pairs are plotted and show that there is an almost 3 orders of magnitude range in values for Au and Ag. The concentrations are from ablation of single unopened fluid inclusions and are all in excess of the detection limits shown for the analysis of Au and Ag in fluid inclusions. Using this data the average concentration for Ag is 32 ppm and Au 41 ppm, but as not all of the Au-Ag particles will have been detected by the ICP-MS we suggest the true concentration of Au and Ag in the fluid inclusions may be towards the higher end of values recorded, c. 100 ppm.

A number of LA-ICP-MS analysis were made on the quartz matrix, but the Au and Ag concentrations are well below 0.5 ppm, confirming all Au and Ag resides in the fluid inclusions. The lack of Au and Ag when ablating the quartz also shows there is no surface contamination affecting the analyses of Au-Ag despite some fluid inclusions being close to the surface.
6 Discussion

The suggestion that gold can be transported as colloids has been proposed for some time (Herrington and Wilkinson 1993; Saunders 1990, 2012) as a means of transporting gold at elevated concentrations greater than is possible in solution. Although there are other constraints on forming giant epithermal gold deposits (Richards 2013) “bonanza” grades (Saunders and Schoenley 1995; Saunders 2012) are often associated with the observation of colloidal gold in the ore veins. Direct evidence of gold colloids in hydrothermal fluids, was first reported by Gartman et al. (2018) in the boiled black smoker fluids from the Lau Basin. Our observation of sub-micron gold particles being carried in a mineralizing fluid, and trapped in fluid inclusions, is consistent with this process.

The concentrations determined here (average Au 41ppm, Ag 32 ppm) are substantially above any reported analyses, or of any theoretical concentrations (Gammons and Williams-Jones 1997; Hurtig and Williams-Jones 2015). However, experimental results of liquid vapour partitioning (Zajacz et al. 2017) at closer to magmatic temperatures show the vapor phase can attain concentrations of a few 10’s ppm Au but still below the values determined in this study.

It is clear that the Au-Ag particles did not precipitate from the fluid once it was trapped as fluid inclusions. The heterogeneity of the LA-ICP-MS analyses and the high concentration of Au and Ag, which can exceed the concentrations of the alkali and alkaline earth elements that are normally most dominant in hydrothermal fluids, is not feasible. Instead we propose that the particulates trapped in the inclusions are the consequence of fluid boiling elsewhere in the mineralizing system and have been accidentally trapped. The fluids and solids were trapped between rapidly growing fibrous quartz, which would create structures similar to fluid-filled tubes, during periods when the fluid was supersaturated with respect to quartz. As pulses of hot low salinity fluid and/or vapor ascended from deeper in the mineralizing system, it cooled due to adiabatic expansion, which led to a decrease in silica solubility as well as that of the metals in solution. Reduction in pressure leading to boiling is also likely to have been a major factor in precipitating different minerals. The calcite coating of the inner walls of the inclusions together with the precipitation of sulphates and sulfides is reminiscent of the associations observed in vein systems with large boiling zones. In the quartz crystals studied, the fluid inclusions provide evidence of pressure transitions from near lithostatic to near hydrostatic conditions, and the presence of flashed fluids (fluids which on rapid pressure drop instantaneously convert to low density vapour) indicates, that there were occasionally periods of transient sub-hydrostatic pressures. Fluids were boiling during these pressure fluctuations and cooled to lower temperatures which is likely to be the reason for the precipitation of the more massive sulfide ores in other parts of the vein systems.

Numerous examples of base-metal and Au, or Au
dominated deposits are present in the Biga Peninsula of NW Turkey, and the fluid inclusion characteristics of those Au-deposits are similar to the low salinity fluids in this study. Other deposits that are base-metals resources, contain fluid inclusions with higher salinities, but also with the same low salinity fluid as in Arapucandere. The previous interpretation that this low salinity fluid had a meteoric origin is clearly incorrect as we have shown. This is most likely a condensed low density vapour or low salinity fluid which separated from more saline magmatic fluids at depth expanding to cooler shallower levels. The presence of particulate gold at high concentrations in these fluids shows their importance in the mineralizing process as they appear to be the main transporter of gold.

Thus, whilst the Arapucandere deposit is a minor one, the direct observation and transportation of Au and Ag in particulate form, and the high concentrations possible, is a significant result with implications for porphyry and epithermal mineralization.

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References

Thermal peak detected in gold-bearing shear zones by a thermo-structural study: a new tool to retrieve fluid flow?

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Abstract. Gold mineralization in the northern part of the Canigou massif (Eastern Pyrenees, France) are localized along regional-scale shear zones. These structures connect the upper metapelitic greenschist facies unit (suprastructure) to the lower migmatitic unit (infrastructure) and are attributed to the late-Variscan tectonic evolution transposing earlier structures. Raman spectroscopy of carbonaceous materials (RSCM) approach documents thermal anomalies in these shear zones with a temperature peak [20 – 100 °C] above the host rocks values. These thermal anomalies are interpreted as recording the upward circulation of a hot fluids. These data point to gold mobilization and transfer controlled by localized deformation and fluid flow at the end of the Variscan orogeny. The nature and origin of the mineralizing fluids, the source(s) of gold, and the mechanisms of ore mobilization-transfer-deposition remain to be determined.

1 Introduction

Fluid flow is known to modify mechanical (Sibson 1992) and thermodynamic features of the crust (Ague 2014). Chemical mass transfer and heat transfer are associated with fluid circulation (Yardley 2005). However, the regional thermal influence of fluid flow remains difficult to retrieve (Ague 2014).

Gold deposits are good evidence of crustal fluid flow. They can provide insights into crustal evolution processes, such as fluid evolution or mass transfer (Philips and Powell 2009). The orogenic gold model implies that metamorphic fluids from the lower crust move upward through trans-crustal shear zones and form gold deposits in the middle and upper crust (Groves et al. 1998; Goldfarb and Groves 2015). However, lower crust levels, where fluids and metal could come from, are rarely exhumed near gold deposits, so their source is difficult to retrieve (Thomkins 2013).

In orogens, metamorphic domes are structures where both upper and lower parts of the crust are exhumed (Whitney et al. 2004). Therefore, they are good targets to retrieve the origin and pathways of former mineralized fluids. Thus, we focused our study on the Canigou dome, in the Axial Zone of the Eastern Pyrenees (France), a late-Variscan metamorphic dome, where the lower levels of the crust are exhumed (Gibson and Bickle 1994; Barbey et al. 2001; Aguilar et al. 2015).

Gold mineralizations have been described in the upper crustal levels of this dome (Blès and Costargent 1985; Polizzi 1990).

2 Geological settings of the Canigou massif

The Canigou massif is located in the Axial Zone of the Pyrenees, where the Variscan basement is exposed. The area consists of a metamorphic dome cored by migmatites designated as the infrastructure with a foliation delineating the shape of the dome. The dome is surrounded by Ediacarian-Cambrian metasediments dominated by metapelites designated as the suprastructure, marked by folding of an S0–S1 foliation into upright F3 folds associated with the development of a subvertical axial planar S3 schistosity. The contact between suprastructure and infrastructure is marked by a zone of transposition interpreted to represent strain partitioning along an attachment zone (Cochelin et al. 2017) (Fig. 1).

In the suprastructure, many gold veins have been described (Blès and Costargent 1985; Polizzi 1990). They are localized along vertical retrogressive mylonite zones (Baillestavy) and reverse faults zones (Glorianes), attributed to the last Variscan deformation stages (Blès and Costargent 1985; Polizzi 1990). The
gold veins are mainly filled with siderite, quartz and arsenopyrite. Native gold (electrum) is present in arsenopyrite-filled fractures (Polizzi 1990).

3 Structural position of gold deposits

3.1 Shear zones and migmatites of the infrastructure

The infrastructure is principally made of metapelites and orthogneiss intruded by the Canigou leucogranite, made of coarse-grained quartz-feldspars-muscovite. The presence of leucosome concordant to the syn-migmatitic foliation in textural continuity with discordant leucosomes localized along W-E trending subvertical shear zones indicates that partial melting and melt segregation were coeval with deformation (Fig. 2b). Moreover, the localization of leucogranite dykes and major quartz veins together with solid-state mylonitic deformation of the Canigou leucogranite along these shear zones suggests that magma emplacement and differentiation occurred during this deformation event (Fig. 2a).

3.2 Shear zones and gold ore-bodies of the suprastructure

Near the NE edge of the Canigou dome, the Baillestavy NW-SE trending dextral shear zone crosscuts the amphibolite facies meta-pelites and carbonates and affects the attachment zone.

Many small ductile to brittle-ductile shear zones are also present in the suprastructure. They crosscut the $S_0$, $S_1$ and $S_2$ foliations and they are syn- to post-$S_3$. Like vertical shear zones of the infrastructure, the shear zones of the suprastructure have a W-E orientation and are mainly filled by quartz veins. The brittle-ductile shear zones are particularly concentrated in the Glorianes-Serrabona area that we designate as the Glorianes-Serrabona shear bands.

Figure 2. a. Vertical quartz vein and leucogranite dyke along vertical shear zones on the Canigou summit. b. Aplitic leucogranite dyke and migmatite collecting zone along vertical shear zone.

Figure 3. a. Vertical quartz-arsenopyrite vein (red) along the $S_3$ main foliation (white), in Glorianes gold deposit. b. Quartz microstructures in vertical quartz-arsenopyrite auriferous vein showing grain-size reduction (GSR) and flattened old grains (FOG); in red, contact between strongly deformed vein and weakly deformed vein.
Gold ore-bodies of the suprastructure are located along the Baillestavy shear zone and the Glorianes-Serrabona shear bands. They consist of siderite-quartz-arsenopyrite vertical veins (Fig. 3a). Microstructures of quartz show an abundant dynamic recrystallization by dislocation creep with strong grain-size reduction (GSR) and flattened old grains (FOG) (Fig. 3b). These microstructures show that the quartz deformed under ductile conditions \((T > 400 \, ^\circ C)\) (Passchier and Trouw 2005). Moreover, microstructural textures show that, at least two quartz filling events occurred in the vein. Indeed, the second deformed quartz vein crosscuts the first deformed quartz vein (Fig. 3b). It suggests that fluid flow was active during the shear strain.

4 Regional thermal gradient

The regional thermal gradient has been determined by the Raman spectroscopy on carbonaceous material (RSCM) method (Beyssac et al. 2002). This geothermometer is based on the structural organization of carbonaceous material. It provides the maximum temperature reached by the rock. Previously obtained RSCM temperatures for the Axial Zone of the Pyrenees are considered to record the Variscan thermal peak (Cochelin et al. 2018). Measurements have been carried out on metapelite samples from the suprastructure and the infrastructure.

The thermal profile from the migmatitic dome core \((ca. \, 620 \pm 20 \, ^\circ C)\) and the external parts of the suprastructure \((ca. \, 380 \pm 20 \, ^\circ C)\) shows a regular decreasing gradient of \(ca. 30 \, ^\circ C/km\) (Fig. 4a, b). However, two thermal anomalies are present along the Baillestavy and the Glorianes-Serrabona shear bands (Fig. 4b, c). The temperature value strongly increases along these structures. It is comprised between \(550 \pm 37 \, ^\circ C\) and \(575 \pm 21 \, ^\circ C\) in the Baillestavy shear zone and between \(464 \pm 18 \, ^\circ C\) and \(521 \pm 41 \, ^\circ C\) in the Glorianes-Serrabona shear bands. They contrast with the thermal peak recorded in the surrounding rocks, where temperature reach \([476 \pm 21 \, ^\circ C - 532 \pm 38 \, ^\circ C]\) and \([413 \pm 12 \, ^\circ C - 448 \pm 15 \, ^\circ C]\), respectively (Fig. 4a, b). Notably, \(\Delta T\) interval is very similar in both Baillestavy and Glorianes-Serrabona shear zones: \([20 - 100 \, ^\circ C]\).

5 Discussion and conclusion

Temperature values obtained by RSCM approach on metapelites are consistent with petrological observations of LP-HT paragenesis. The temperature peaks identified could reflect local exhumation accommodated by conjugate faults. However, such faults have not been identified in the field. According to recent studies, shear heating may also be invoked to explain thermal anomalies identified by RSCM approach (Souche et al. 2013; Fauconnier et al. 2014). However, this process might be only valid for major crustal shear zones or supradetachments (Duprat-Oualid, pers. comm. 2018). Another possible source for anomalously high temperatures at depth may be represented by exothermic reactions during chloritization of biotite, but it seems difficult to generate temperature anomalies reaching tens of degrees Celsius. As an alternative, we thus propose that the Baillestavy and Glorianes-Serrabona thermal anomalies reflect localized heating caused by circulation of a hot fluid in the shear zones. This interpretation is consistent with quartz microstructures in the mineralized veins, which show a deformation under ductile regime during fluid circulation.

Such fluids could originate from different sources that are not mutually exclusive. Indeed, they could represent meteoric fluids penetrating the upper crust down to the brittle-ductile transition, where they were heated before migrating upwards, as typically identified in metamorphic core complexes (Morrison and Anderson 1998; Siebenaller et al. 2013). The fluids could also be generated by dehydration metamorphic reactions as proposed for mineralizations in the Vall de Ribes district, on the south flank of the Canigou dome, where fluid inclusions revealed an \(H_2O-NaCl\) chemistry and trapping conditions under \(350-400\, ^\circ C\) and \(2\, kbar\) (Ayora et al. 1992). In that case, upwelling fluids probably incorporated gold from disseminated sulphides of the meta-sedimentary pile. Such auriferous disseminated sulphides have been observed in the Vall de Ribes district as well (Ayora and Casas 1986). Moreover, this
model involves a preexisting gold metal stock in metapelites and carbonates (Gaboury 2013), as proposed for the nearby Salsigne gold deposit (Montagne Noire, France) (Courjault-Radé et al. 2001). At last, the mineralizing fluids might originate from crystallization of the migmatites and granites forming the core of the Canigou dome. Constraining the origin of the mineralizing fluids requires fluid inclusion analyses.

In conclusion, our study shows that gold deposits of the Canigou massif formed during the late tectonic evolution of the Variscan orogenesis. Upward gold-forming fluid flow used vertical shear zones, which crosscut both the infrastructure and the suprastructure, as pathways. According to our structural model, the crustal thickness between gold deposits and migmatites is ca. 5 km. This contrasts with the transcrustal fault system controlling fluid flow and gold mobilization-transfer-deposition invoked in the orogenic gold model proposed by Groves et al. (1998).

By combining structural observations and RSCM data, we were able to detect the thermal signature of fluid flow along structures which were difficult to retrieve by a classical petro-structural study. Using this thermo-structural approach at a regional scale could be a useful tool for detection of ore deposits in faults and shear zones and to a better understanding of former fluid flow in the orogenic crust. It could also be a useful tool to identify areas with potential ore deposits for exploration.

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REE geochemistry of the sulfides and native gold of the Olympiada deposit (Russia, Siberia)

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Abstract. The paper provides data for a study of REE distribution in sulfides and native gold of the Olympiada deposit (Russia, Siberia), the largest gold producer in Russia. Pyrite, pyrrhotite, arsenopyrite, and native gold are characterized by similar patterns of distribution of lanthanides, which are close to host rock REE patterns. For antimony minerals, a different type of distribution of rare earth elements is established, with a spectrum exhibiting enrichment in some MREEs. It is assumed that gold-sulfur-arsenic mineralization is formed with involvement of the upper crust, while the formation of antimony involved mantle fluids.

1 Introduction

Due to the development of high-accuracy precision analytical methods (ICP-MS, LA-ICP-MS, SIMS, etc.), great attention is paid to the study of trace-elements in mineral deposits and their host rocks. Data for the distribution of trace elements as well as precious metals allow us to obtain information on the source of metals substance, and forms a finding of ore components in minerals and ore-forming processes in general (Goryachev et al. 2008; Guangzhou et al. 2009; Nekrasova et al. 2010; Kun et al. 2014; Volkov et al. 2016; Silyanov et al. 2018).

In this paper, we provide information on the distribution of REE in ore minerals and native gold of the Olympiada deposit, one of the largest Au deposits in Russia.

2 Geological Characteristics of Deposit

The Olympiada Au deposit is located within the Yenisei Ridge (Russia, Siberia), a 200-km-wide Neoproterozoic accretionary-collisional orogeny, extending for 700 km along the western margin of the Siberian craton. The deposit is confined to the silicate and carbonate band of the Lower Riphean Kordinskaya suite. Granitoids are distributed at 1.5 km and above from the deposit. Introduction of intrusions in the Tatar-Ishimbinskaya tectonic zone assisted in the formation of compensation synformal depressions (Innokentyevskaya and Chirimbinskaya synclines) in the contact zones of intrusions united by the antiformal rock unit (Medvezhinskaya anticline). These connected W-shaped structural elements represent the structure of the ore field. Subhorizontal shifts in the area shaped the magmatogene structure into a tectonic syncline and anticline folds.

The ore bodies are concentrated in fold hinges and parasitic folds along limbs. The micaceous-quartz-carbonate matrix of the sulfide-disseminated ores has been boudinaged, mylonite-altered and folded into minor folds up to goffering Ore minerals (main minerals – arsenopyrite, pyrite, pyrrhotite, stibnite, and native gold) form disseminations and veinlets in the host rocks.

The ores are divided into gold-arsenic and gold-arsenic-antimony ores separated spatially and temporally. The industrial ores of gold-arsenic composition have an age (Ar-Ar) of 803–758 Ma, and the gold-arsenic-antimony ores dated (Ar-Ar) at 795–660 Ma (Sazonov et al. 2019; Gibsher et al. 2019).

3 Samples and Methods

Specimens of sulfide minerals (arsenopyrite – Apy, pyrrhotite – Po, pyrite – Py and stibnite – Stb) and native gold (Au) were collected from small technological and drill samples from the Eastern section of the Olympiada deposit. The process of sample preparation is described by Silyanov et al. (2018).

Trace elements analyses were carried out using an Agilent 7500cx ICP-MS (Agilent Technologies). Before analysis, using the incremental decomposition technique the weighted sulfide probes were digested using AquaRegia. The quality of the measurements was monitored using BCR-2, BHWO, SSL-1 and other standards. The analyses were performed in Analytic Center for Natural Systems Geochemistry, Tomsk State University, Tomsk, (analysts E.V. Rabtsevich and E.I. Nikitina).

4 Results

Maximum REE concentrations were exhibited for arsenopyrite (37.04 ppm) and stibnite (41.15 ppm); pyrite, pyrrhotite and native gold have low ΣREE: 7.93, 2.72 and 1.64 ppm, respectively (Table 1). Specimens are characterized by LREE enrichment (83-99%) and a slight predominance of HREE relative to MREE (~8% vs. ~3%). In the group of LREE, La and Ce dominate. For arsenopyrite, pyrite, pyrrhotite and native gold, La prevails over Ce, while stibnite shows a reverse tendency.

Chondrite-normalized (McDonough and Sun 1995) REE profiles for sulfides and native gold are characterized by LREE-enrichment...
LaN/YbN (0.6-1.3), LaN/SmN (0.9-1.8), and GdN/YbN (0.6-1.3) approaches values of 1. Stibnite is characterized by a distinctly different chondrite-normalized REE pattern due to the predominance of Gd, Tb and Dy (Fig.1). The sample is also characterized by elevated concentrations of La, Ce and Pr.

Table 1. Content of REE (ppm) and indicator ratios in the studied samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Stb</th>
<th>Apy</th>
<th>Po</th>
<th>Py</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>38.817</td>
<td>8.100</td>
<td>0.551</td>
<td>2.006</td>
<td>0.445</td>
</tr>
<tr>
<td>Ce</td>
<td>1.775</td>
<td>17.604</td>
<td>1.308</td>
<td>3.100</td>
<td>0.758</td>
</tr>
<tr>
<td>Pr</td>
<td>0.085</td>
<td>1.527</td>
<td>0.100</td>
<td>0.297</td>
<td>0.060</td>
</tr>
<tr>
<td>Nd</td>
<td>0.067</td>
<td>5.333</td>
<td>0.357</td>
<td>1.161</td>
<td>0.196</td>
</tr>
<tr>
<td>Sm</td>
<td>0.015</td>
<td>1.118</td>
<td>0.092</td>
<td>0.260</td>
<td>0.037</td>
</tr>
<tr>
<td>Eu</td>
<td>0.005</td>
<td>0.191</td>
<td>0.015</td>
<td>0.055</td>
<td>0.010</td>
</tr>
<tr>
<td>Gd</td>
<td>0.062</td>
<td>1.039</td>
<td>0.086</td>
<td>0.264</td>
<td>0.035</td>
</tr>
<tr>
<td>Tb</td>
<td>0.016</td>
<td>0.156</td>
<td>0.013</td>
<td>0.043</td>
<td>0.006</td>
</tr>
<tr>
<td>Dy</td>
<td>0.275</td>
<td>0.920</td>
<td>0.078</td>
<td>0.276</td>
<td>0.040</td>
</tr>
<tr>
<td>Ho</td>
<td>0.003</td>
<td>0.173</td>
<td>0.016</td>
<td>0.060</td>
<td>0.008</td>
</tr>
<tr>
<td>Er</td>
<td>0.012</td>
<td>0.431</td>
<td>0.048</td>
<td>0.173</td>
<td>0.022</td>
</tr>
<tr>
<td>Tm</td>
<td>0.002</td>
<td>0.058</td>
<td>0.007</td>
<td>0.027</td>
<td>0.003</td>
</tr>
<tr>
<td>Yb</td>
<td>0.011</td>
<td>0.339</td>
<td>0.040</td>
<td>0.183</td>
<td>0.018</td>
</tr>
<tr>
<td>Lu</td>
<td>0.003</td>
<td>0.048</td>
<td>0.006</td>
<td>0.028</td>
<td>0.003</td>
</tr>
<tr>
<td>ΣREE</td>
<td>41.15</td>
<td>37.04</td>
<td>2.72</td>
<td>7.93</td>
<td>1.64</td>
</tr>
<tr>
<td>ΣLREE</td>
<td>40.74</td>
<td>32.56</td>
<td>2.32</td>
<td>6.36</td>
<td>1.46</td>
</tr>
<tr>
<td>ΣMREE</td>
<td>0.25</td>
<td>1.31</td>
<td>0.11</td>
<td>0.31</td>
<td>0.05</td>
</tr>
<tr>
<td>ΣHREE</td>
<td>0.39</td>
<td>3.16</td>
<td>0.29</td>
<td>1.05</td>
<td>0.14</td>
</tr>
<tr>
<td>ΣLH</td>
<td>105.75</td>
<td>10.29</td>
<td>7.90</td>
<td>6.24</td>
<td>10.72</td>
</tr>
<tr>
<td>Eu/Eu*</td>
<td>0.48</td>
<td>0.54</td>
<td>0.52</td>
<td>0.64</td>
<td>0.82</td>
</tr>
<tr>
<td>Ce/Ce*</td>
<td>0.24</td>
<td>1.21</td>
<td>1.35</td>
<td>0.97</td>
<td>1.12</td>
</tr>
<tr>
<td>Tm/Tm*</td>
<td>1.32</td>
<td>0.98</td>
<td>1.00</td>
<td>0.98</td>
<td>1.08</td>
</tr>
<tr>
<td>TE3</td>
<td>7.09</td>
<td>0.02</td>
<td>0.05</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>TE4</td>
<td>0.24</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>Sm/Nd</td>
<td>0.22</td>
<td>0.21</td>
<td>0.26</td>
<td>0.22</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Note: Stb – stibnite, Apy – arsenopyrite, Po – pyrrhotite, Py – pyrite, Au – gold; Eu/Eu* = Euν/√(Sm*,Gd); Ce/Ce* = Ceν/(La*,Prν); Tm/Tm* = Tmν/√(Erν,Ybν);
Calculation of the tetrahedral effect of REE fractioning (TE3, TE4) performed using the formulas borrowed from (Monecke et al. 2002).

For regionally metamorphosed rocks of the Kordinskaya suite (RF1kd), not affected by hydrothermal processes, all minerals considered are significantly depleted in REE (Kordinskaya suite rock composition borrowed from the work Likhanov et al. (2006), average for two specimens E-8 and E-10). The shape of the REE profiles for Apy, Po, Py, and Au are similar to the host rocks, as evidenced by substrate-normalized values of Lan/Nbν (0.6-1.3), Lan/Smν (0.9-1.8), and Gdν/Ybν (0.6-1.3) approaching values of 1.

All analyses of sulfides and gold are characterized by negative Eu-anomalies (0.52-0.82) and slightly to moderate (or unremarkable for Py = 0.97) positive Ce-anomalies (1.12-1.35) (Table 1, Fig. 1). Stibnite exhibits negative Eu- and Ce-anomalies – 0.48 and 0.24, respectively.

Sm/Nd ratios range from 0.19 to 0.26 (Table 1). For pyrite, this ratio is close to the lower crust (LC=0.25), and for gold to the upper crust (UC=0.17), the Sm/Nd ratio of the host rocks are also close to the upper crust (RF1kd=0.18). Other specimens are characterized by intermediate values of Sm/Nd ratio (0.21-0.22).

Stibnite is characterized by the presence of tetrad effect of REE fractionation (M-type) in the third (TE3=7.09) and fourth (TE4=0.24) tetrad, respectively (Table 1, Fig. 1). Fractionation of HREE in stibnite is confirmed by weak positive thulium (1.32), or negative Yb anomaly (0.69).

5 Discussion

It is thought that most of the REE in ore minerals is concentrated in fluid inclusions (Kun et al. 2014; Qiaoqin et al. 2006). Thus, the REE composition characterizes the ore-bearing fluid in equilibrium with this mineral, which allows the use of REE-characteristics in interpreting the source of fluid and its physicochemical parameters (Wang et al. 2016). However, this cannot exclude the possibility of isomorphous entry of lanthanides into the lattice of ore minerals (Qiaoqin et al. 2006), as well as the presence of REE-containing micro inclusions (Silyanov et al. 2018).

The similarity of the chondrite-normalized profiles for pyrite, pyrrhotite, arsenopyrite and native gold to signatures for the host rocks suggests an influence of the substrate on the ore-forming fluid, and an upper crust source of ore metals (Kun et al. 2014; Liu et al. 2015). This is also indicated by the Sm/Nd ratio in gold, pyrrhotite and arsenopyrite, which are close to upper crustal values. However, the high Sm/Nd ratio in pyrite does not exclude the participation of the lower crust in ore formation.

Stibnite is characterized by a different REE pattern, which, together with the geological setting of antimony mineralization in the deposit, suggests a different source. This source can be magmatic fluids, as indicated by the appearance of tetrad effects on REE fractionation in stibnite (Monecke et al. 2002).
It has been shown that scheelite, in association with antimony minerals, is characterized by the enrichment of MREE relative to other lanthanides. The authors suggest the participation of two fluid sources during ore formation: an early fluid depleted in REE and a later enriched REE fluid.

An interesting feature is also the appearance of the thulium anomaly, which was noted for pyrrhotite in the Panimba deposit (Yenisei Ridge, Russia) (Silyanov et al. 2018). A similar anomaly was described by Nekrasova et al. (2010) for gold in deposits of the Yenisei-East-Sayan province.

It is assumed that the behavior of europium and cerium in the hydrothermal fluids is controlled by the redox potential of the environment. The combination of positive Ce-anomaly and negative Eu-anomaly, as confirmed by the studies of fluid inclusions in quartz and ore minerals (Naumov et al. 2019) in ore minerals, and He in fluid inclusions, imply that metals were derived from the host rocks and a significantly upper crust source.

At the same time, the late antimony mineralization was formed by a fluid of a different source, as evidenced by the sharply different shape of the chondrite-normalized spectrum for REE distribution in stibnite. Based on the presence of tetrad effects influencing REE fractionation, we assume that the mineral is formed with the participation of mantle fluids (Taylor and McClennen 1985; Monecke et al. 2002).

Our data on the polygenic nature of metal sources are confirmed previous studies of the isotopic composition of Pb (Savichev et al. 2006; Kryazhev 2017), Os (Naumov et al. 2015) and S (Kryazhev 2017; Gibsher et al. 2019) in ore minerals, and He in fluid inclusions in quartz and ore minerals (Naumov et al. 2015; Kryazhev 2017).

Analysis of the Eu- and Ce-anomalies indicates that the early gold-sulphide associations formed under reducing conditions; the formation of late antimony parageneses was accompanied by a change in the redox potential, as confirmed by the studies of fluid inclusions.

6 Conclusions

Our data show that sulfides and gold are characterized by REE patterns similar to those of their host rocks, implying that metals were derived from the host rocks and a significantly upper crust source.

Based on the present of tetrad effects influencing REE fractionation, we assume that the mineral is formed with the participation of mantle fluids (Taylor and McClennen 1985; Monecke et al. 2002).

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Ore-stage calcite veins in the Carlin-type Au-deposits of the Nadaleen trend, Yukon: a new addition to the economic geologist’s tool-kit.

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Abstract. Readily-identifiable, ultraviolet-fluorescent (UVF) calcite veins in the Carlin-type Au-deposits of the Nadaleen trend, Yukon, are linked to Au-mineralization by their spatial distribution, mineralogy, isotopic signature and chemistry. They offer exciting opportunities to study the evolution of Carlin-type ore fluids and can be used to aid exploration for these typically large, high-grade deposits. UVF veins cut fault fabrics associated with thrusting and folding, providing age constraints relative to deformation. U-Pb dating of UVF calcite provides a preliminary Eocene Au-mineralization age, which is long after any known regional magmatism, suggesting an amagmatic genesis. The orientation of UVF veins provide support for a vertically-focused ore fluid-flow regime that exploited pre-existing fold-fracture networks that parallel steeply-plunging fold hinges. UVF calcite likely formed as a product of decarbonatization of host limestones during the sulfidation reaction that deposited the Au.

1 Introduction

Carlin-type Au-deposits (CTGDs) are epigenetic carbonate-replacement deposits named after the large high-grade occurrences in northern Nevada (Cline et al. 2005). The host rocks to CTGDs are dominantly sedimentary carbonate rocks within exhumed, inverted basins (Cline et al. 2005). Decarbonatization (removal of carbonate) and subsequent silicification and argillization of carbonate host rocks are the most common alteration indicators, along with late ore-stage mineralization of realgar, orpiment and calcite, and associated geochemical enrichments in Sb, Hg, Tl and particularly As (Cline et al. 2005). Gold occurs as sub-micron domains within the rims of As-rich pyrite, and is thought to be deposited via sulfidation of an Fe-rich wall-rock by a fluid carrying Au as bi-sulfide complexes (Cline et al. 2005). Despite their economic significance, the genesis of CTGDs is still poorly understood (Muntean et al. 2011, Ilchik and Barton, 1997).

Calcite veins are generally considered unimportant in CTGDs as they do not host any Au. However, it has been previously suggested that some calcite veins may be genetically related to Au-mineralization based on the presence of realgar, C and O stable isotope signatures, and/or trace-element enrichment relative to background values (e.g. Hofstra and Cline, 2000; Vaughan et al. 2016). Difficulty in recognizing these veins has hindered attempts to assess their significance. Here we present evidence for ore-stage calcite veins that fluoresce under short-wave ultraviolet (UV) light from the Nadaleen trend CTGDs, Yukon, Canada. These UV-fluorescent (UVF) veins can be linked spatially, temporally and chemically to the Au-mineralizing event. They provide critical information on the timing of the Au-mineralizing event, the temperature of ore-fluids, salient ore-fluid controls and the physicochemical evolution of ore-fluids along the flow path. Critically, they are easy to identify in the field with a UV-lamp, allowing them to be used as an exploration tool.

2 UV-fluorescent ore-stage calcite veins

Ore-stage calcite veins fluoresce pink to orange under shortwave UV light (Fig. 1). UVF veins can exhibit homogenous, patchy, or concentrically zoned fluorescence (Fig. 1a), and frequently occur as veinlets within pre-existing non-fluorescent calcite veins (Fig. 1b). Both the density of calcite veining and calcite vein characteristics in visible light are invariant with distance from the ore-zone. Petrographically, UVF veins are indistinguishable from non-fluorescent calcite veins. They dominantly comprise blocky crystal and rarely exhibit crack-seal growth textures, such as syntaxial growth. UVF veins exhibit a bright red cathodoluminescence (CL) response, and concentric zoning is also distinguishable in CL responses.

Detailed core-logging through sixteen diamond drill-holes reveals the spatial distribution of UVF veins to be restricted to within a few metres of Au-mineralization or alteration. Therefore, UVF veins can be used as an indicator of spatial proximity to ore-stage hydrothermal fluid flow, and may be a useful vector towards ore zones. A temporal link to Au-mineralization is established through the presence of rare syntaxial coprecipitation of realgar with UVF calcite (Fig. 1c).

3 Vein chemistry

Interaction between ore-stage fluids and carbonate host-rocks in CTGD systems results in the isotopic alteration of the latter relative to rocks distal to hydrothermal activity (Barker et al. 2013). Hydrothermally altered rocks have anomalous δ¹³C and depleted δ¹⁸O signatures relative to background values (Barker et al. 2013). Figure 2 shows δ¹³C and δ¹⁸O values for calcite vein—wall-rock sample pairs drilled from two different host-limestones: the Conrad and Osiris limestones. UVF veins (shown in pink) have a δ¹³C...
signature between -1 and -4‰. In $\delta^{18}O$ space, UVF veins are generally depleted relative to the adjacent wall-rock. The wall-rock values lie within the non-mineralized background range of 17 to 24‰, determined from regional non-altered samples (Moynihan et al. 2019). These $\delta^{13}C$ and $\delta^{18}O$ values suggest limited isotopic exchange between UVF vein-forming fluids and wall-rock. Since UVF veins are depleted relative to the Conrad limestone and enriched relative to the Osiris limestone, the initial $\delta^{13}C$ composition of the fluid is constrained between -1 and -4‰.

UV- and cathodo-luminescence intensity is controlled by the concentrations of Mn (a luminescence activator) and Fe (a luminescence quencher; Rakovan and Waychunas, 1996). Non-altered host rocks and non-UVF veins have Mn and Fe concentrations of a few hundred ppm and several thousand ppm to over 1%, respectively. UVF veins are enriched in Mn by up to two orders of magnitude, with concentrations between 1000ppm and nearly 5%. Fe in UVF veins is significantly lower than non-altered wall-rock, with Fe concentrations generally <700ppm. This high Mn:Fe ratio causes the veins to fluoresce under UV light and to be cathodoluminescent. Collectively, the spatial distribution of UVF veins, their $\delta^{18}O$ and $\delta^{13}C$ signatures, their Fe and Mn chemistry and the co-precipitation of UVF calcite and realgar provide a robust genetic link to the ore-stage hydrothermal activity.

4 Timing, temperature and geological controls of ore-fluid flow

Cross-cutting relationships of UVF veins and fault fabrics indicate that Au-mineralization occurred post folding and thrusting. An Eocene U-Pb date for UVF vein calcite provides a preliminary age for hydrothermal fluid flow and mineralization along the Nadaleen trend of CTGDs. This age is consistent with apatite fission track (AFT) dates from the ore-zone interpreted to be thermal resetting temperatures since they are younger than regional cooling ages (Tucker, 2015; Hickey et al. 2014b). The temperature of vein-forming fluids can be determined from clumped isotope thermometry (CI). CI measures the “clumping” of heavy $^{18}O$ and $^{13}C$ bonds relative to predicted stochastic distribution. The difference is thermodynamically controlled and can be back-calculated to give a carbonate precipitation temperature (Huntington and Lechlar, 2015). We undertook a pilot CI study at Isolab at the University of Washington, USA, yielding a UVF calcite precipitation temperature of ~150°C determined using a modified calibration after Kluge et al. (2015) with Brand et al. (2010) parameters. AFT modelling indicates little post-Eocene exhumation, so C-O bond reordering through solid-state diffusion in UVF veins is unlikely (Stopler and Eiler, 2015). This 150°C temperature is lower than the 180-240°C main ore stage fluid temperatures determined in Nevada, but similar to fluid inclusion temperatures from late ore-stage calcite (Cline and Hofstra, 2000).
UVF veins are predominantly either bedding-normal or bedding-parallel. This is typical of a buckle-fold—fracture network in which initial Mode-I fracturing occurred along horizontal bedding-planes and layer-parallel extension during subsequent folding of thick carbonate layers created a bedding-normal fracture set (e.g., Cosgrove, 2015). However, the age of folding is Cretaceous, and UVF veins cut fault fabrics on faults that post-date folding. Therefore, we interpret that the ore-fluids exploited a pre-existing fold-fracture network. This is consistent with the distribution and style of visible alteration in drill-core, soil As anomalies and wall-rock δ¹⁸O and δ¹³C signatures, which all indicate that fracture-controlled fluid flow is the dominant flow regime, particularly in fold-hinges. The majority of UVF veins are steeply-oriented and the folds in which they form are steeply-plunging. Thus, the fluids mainly flowed up into the deposit through this steep fracture-network.

5 Genetic model for UVF vein formation

Mn in the vein-forming fluids is thought to have been derived from decarbonatization (dissolution) of host limestones by acidic ore-fluids. Micro X-ray fluorescence element maps show that Mn is depleted in decalcified zones, which is consistent with previous observations from the CTGDs in Nevada (Vaughan et al. 2016; Cail and Cline, 2001). Gold deposition accompanies decarbonatization via the sulfidation of Fe released from the dissolving carbonate. Decarbonatization, therefore, results in a Ca- and Mn-depleted, Au-enriched, carbonate dissolution zone (CDZ), and a discharging, Ca- and Mn-enriched, hydrothermal fluid (Fig. 3). The precipitation of UVF calcite outside the CDZ likely reflect some physicochemical change in the fluid, possibly CO₂ degassing. This change causes calcite to become insoluble and the ore fluid switches from dissolving calcite to precipitating calcite. Where this fluid flows pervasively through the carbonate host rock, it precipitates Mn-rich calcite as pseudomorphs of existing calcite to form the carbonate replacement zone (CRZ; Vaughan et al. 2016). Fluids that travel further outboard of the CRZ by exploiting pre-existing fracture networks deposit UVF calcite in veins.

UVF veins are largely representative of a fold-fracture network, yet formed long after folding (>30 Myr). This suggests that the majority of UVF calcite grew as pseudomorphs of existing calcite. The observation that the density of veining does not increase towards dissolution zones is additional evidence for the replacement of pre-existing veins rather than the formation of a new CTGD-related fracture network. However, the presence of concentric luminescent zoning and syntaxial co-growth of UVF calcite with realgar indicate that some primary UVF calcite growth did occur. We propose that a minor deformation event re-fractured existing veins owing to the rheological contrast between vein and wall-rock. The Mn-rich fluids used these small fractures to travel beyond the CRZ while pseudomorphing adjacent calcite crystals, and precipitated new crystals in any open fracture spaces.

6 Implications

Our preliminary Eocene age for Au-mineralization at Nadeleen is nearly 20 Myr after the last episode of magmatism in the Selwyn basin (Kingston et al. 2010), suggesting that gold is unlikely to be sourced directly from magmas, as has been previously suggested for the deposits in Nevada (Ressel and Henry, 2006; Muntean et al. 2011). The vertically-focused, fracture-controlled fluid-flow in the Nadeleen trend is also different to the CTGDs in Nevada, where lateral fluid flow through confined aquifers was dominant (Hickey et al. 2014a). These differences highlight that the structural framework prior to Au-mineralization is important for promoting fluid flow into a deposit, and that magmatism perhaps is not an essential component in CTGD genetic models.
**Figure 3.** Idealized physicochemical evolution of the Carlin ore-fluids at Nadaleen (after Vaughan et al., 2016). Changes in the relative Mn, Ca and Au content of both rock and fluid as a result of fluid:rock interaction are shown above. The dashed black line represents the boundary between calcite solubility and insolubility in the ore-fluids.

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Advances in 4D X-ray microtomography: new experimental tools for hydrothermal processes and materials

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Abstract. A novel suite of experimental environments have been developed to explore chemical and physical processes in-situ in experiments using 4D X-ray microtomography. These experimental environments are designed to enable investigation of fluid-rock reaction, fluid transport, coupled chemical, mechanical, thermal and hydraulic processes and the evolution of geological samples towards mechanical failure. Four dimensional data acquired in such experiments can provide novel insights into processes of importance to geological and engineering applications. Experimental access to the hydrothermal temperature range, along with the ability to chemically react and to deform samples means these cells are applicable to studies of materials and processes relevant to economic geology, mineralisation and mining.

1 Introduction

The application of non-destructive 3D imaging using X-ray microtomography (µCT) has made a significant impact across the Earth Sciences over the last decade or more. These applications have included studies of ore deposit geology and investigations of mineral processing (e.g. Godel 2013; Kyle and Ketcham, 2015). A particular virtue of µCT imaging is the ability to process the digital image data produced to obtain quantitative information about, inter alia, the distribution, size, shape and orientation of materials. The analysis of such data can be considered to be the equivalent of examining multiple 2D thin sections in a non-destructive way. Thus for sparsely distributed minerals, like gold, µCT analysis is advantageous in order to acquire a statistically representative sample of grains for analysis (Kyle and Ketcham 2003). Other recent ore-related applications of µCT have included the observation of the relationship between metasomatic reaction haloes and base metal or PGE-rich sulfides in mantle xenoliths (Hughes et al., 2016) and the optimization of preparation methods for chemical and isotopic analysis of metal sulfide inclusions in diamonds (McDonald et al., 2017).

While 3D analysis of materials can offer new insights not available from conventional 2D techniques, the most exciting and potentially transformative experimental applications of µCT techniques have come from 4D approaches. In 4D microtomography the 4th dimension indicates resolution in time or another progress variable for a reaction or physical change in a sample. Continuous X-ray imaging of progressive change means that a single 4D experiment can be the equivalent of 10s-100s of conventional batch experiments which are analysed post-mortem. While 4D experiments have found considerable application in the context of oil & gas and other reservoir-related studies (e.g. Al-Khulaifi et al., 2017; Andrew 2015) and in some fluid-rock reaction studies (e.g. Zhu et al., 2016; Bedford et al., 2017), there have been few studies which focus upon economic mineralization, although the method has been employed in some mineral process investigations (e.g. Dobson et al., 2017). In 4D experiments an experimental cell provides the pressure, temperature and chemical environment required to promote change in the sample. In part this paucity of studies relating to mineralisation reflects the lack of experimental environments that can operate within a µCT instrument, or a synchrotron beamline and which are capable of providing the conditions of elevated temperature, pressure and reactive fluid access typical of many ore forming environments.

Herein we describe a suite of new experimental environments designed and built at the School of Geosciences, University of Edinburgh which facilitate experiments at elevated temperature and pressure, with differential applied stress and with access for reactive fluids. We illustrate the capability of each cell with example data which have been produced through...
studies of fluid rock reaction, coupled processes and dynamic failure of rocks. Our purpose in presenting is to illustrate that tools for experimental studies of processes in-situ at elevated pressures and temperatures consistent with subsurface applications and mineralisation have become recently available and to explore, with the mineral deposit, mineral processing and mining engineering community, their potential to be used to obtain new insights to processes and materials of importance to economic geology using µCT methods.

2 Apparatus for 4D X-ray microtomography

The three experimental environments are shown in figure 1. Each environment has different capabilities and has built in modularity for flexibility of use in a range of studies. These experimental environments are designed and optimized for use with synchrotron light sources (Fusseis et al., 2014a) and each has been successfully employed during experimental campaigns the Advanced Photon Source (APS, Chicago, USA), the Diamond Light Source (DLS, Oxfordshire, UK), the Swiss Light Source (SLS, Villagen, Switzerland) and the Soleil synchrotron (Saint-Aubin, France).

2.1 Sleipnir – fluid flow and fluid-rock reaction at elevated P & T.

Sleipnir (Fusseis et al., 2014b & Fig. 1), was developed as a fluid-rock reaction cell and has been used for in-situ investigations of carbonate mineral formation during reactions of carbonate-rich fluids with olivine (Zhu et al., 2016), and for investigations of gypsum dehydration at elevated pressure and temperature (Bedford et al., 2017). In addition Sleipnir has been employed for highly time-resolved investigations of multiphase fluid infiltration in porous media (Yang et al., 2018).

Sleipnir can accommodate a 3 mm diameter cylindrical sample up to 20 mm in length, which is located between two static pistons and jacketed with a flexible silicone sleeve. The cell can operate to 230°C and 20 MPa confining pressure for reaction durations of 150 hours. Pressurised fluid can be introduced from either end of the sample. Thus the cell is able to access the lower range of temperatures and pressures associated with the formation and hydrothermal reprocessing of hydrothermal ores. The flexibility of the cell design allows each component of the cell to be replaced subject to the demands of fluid compatibility, or if enhanced x-ray transparency is required.

Experimental results produced by Zhu et al., (2016) using Sleipnir as a fluid-rock reaction cell are shown in Figure 2. In these experiments San Carlos olivine (Fo90) was reacted with a 1.5M bicarbonate solution at 200°C. The reaction product was magnesite. The use of µCT imaging enabled visualization of the volumetric change on magnesite formation and the way that expansion and microfracturing created fresh reactive surface to enable continued reaction progress. Moreover, analysis of crystal size from time resolved tomographic data demonstrates that this technique can provide both spatially distributed and bulk kinetic data for complex reactions in heterogeneous media. Rate data such as this cannot readily be obtained using conventional analytical methods.

2.2 Mjölnir – fluid–rock interaction at elevated T with triaxial stress.

Mjölnir (Butler et al., 2017 & Fig. 1) was designed as a triaxial deformation cell and adapted for multicomponent studies by the addition of fluid access via pistons and sample heating. This has enabled the cell to be used for studies of coupled thermal, hydraulic, chemical and mechanical processes involving geological media.

Mjölnir can accommodate a 3 mm diameter cylindrical sample up to 10mm long, which is located between two pistons and jacketed with a silicone sleeve. The upper piston is driven by a hydraulic actuator and can apply constant or increasing axial load to the sample. The cell is able to confine samples at up to 50 MPa, with applied axial loads of up to 700 MPa in order to perform triaxial rock tests coupled with high resolution imaging of pre- and post-failure processes. Sample temperatures up to 150°C can be attained.

Coupled process data acquired by using Mjölnir at beamline 2-BM of the Advanced Photon Source is shown in Figure 3. A 3mm diameter sample of gypsum was confined at 15 MPa and loaded to 40 MPa differential stress. The sample was heated to 115 °C.
Between 198 minutes and 204 minutes the sample failed along a shear plane, which created a conduit for fluid expulsion. The fluid conduit enabled water from dehydration of gypsum (CaSO₄·2H₂O) to basanite (CaSO₄·½H₂O) to be transported from the reaction site, facilitating the pervasive conversion of gypsum to basanite seen between 222 minutes and 270 minutes. Progressive healing of the initial shear plane was observed between 270 and 295 minutes. We note that the dehydration of gypsum to bassanite is itself an important industrial process as well as being a source of fluids during thin-skinned tectonic processes.

Figure 3. Time sequence of a mineral reaction (dehydration of gypsum to bassanite, coupled to increasing sample porosity) coupled to the shear failure of the sample and progressive healing of the failure plane (diagonal blue arrows). The red and yellow stars each mark the position of an equivalent point in the sample as the structure evolves.

2.3 Stór Mjölnir – triaxial deformation with acoustic monitoring.

Stór Mjölnir (Fig. 1) was built in 2018 and is a triaxial deformation cell, akin to a full-size rock deformation apparatus in which the principal stresses are configured as \( \sigma_1 > (\sigma_2 = \sigma_3) \). The sample size is a 10 mm diameter by 25 mm long cylinder, which can be confined at up to 50 MPa (\( \sigma_2, \sigma_3 \)) and axially loaded to 500 MPa (\( \sigma_1 \)). Pore fluid pressure can be applied at pressures <\( \sigma_2 \). The addition of a linear variable displacement transducer enables stroke control of the hydraulic actuator for experiments performed at a constant strain rate. Two acoustic transducers are located axially at either end of the sample in order to be able to measure i) p-wave velocity during deformation and ii) to acquire acoustic waveforms and event rates of seismic signals produced as a consequence of deformation.

Data from the triaxial deformation of Berea Sandstone are shown in Figure 4 for a sample confined at 15 MPa with 5 MPa pore fluid pressure and deformed at a strain rate of \( 10^{-3} \) s⁻¹. The AE event rate tracks progressive accumulation of stress induced damage with the sample and peaks at the point of failure (~1.25% axial strain) with continual damage generated during frictional sliding of the failure surface. The before and after slices cut vertically through the tomographic image of the core illustrate barreling of the sample and the locus of the shear failure. The time–resolved sequence of tomographic volumes acquired continuously during deformation can be analysed using digital volume correlation methods to establish the localized distribution of volumetric and shear strain as well as localized strain rates. Our aim is to develop improved micromechanical models for the localization of failure.

3 Summary and developments in progress.

The experimental environments described were not developed specifically for application to mineral deposit related research. Nevertheless the studies highlighted illustrate that a combination of fast x-ray synchrotron microtomography with new experimental technology is able to offer unique insights into deformation processes, fluid rock reaction and complex, coupled processes, all of which are relevant to industrial and ore minerals, mineral deposition and mining engineering.
At the present time, our equipment development is focused upon the extension of the operational range for our experimental environments towards 450 °C and 100 MPa, while maintaining capability for axial deformation and the introduction of reactive fluids. These temperature and pressure targets are not technically demanding for conventional experimental vessels, but are restrictive in the context of materials with low x-ray attenuation. These developments will access much of the hydrothermal pressure and temperature range, fully opening the potential for new experimental approaches to understanding hydrothermal mineralisation processes and the properties of geological materials critical to mining and mineral processing.

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References

Carbonatization of the Antimony line in the Murchison reenestone Belt (South Africa): geochemical investigations along two drill cores.

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Abstract. Alteration of the host rock is a common process during ore genesis. Penetrative carbonatization can be observed along the Antimony Line of the Murchison Greenstone Belt (South Africa). The alteration shows zonation from proximal strongly carbonatized and mineralized carbonate-quartz schist in the vicinity of Sb-Au mineralized zones to distal, slightly carbonatized talc-chlorite-quartz schists. It is assumed that the Sb-Au veins played a major role with respect to the formation of the alteration zones. First results show high contents of MgO and Sb in Sb-mineralized zones of the Antimony Line compared to adjacent sections. However, K2O and Al2O3 contents are relatively low. Due to exceptionally high MgO contents, the precursor rock of the alteration zones was presumably an ultramafic, komatiitic rock. Major variations in MgO and Al2O3 ratio within the Antimony Line likely indicate compositional variation in volcanic lava flows or sections of intense alteration in which Al is relatively immobile. Higher contents of K2O in the Antimony Line are likely due to a late-stage potassium metasomatism and gave rise to fuchsite mineralization.

1 Introduction

The antimony (-gold) vein deposit of the Antimony Line in the Murchison Greenstone Belt (MGB) was in the 1970’s the largest producing area of antimony in the world (Pearson & Viljoen 1986). In the vicinity of the deposit, the host rock was altered by intense carbonate alteration. Carbonatization is promoted by fluids with high partial pressure of CO2 (e.g. Fyon et al. 1984). In Archean greenstone belts, carbonatization is often accompanied by silicification due to seafloor alteration (e.g. Hofmann et al. 2017) and/or hypogene hydrothermal magmatic or mantle-derived metamorphic fluids.

With respect to the genesis of the Antimony Line and the related alteration zones, many models have been proposed. An early model of a sedimentary origin of the carbonates (Hall 1912; Mendelsohn 1938; van Eeden et al. 1939) was replaced with current theories of mineralization by epigenetic magmatic derived ore-forming fluids (Boese 1964; Kedda 1992), syngenetic volcanogenic exhalative fluids (Muff 1978) or syngenetic hot spring systems (Minnitt 1975), and syndeformational metamorphic derived fluids (Pearson 1980; Boocock 1984; Pearson & Viljoen 1986).

In the Antimony Line in the MGB, different textures and ore minerals were observed. After Muff (1978) they can be distinguished as stibnite (Sb2S3) ore, berthierite (FeSb2S4) ore, and iron sulphide rich ore. Muff & Saager (1979) described more than 40 ore minerals from the Antimony Line.

Close to mineralized veins the host rock commonly consists of mineralized cherty quartz-carbonate rocks. In more distal parts the rocks change to green fuchsite-quartz-carbonate schists, gray quartz-carbonate schists, talc-carbonate-quartz schists, talc-chlorite-quartz-carbonate schists, and chlorite-quartz-carbonate schists (Pearson 1980). However, due to shearing and multiple veining in the Antimony Line, this zonation is not well pronounced in most areas.

The aim in this project is to provide a reliable mass balance of altered/unaltered rock to establish a geochemical fluid modeling in order to characterize the mineralizing and altering fluid, which should combined with stable isotopic studies (e.g. Jaguin et al. 2014) and thermodynamically fluid modeling (Blauweibrook 2016) contribute to a holistic view of the fluid system.

This study provides an insight into the geochemical evolution of alteration zones along two drill cores, “Free State Mine drill core” (FS drill core) and “Weigel Shaft drill core” (WS drill core) of the Antimony Line and adjacent sequences. Preliminary analyses were carried out by a portable XRF. The examined rocks are strongly altered by carbonatization. However, different units could be distinguished with different geochemical and mineralogical features.

2 Geological setting

The Antimony Line is situated in the MGB in the northeastern part of South Africa. The MGB is divided into several tectonostratigraphic domains (Fig. 1).
These units were subjected to greenschist- to amphibolite-facies metamorphism (Vearncombe 1988) during the first deformation stage D1, which is considered to be the main deformational event in the MGB (Boocock 1984).

The central portion of the MGB is made of the 3.07 Ga old Weigel Formation, which hosts the Antimony Line. It consists of steeply N-NNW dipping metasediments and carbonatized mafic to ultramafic volcanic and subvolcanic rocks subjected to greenschist facies metamorphism (Vearncombe et al. 1992). Along a 50 km shear zone in the center of the Weigel Formation, the WSW-ENE oriented Antimony Line (Sb-Line) (Fig. 1) exposes several districts of Sb- and Au-enriched ore bodies in massive hydrothermal quartz-carbonate veins.

### 3 Portable XRF analyses of drill cores of the Antimony Line

XRF analyses were obtained from two drill cores that are representative of rocks of the Antimony Line and adjacent sequences. The obtained data show a geochemical trend of altered rocks and give indications for significant changes of whole rock geochemistry and the possible precursor rock.

The analyzed cores both comprise mineralized zones and characteristic alteration zones can be distinguished. Talc-chlorite-carbonate-quartz-fuchsite (talc-chl-carb-qtz-fuchs) bearing schists with different compositional and textural features were observed. They were defined as qtz-carb schist, talc-carb (-qtz) schist, talc-chl-qtz-carb schist, fuchs-qtz-carb schist, talc-chl schist and chl-qtz-carb schist with varying modal mineral proportions. MgO, Al₂O₃, K₂O, and Sb were used to represent the significant changes in rock composition. Rocks of the Antimony Line are accompanied by strongly pronounced carbonatization and silicification as well as continuously detectable values of Sb (>38 ppm).

#### 3.1 XRF analyses of the Free State (FS) drill core

The FS drill core was drilled in the Free State mining area of the MGB (Fig. 1) and comprises a profile through the Antimony Line from N to S in this area. The majority of the rocks (Fig. 2) in the Free State drill core are representative for rocks of the Antimony Line. However, the chl-qtz-carb schists at the base of the drill core exhibit different geochemical features and likely represent a sheared sedimentary unit. The dotted line in figure 2 displays a major change in lithology which is accompanied by a decline of MgO and Sb contents as well as higher contents of Al₂O₃ and K₂O.
The Antimony Line, however, exhibits constantly high MgO values and relatively low Al₂O₃ values. Three analysis at 51 m, 73 m, and 97 m depth in the Antimony Line show slightly higher values of Al₂O₃ compared to MgO. These changes could indicate intraformational variations in lithology or degree of alteration. The K₂O contents are below detection in most of the core. From 100 m to 120 m depth K₂O is enriched. This enrichment is accompanied by a distinct Sb enrichment in the same depth. Sb was detected over the whole range of the Antimony Line up to 1000 ppm. Besides, several stibnite-enriched mineralization zones were observed in different sections of the drill core. These are not displayed in Fig. 2, as the main priority of this study is to explain the formation of the alteration zones.

3.2 XRF analyses of the Weigel Shaft (WS) drill core

The WS drill core was drilled in the Athens-Weigel mining area in the central part of the Antimony Line, approximately 3 km west of the Free State drill core (Fig. 1).

The drill core intersected a variety of schists (Fig. 3). The dotted line in figure 3 divides the rocks into two units. In the upper unit, which consists of qtz-carb (-chl) schist and talc-chl (-qtz) schist, Sb was barely detected. However, the carb-talc-qtz schist and talc-chl-carb-qtz schist in the lower unit are considered to be representative for the Antimony Line due to higher contents of Sb up to 1500 ppm. In the main mineralized zone from 128.5 m to 136 m Sb contents up to 8.83 % were detected (Unpublished data - Consolidated Murchison Ltd.). In the upper unit, the drill core exhibits higher Al₂O₃ values than MgO. After a 20 m transition zone from about 90 m to 110 m depth, where Al₂O₃ and MgO show similar values, the ratio changes in the Antimony Line to concentrations of higher MgO and lower Al₂O₃. K₂O contents are fairly high in the upper unit compared to the K₂O contents in the lower unit, where K₂O was barely detected. However, right below the contact of upper and lower unit in the Antimony Line, a small enrichment peak of K₂O was identified.

4 Discussion

High MgO and low Al₂O₃ contents were observed in the Antimony Line compared to non-Sb-bearing sections. After Pearton (1980) the rocks in the Antimony Line contain 20-36 % of MgO but only 4-6 % of Al₂O₃. This difference is evident in the displayed XRF analyses.

Because of high MgO contents, an ultramafic, komatiitic precursor rock is assumed, as previously proposed by several authors (Minnitt 1975; Pearton 1980; Pearton & Viljoen 1986). This assumption is supported by the occurrence of fuchsite indicating high contents of Cr and, therefore, an ultramafic precursor rock.

According to the map of Wilson & Viljoen (1986), the upper unit of the WS drill core should consist of chlorite-quartz schists and phyllites. This study, however, revealed that these sequences are fairly carbonatized and enriched in talc as well.

K₂O was not detected in broad sections of the Antimony Line. Close to the boundary of the sequences both drill cores show a small enrichment of K₂O and Sb which is accompanied by an enrichment of fuchsite in the FS drill core. According to Pearton (1980), a late-stage potassium alteration took place, whereby fuchsite was generated. This indicates that potassium was introduced into the Antimony Line by hydrothermal solutions and would, therefore, have only to a minor extent a primary origin in the host rock.

The variation in MgO and Al₂O₃ contents in three analysis of the FS drill core could indicate a heterogeneous composition of the ultramafic sequence. Komatiitic lava flows exhibit pronounced variation in chemical composition with regards to the position in the lava flow pile (e.g. Arndt 1986). The variation, therefore,
could represent compositional variation in the komatiitic lava flows. It is also possible that mafic to andesitic lava flows are interlayered with the komatiites. The portable XRF data show relative variations of some major and trace elements, but do not provide sufficient accuracy to classify the rocks. Another approach to explain the varying ratio of MgO and Al₂O₃ is intense alteration which led to an enrichment of immobile elements (Al) (MacLean and Kranidiotis 1987).

5 Outlook

The presented data are preliminary results of further quantitative XRF investigations as part of an MSc project. Samples of both drill cores will be analyzed by XRD, ICP-MS, and XRF to obtain reliable data for the zonation in the alteration assemblage. The compositional variation of trace and main elements from proximal to distal alteration zones should contribute to the understanding of the formation of the carbonate alteration in the MGB. Furthermore, petrographic analyses will be conducted in order to examine textural features of the alteration zones and to gather detailed information of mineralogy of the rocks.

Obtained data will be used to set up a mass balance of altered/unaltered rocks and fluid modeling of the mineralizing and altering fluid.

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Ore mineralogy, trace element distribution and 3D X-ray tomography of the polymetallic sulphide deposits at Mavres Petres and Piavitsa, Greece

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Abstract: The Mavres Petres mine, operated by Hellas Gold, and the Piavitsa prospect are both located along the Stratoni fault in the Kassandra mining district, northern Greece. These Tertiary deposits are brecciated, carbonate replacement Pb-Zn-Ag-(Au) mineralisations and the Piavitsa deposit is also associated with Au-rich epithermal veins. Both mineralisations were variably overprinted by later fluids as well as ductile and brittle deformation affecting ore mineralogy and trace element distribution. Galena is the main Ag-carrier, contains significant concentrations of Sb and Bi and is locally associated with a suite of Sb-As-Bi phases. Sphalerite is either massive or occurs as a later cockade-textured type. Both varieties are variably enriched in Mn and can exhibit elevated concentrations of In and Ga. In Piavitsa, alabandite is present as small euhedral crystals or in veins in fractured sphalerite. Pyrite is ubiquitous and is either present as disseminations, massive to skeletal aggregates or as a matrix in breccias. It is often arsenic-bearing and even more so towards the later stages. Arsenopyrite appears to be a late phase and occurs interstitial to pyrite and as euhedral crystals. While both arsenopyrite and arsenian pyrite can be enriched in Au, As-minerals are not necessarily associated with Au.

2 Geological setting

The mineral deposits in the Kassandra mining district in northern Greece are hosted by the Serbo-Macedonian and Rhodope terranes (Figs. 1 and 2). In this area mining activities date back thousands of years, and both exploration and production of base and precious metals are still on-going (e.g. Voudouris et al. 2017).

Figure 1. Simplified geological map of the Chaldiki area, northern Greece. The Mavres Petres and Piavitsa deposits are located along the Stratoni fault in the Kassandra mining district (modified after Melfos and Voudouris 2017 and Siron et al. 2018).

The Serbo-Macedonian and Rhodope terranes are continental fragments accreted to the Eurasian margin during the Hellenic orogeny (Pe-Piper and Piper 2006). In the Kassandra mining district (Fig. 2) the mineralisations occur in the Kerdilion and the Vertiskos units within the Serbo-Macedonian Terrane. The Kerdilion unit encompasses a Permo-Carboniferous magmatic arc and Paleotethyan carbonates that are juxtaposed with the Ordovician to Silurian gneisses and leucogranites of the Vertiskos unit (Siron et al. 2018). Accretion of this unit in the Late Cretaceous caused thrust faults and metamorphism that reached greenschist to amphibolite facies (Kydonakis et al. 2016). Amphibolite facies metamorphism in the Kerdilion unit occurred in middle Eocene, later to be overprinted by retrogression into greenschist facies.
Mineralisation in both the Vertiskos and the Kerdilion units occur in shear zones and faults and are associated with intrusions that are present along a NE trending corridor (Fig. 2). These intrusions were formed during two pulses of post-collisional magmatism in a back arc extensional setting in the Oligocene and Miocene, respectively (e.g. Siron et al. 2018). The shear zones and faults were either initiated or reactivated during extensional tectonics that commenced in the middle Eocene and continued into the Neogene. Many of the mineralisations are interpreted to be related to shear zones, detachment faults and subsequent magma intrusions (Voudouris et al. 2017). In the Kassandra mining district, the most important mineralisation types include Cu-Au porphyry deposits (Skouries, Fissoka, Tsikara), skarn and manto-type carbonate replacement mineralisations (Mavres Petres, Madem Lakkos, the Au-Ag-Pb-Zn Olympias deposit and the Piavitsa prospect, which is also associated with Au-rich veins).

### 2.2 Piavitsa

The Piavitsa prospect is located c. 5 km from Mavres Petres further to the west along the Stratoni Fault (Fig. 2). It is a siliceous-manganese carbonate replacement mineralisation associated with epithermal Au-rich veins (Siron et al. 2016) that was historically explored and mined from the surface for manganese. It has an estimated resource of 10.54 Mt at 57 g/t Ag and 5.7 g/t Au (Eldorado Gold Corporation 2018). Similar to the Mavres Petres deposit, it is largely controlled by the Stratoni Fault and massive sulphide mineralisation is located both within the fault as well as in the footwall, replacing the marble under the overlying hanging wall amphibolite. The mineralisation occurs mainly as brecciated, massive to semi-massive sulphide lenses affected by a later hydrothermal brecciation with clasts of altered marble and sulphide as well as epithermal quartz-kutnahorite/rhodochrosite-gold veins (Siron et al. 2016; Melfos and Voudouris 2017).

### 3 Mineralogy

The ore mineral assemblages at Mavres Petres and Piavitsa are being investigated by optical reflected light and electron microscopy, EDS and WDS X-ray spectroscopy, LA-ICP-MS and Geocore X10 drill core scanning developed by Orexplore in Kista, Sweden. The characterisation of the ore mineralogy will be used in further development of the GeoCore X10 in addition to assess the critical metal potential of these deposits.

The GeoCore 10X uses a novel technique by combining XRT and XRF measurements, together with automatic weight measurements to scan drill core with a diameter of up to 50.6 mm. The generated 3D-tomographical visualisations display the distribution of minerals with contrasting density in the cores with a resolution of down to 200 µm (Fig. 3). Using Orexplore software the tomography scan can be rotated in three directions whereby various textures and structures can be highlighted. The XRF measurements give concentrations for most elements heavier than S with a resolution of between 10 and 100 ppm.

### 3.1 Ore mineralogy, textures and trace element distribution at Mavres Petres

At Mavres Petres galena occurs together with sphalerite and pyrite and is mainly present as rather coarse-grained, locally highly strained aggregates. It is also observed as irregular inclusions in the former two variations between imbricated marble lenses (Siron et al. 2018), which resulted in a massive sulphide replacement mineralisation (Melfos and Voudouris 2017). This is dominated by galena and sphalerite with lesser amounts of pyrite and arsenopyrite. During a second stage the mineralisation was sheared and brecciated and overprinted by later fluids that led to, among others, pyrite disseminations. Pyrite also comprises the matrix to brecciated ore and gangue.
Ag-enriched (100-2000 ppm) and the Ag content appears to be higher in outer parts of unstrained crystals. When Bi is present it has a negative correlation with Sb, of which the latter may reach 2000 ppm. Selenium has only been detected in a few of the analysed galenas, featuring concentrations up to 3500 ppm. In some grains the Zn content is rather high (3.5 wt.%) accompanied by increased contents of Cd (up to 640 ppm).

There are at least two generations of sphalerite. The first generation is massive, coarse-grained and occurs together with massive galena and pyrite. These phases are also common as inclusions along with numerous micro-inclusions of chalcopyrite (“chalcopyrite disease”). This sphalerite generation is invariably brecciated and intermittently overgrown by a second generation of euhedral to subhedral crystals exhibiting cockade texture and oscillatory growth zoning (Fig. 4a).

The Fe concentration in both sphalerite generations ranges between 5 and 10 wt.%, they are Mn-bearing (6000-8000 ppm), have Cd contents of c. 3000 ppm and Ga concentrations typically around 20 ppm, reaching 75 ppm locally. Both generations are also variably enriched in In ranging from a few ppm up to 155 ppm even within the same grain.

Pyrite is either massive, present as small inclusions in sphalerite and galena or occurs as disseminated subhedral to euhedral crystals. The massive pyrite is typically less than 1 mm in grain size and occurs in the matrix of brecciated sphalerite and galena and the disseminated pyrite is up to several centimeters in size. Pyrites of both types are characteristically zoned and occur together with the less abundant arsenopyrite. The zoning reflects an increasing As content towards the margins of the grains (Fig. 4b). This As-zoned pyrite is locally overgrowing an earlier stage of As-poor pyrite.

It is also common that As-rich, platy-shaped pyrite is succeeded by free-growing, comb textured arsenopyrite.

In the disseminated pyrite, the increase in As covaries with Au, from a few ppm in the cores of the crystals, up to about 20 ppm Au in As-rich rims. However, early-formed slightly As-enriched pyrite appears to be barren in Au.

Arsenopyrite is a late phase that occurs interstitial between pyrite grains, projecting into open cavities, or as euhedral sub-millimeter sized crystals in the host-rock. Gold is heterogeneously distributed in it and in general ranges between 3 and 25 ppm although concentrations of up to 135 ppm Au have been measured. The Sb concentration is between 200-2000 ppm and there are traces of Co (2-15 ppm), Cu (2-40 ppm, Ag (2-35 ppm) and Te (2-18 ppm).

LA-ICP-MS analyses of both pyrite and arsenopyrite typically exhibit smooth down-hole profiles indicating that Au is lattice-bound in both these phases.

In a sphalerite-rich part of the ore, argentian tetrahedrite has been observed as inclusions in galena in addition to various Pb-Sb-Bi-Ag-(As) phases that likely represent solid solutions between galena-stibnite-matildite components (cf. George et al. 2015).
3.2 Ore mineralogy, textures and trace element distribution in the carbonate replacement ore at Piavitsa

The main ore mineral assemblage studied is represented by an assemblage of sphalerite, pyrite, arsenopyrite, galena and alabandite in a matrix dominated by carbonates. Isolated galena grains are corroded, often fractured and rimmed by reaction zones, potentially consisting of cerussite, towards the host carbonates (Fig. 6). Analysed grains have Ag contents of about 2000 ppm and inclusions of Pb-Sb-Ag-As-phases are common. The sphalerite is also corroded and typically contains fractures that are filled with carbonates. Micro-inclusions of chalcopyrite occur sporadically. Pyrite is sub- to euhedral and is often rich in inclusions of galena and sphalerite. Alabandite occurs mainly in the carbonate, often as small, euhedral to subhedral crystals (Fig. 6), and is also present in the sphalerite-hosted fractures. Arsenopyrite is mainly present in late veins, often together with pyrite and galena.

4 Summary

A combination of optical and electron microscopy, EDS and LA-ICP-MS analyses have been used to characterise the ore, and the host and distribution of important trace elements in the Mavres Petres and Piavitsa deposits. The results will be used to further improve the development of the GeoCore X10 technology and its application in mineral exploration.

The present observations show that sphalerite from the Mavres Petres deposit is variably enriched in In, hosted by two generations of sphalerite that are also modestly enriched in Ga. Galena is not only the main Ag-host but also carries Sb and Bi in locally considerable concentrations. These trace elements are heterogeneously distributed and exsolution of sulfosalts is rather common. Gold occurs lattice-bound in arsenopyrite and at the rims of compositionally zoned arsenian pyrite. Early formed pyrite appears to be Au-poor. Gold is always associated with As, but As is not necessarily associated with Au.

Galena and sphalerite in the carbonate replacement ore at Piavitsa prospect are corroded, which is likely to be a result of fluids that formed the later epithermal Au-enriched vein mineralisation. Disseminated, inclusion-rich pyrite and small euhedral alabandite post-date the main ore-forming stage.

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References


Diversity of Devonian Lahn-Dill-type iron ores from the Rhenish massif, Germany: evidence from petrography and geochemistry

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Abstract. Deposition of the Lahn-Dill-type iron ores took place during the Devonian in a marine environment with mineralisation being related to volcanic and volcaniclastic rocks.

Field work and petrographical studies reveal different depositional environments for Lahn-Dill-type iron ores that took place either in basinal sediments or reef carbonates. Also, modes of mineralization are diverse: Shrinking textures in jasper-like hematite assemblages indicate synsedimentary (or early diagenetic) formation, while replacement textures of carbonates by hematite in limestone are evidence for metasomatic mineralisation.

Geochemical analyses of Lahn-Dill-type iron ores yield a significant volcanogenic component (transition metals, HFSE, Eu anomaly) as well as a (Devonian) seawater REE+Y signature. Few differences between REE+Y of Lahn-Dill ores and youngest iron formation (e.g. Red sea, Neoproterozoic and Cambrian iron ores) is apparent regarding LREE depletion, anomalies in La, Eu and Y and lack of pronounced negative Ce anomaly.

1 Introduction

Stratiform mineralisation in submarine settings represents one of the most important sources for iron (Bekker et al. 2010). These iron ores are widely used as proxies for local to global marine depositional environments, despite the fact that deposits often experienced extensive tectonometamorphic overprint, hydrothermal alteration or weathering (Bekker et al. 2010, and references therein).

Stratiform iron ores of the Lahn-Dill-type sensu stricto are a peculiar deposit type: these ores are exclusively associated with Middle Devonian to Lower Carboniferous submarine basaltic volcanism (Quade 1968), without showing any link to massive sulfide occurrences. Ore layers can reach thicknesses up to several meters and lateral extensions of several hundreds of meters (Lippert and Flick 1998). Typically, siliceous or carbonate-rich, these oxide ores have variable iron grades which in places reach up to 60 wt.% Fe, arguably representing the most enriched iron accumulations in any sedimentary setting (Quade 1976).

In these ores, early (primary or diagenetic) textures are preserved related to a generally low metamorphic overprint reaching only lower greenschist facies (Massonne 1995). Thus, these rocks may provide the possibility to decipher modes of iron oxide (trans-) formation. Understanding these ores will yield insight into precipitation and diagenetic regimes with regard to the interplay of marine, volcanic, microbial and hydrothermal processes in the Devonian and Carboniferous marine basins.

Numerous genetic models for the Lahn-Dill-type iron ores have been proposed during the past 140 years, though, a systematic approach using advanced analytical methods does not exist currently.

Here, we present field, petrographical and geochemical data from hematite ores located within the Lahn-Dill area in western Germany.

2 Geological setting and stratigraphy

Lahn-Dill-type iron ores were deposited within the Rhenohercynian Ocean along the southern shelf of the Old Red Continent (Königshof et al. 2010). Footwall rocks consist of mafic volcanic and volcaniclastic rocks, geochemically corresponding with alkali basaltts (Nesbor et al. 1993). These mafic rocks are part of an extensive submarine volcanic event at the Middle to Upper Devonian boundary (Givet-Adorf phase), which occasionally reached sea level facilitating reef development (Nesbor et al. 1993). In basinal settings, clastic sediments were deposited on top of the volcanic and volcaniclastic rocks.

The orebodies are located at four different positions (Position I–IV) within the volcano-sedimentary sequence: (I) concordantly intercalated with Middle Devonian volcanic and volcaniclastic rocks (Lippert 1997); (II) at the top of the volcanic and volcaniclastic rocks with hanging wall rocks either being composed of reef carbonates or clastic sediments (Lippert 1997); (III) as layers within the Upper Devonian clastic sediments (Lippert 1997) or as resediment ores in local subbasins (Rösler 1962); (IV) in layers and lenses overlying tholeiitic volcanic rocks that were emplaced during a Lower Carboniferous volcanic phase (Hein 1998). Because Position II iron ore represents the main mineralisation regarding extent, grade and abundance, it will be the focus of this study.
3 Ore type classification

Field observations, optical microscopy, SEM and XRD analyses reveal that Lahn-Dill-type iron ores are mainly composed of hematite (locally magnetite) that forms assemblages with either quartz (siliceous iron ores "kieselige Roteisenzerze") or carbonates including calcite, siderite and ankerite (carbonic iron ores "Flusseisensteine"). Minor components are pyrite, Fe-Mg chlorite, greenalite and bitumen. According to Quade (1976) dolomite and stilpnomelane occur rarely.

3.1 Siliceous iron ores

Siliceous ores are subdivided into hematite- and jasper-rich ores. These subtypes differ with regard to occurring mineral assemblage and textures.

Jasper-rich ores show nano-scale hematite needles that form dense accumulations appearing as masses. These masses form schlieren and clasts. Nests of hematite blades are also present. Furthermore, a distinct hematite-quartz assemblage is present where nano-scale hematite occurs as homogeneously distributed needles within quartz. The hematite-quartz dispersions range in Fe from 5 to 45 % and form schlieren, spherulites and clasts. Another assemblage is jasper-like quartz with <5 % Fe forming clasts, veinlets and schlieren.

Hematite-rich ores consist dominantly of nano-scale hematite needles that form dense accumulations appearing as masses. Quartz is a minor component.

3.2 Carbonatic iron ores

Carbonatic iron ores are subdivided into carbonate/quartz- and hematite-rich ores. These subtypes differ not only in assemblage and texture, but also in temporal relationship.

Carbonate/quartz-rich ores show microscopic textures where hematite occurs as masses forming schlieren, as blades distributed homogenously across the sample, or locally as radial fibres. In this subtype quartz is present.

In contrast, hematite-rich ores are hosted within limestone, where the ore has replaced reef carbonates metasomatically. In these replacement ores, hematite is present as blades which can form masses, around calcite grains, fills cracks and fissures. Macro- (Fig. 1) and microfossils are completely or partly replaced by hematite.

4 Whole-rock geochemistry

We present unpublished whole rock and trace element analysis of 27 and REE analysis of 16 iron ore samples (by H.D. Nesbor and H. Quade; data from the 1990s). Thirteen samples are from selected exploration drill cores located in the eastern Dill-syncline, and 14 samples from the Fortuna mine (northern Lahn-syncline) representing a vertical profile of an ore layer (8 m thickness).

4.1 Major elements

Siliceous iron ores show Fe contents of 22 to 62 wt.%, and 1 to 31 wt.% Si. They show average Al content of 1.2 wt.% and 0.5 wt.% Mg, locally reaching up to 4 wt.% Al and 1.3 wt.% Mg implying the occurrence of chlorites from the chamosite-clinochlore series. Titanium averages 0.15 wt.%. Manganese shows an average of 0.7 wt.% as well as a positive correlation with Fe.

Carbonatic iron ores with more than 10 wt.% Ca and 3 – 13 wt.% Si show Fe contents varying from 20 to 39 wt.% Fe. Aluminum and Ti show higher average values than siliceous ores with 2 wt.% and 0.2 wt.%, respectively. Magnesium averages 0.4 wt.% and Mn 0.03 wt.%.

Iron and Ca show a distinct vertical variation within the Fortuna-profile. The Fe/Ca ratio decreases towards the top.

4.2 Trace elements

Lahn-Dill iron ores are rich in trace elements with respect to V, Cr, Ni and Zr compared with various chemical iron formations. Recent iron-rich sediments show a comparable trace element enrichment as the Lahn-Dill ores.

Lahn-Dill-type iron ores show V values that average 256 ppm. Chromium shows average values of 91 ppm, and Ni of 125 ppm which is in good agreement with average values of mined ores (Doutch 1977). Zirconium content can be as low as 7 ppm but reaches up to 240 ppm in samples. Strontium averages 81 ppm. Within Lahn-Dill ores a negative Si correlation with V, Ni, Zr and Sr is present. Iron shows positive correlations with Sr and Ba.
4.3 Rare earth elements

The Lahn-Dill samples reveal quite uniform REE fractionation patterns (Fig. 2A). They all show minor LREE depletion and rather flat HREE (PAAS-normalized). A number of samples have a positive La, Eu and Y anomaly, and in some samples a weak negative Ce anomaly may be present. Carbonatic and siliceous iron ore also show similar patterns.

REE appear to be largely tied to a detrital or volcanogenic component (positive correlation of $\sum$REE with Al, Ti, Zr). Additionally, a positive correlation with P is present evidence for a local relation of REE with apatite.

5 Discussion

5.1 Syn- versus epigenetic depositional environment

Deposition of the Lahn-Dill iron ores took place in an open marine setting with a large seafloor relief due to extensive volcanism (Nesbor et al. 1993). In environments where volcanic rises reached sea level and reef development was facilitated, carbonates overlying volcanic and volcaniclastic rocks (Königshof et al. 2010). Here, hematite mineralisation occurs heterogeneously within limestone and replacement of calcite by hematite took place indicating metasomatic processes.

Contrastingly, hematite mineralisation also occurs in basinal settings where clastic sediments represent the hanging wall (Lippert 1997). In these ores relative timing of hematite microtextures is ambiguous. Observed shrinking structures in jasper-like textures are indicative of sedimentary or early diagenetic formation. Thus, this hematite and quartz assemblage may have been precipitated from a syngenetic Fe- and Si-rich gel (Cissarz 1924). Furthermore, in hanging wall rocks younger resedimented ores occur and are composed of hematite-rich clasts providing evidence for syngenetic deposition as well.

In both mineralisation settings, however, well-crystallised hematite textures may be products of prograde ripening or fluid-aided redistribution during late diagenesis or very low-grade metamorphism.

5.2 Geochemical comparison with other submarine iron ores

Lahn-Dill-type iron ore are rich in trace elements, though showing slightly lower values compared to their footwall rocks (c.f. Doucht 1977).

Lahn-Dill ore samples all show similar REE+Y patterns (Fig. 2A) with fractionation resembling its footwall rocks (Fig. 2B) indicating a strong volcanogenic component. Hanging wall rocks show a HREE depletion not typical for a marine environment.

Positive Eu anomalies in ores are either related to high temperature hydrothermal fluids (Bau and Dulski 1999) or inherited from volcanogenic components.

Lahn-Dill ores show a comparable fractionation pattern with Devonian microbilites (LREE depletion, La- and Y anomalies) evidence for a seawater signature (Nothdurft et al. 2004). However, a small negative Ce anomaly within Lahn-Dill ores may indicate a non-oxidized marine environment (c.f. Alibo and Nozaki 1999). Rare earth elements in Lahn-Dill ores show similarities to iron oxide muds from the Red sea (Laurila et al. 2014), Taxkorgan BIF (Li et al. 2018) and Urucum BIF (Angerer et al. 2016).
a lack of negative Ce anomalies indicating brine composition without seawater mixing (Laurila et al. 2014). Rapitan-type BIF as well as Cambrian “Algoma-type” BIF are assumed to have formed in ferruginous marine subbasins under anoxic conditions (Angerer et al. 2016; Li et al. 2018). These chemical iron sediments are interpreted to have formed under different conditions, nevertheless similarities in their REE+Y fractionation patterns exists.

6 Conclusion

Lahn-Dill-type iron ores represent a peculiar deposit type regarding their depositional environment as well as their geochemical composition.

Two distinct processes are involved in the formation of these iron ores. They show features characteristic for a synsedimentary formation as well as for mineralisation related to metasomatic replacement in reef carbonates, thus being related to epigenetic processes.

Lahn-Dill iron ores show REE+Y patterns indicating a strong volcanogenic component as well as a seawater signature. However, a distinct negative Ce anomaly is absent suggesting a marine environment that may not have been oxidizing. Comparison with recent iron ore deposits, Cambrian and Neoproterozoic BIF show patterns with some resemblances.

A minor heterogeneity between the two sets of data (c.f. Nesbor and Quade data) is present regarding Eu anomalies highlighting the importance of new data.

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References


Evidence for late Lufilian orogenic mineralizing fluids at the Kamalondo Cu-Co deposit (Tenke Fungurume, Democratic Republic of the Congo)

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Abstract. The Democratic Republic of Congo, part of the Central African Copperbelt, contains numerous Neoproterozoic world-class Cu-Co deposits. The Kamalondo Cu-Co deposit, located in the Tenke Fungurume Mining District, is a mega-fragment of the Mines Subgroup. The Cu-Co mineralization is characterized by a multistage origin, from a diagenetic mineralization, to a syn-orogenic phase (carrollite, chalcocite, chalcopyrite, bornite), and a final supergene enrichment (chrysocolla, heterogenite, malachite). The late Lufilian orogenic Cu-Co mineralization shows carbonate veins (brittle stage 5) crosscutting both carbonate and quartz veins related to brittle stages 1 to 4. The petrography of fluid inclusions reveals the presence of two-phase (liquid and vapor), three-phase, and four-phase inclusions (liquid, vapor and solids, such as anhydrite, halite and sylvite). The fluid inclusions microthermometry indicate that the Cu-Co mineralization formed from a fluid with a minimum temperature of 60°C and a salinity ≥26.5 eq. wt.% NaCl. These temperature and salinity data are lower than the values typically recorded from the late diagenetic and syn-orogenic stages (homogenization temperature ≥270°C; salinity between 35-45.5 eq. wt.% NaCl).

1 Introduction

The Neoproterozoic Katanga Supergroup in the Central African Copperbelt (CACB) contains several Cu-Co (U) and Pb-Zn-Cu (Ge) sediment-hosted ore deposits (Cailteux et al., 2005, Dewaele et al., 2006; Schuh et al., 2012; Sillitoe et al., 2017; Twite et al., 2019). These sedimentary rocks are a succession of carbonate and detrital rocks deposited in a paleorift (Batumike et al., 2007; Mambwe et al., 2019). The Kamalondo Cu-Co deposit is located in the Tenke Fungurume Mining District (TFMD) in the CACB. The Cu-Co mineralization is hosted in the Mines Subgroup of the Roan Group. At a local scale, this deposit is part of the alignment forming the southern limb of the larger Dipeta syncline together with the Kansalawile and Mambilima deposits, while the Mwadinkomba and Shadirandzoro deposits occur in the northern limb.

The sediment hosted stratiform Cu-Co deposits in the CACB are generally thought of having a multistage origin (Dewaele et al., 2006; Haest and Muchez, 2011), however, also one mineralization phase has been proposed (Sillitoe et al., 2017). This single phase spans a time period of 50 Ma. Cu-Co mineralization started with diagenetic hydrothermal stages, followed by syn-orogenic (early to late) to post-orogenic stages. The diagenetic phases dated at ~800 Ma (Muchez et al., 2015), caused the precipitation of Cu-Co sulfides during burial of the Roan strata. The Th values of the fluid inclusions range between 115 and 220 °C, with a salinity between 11.3 and 20.9 eq. wt.% NaCl (El Desouky et al. (2009, 2010). The late diagenetic to syn-orogenic fluids have a minimum temperature of 270°C and high salinities (35-45.5 eq. wt.% NaCl).

During the Lufilian orogeny, a remobilization of the stratiform ore deposit occurred, causing the formation of stratabound deposits (Van Wilderode et al., 2015). A mineralization/remobilization phase is proposed to have occurred between ~720 to ~670 Ma by hydrothermal fluid convection during the Nguba proto-oceanic rifting or early stages of the Congo-Kalahari craton convergence (Decrée et al., 2014). The main mineralization/remobilization stage of Cu and U took place between 652 Ma and 530 Ma (Loris et al., 1997) in the Congolese part of the Copperbelt. In the Zambian Copperbelt, remobilization of Cu mineralization has been dated at 583 ±24 Ma (Barra et al., 2004) and at ~550 to ~530 Ma (Eglinger et al., 2013). An event dated at ~510 to ~500 Ma was related to Ca- and Na-rich metamorphic fluid (Eglinger et al., 2014). The 540– 490 Ma ages of Cu-Mo mineralization (Sillitoe et al., 2017) are likely related to the syn- to post-orogenic timing of mineralization/remobilization.

The brittle stages 1 and 2 as defined by Kipata et al. (2013) belong to the Kolwezian orogeny-D1 and are characterized by folding and thrusting (Kampunzu and Cailteux, 1999; Kipata et al., 2013). The Monwezian phase-D2 is characterized by transpression, transtension and arc-parallel extension deformation,
which are recorded in respectively brittle stages 3, 4 and 5 (Kipata et al., 2013). These Lufilian phases control the mineralization in the Katanga Supergroup (Haest and Muchez, 2011; Mambwe et al., 2017a; b).

This study aims to characterize the nature and origin of the Cu-Co mineralizing fluids during the late stages of the Lufilian orogeny in the CACB. Using the Kamalondo deposit as an example (fig.1), the results will be compared with previous studies (El Desouky et al., 2009; 2010).

Figure 1. Geological map of the northern part of the Lufilian arc showing the Tenke Fungurume Mining District and Kamalondo Cu-Co deposit.

2 Methodology

Fieldwork, followed by detailed petrography and mineralogy, was completed at the Kamalondo Cu-Co deposit on both outcrops and cores. The characterization of fluid inclusions focused on dolomite veins mineralized with chalcocite, bornite, chalcopyrite and carrollite, hosted in a stratified siliceous dolomite. A representative sample was collected from the KAMA0052 borehole at a depth of 216.5m (Figs. 2, 3). This borehole was drilled in the western part of the deposit. Two doubly polished thick sections were made from the vein with hypogene Cu-Co sulfides.

The petrography of the fluid inclusions was completed on Olympus (BX41 and BX60) microscopes, and the microthermometry was done using an Olympus BX51 microscope equipped with a LINKAM MDS heating-cooling stage coupled to a computer. Calibration of the stage was done using glass standards with fluid inclusions of H₂O-CO₂ (TmCO₂ = -56.6°C), H₂O-NaCl (Te = -21.2°C), H₂O-KCl (Te = -10.4°C) and H₂O (Tm = 0.0°C). The detailed petrography and fluid inclusion microthermometry were completed at the Geodynamics and Geo Fluids Research Group of the KU Leuven.

3 Results

3.1 Cu-Co mineralization

Several generations of Cu-Co mineralization are observable in the Kamalondo deposit. The initial phase is characterized by nodules of dolomite-bearing carrollite or chalcopyrite with minor bornite, and disseminated pyrite, chalcopyrite and carrollite. This phase is followed by multiple generations of dolomite and quartz veins. The formation of the latter veins can be linked to the D1 tectonic phase (cf. Kampunzu and Cailteux, 1999). The mineralized zone is controlled by a strike-slip fault, interpreted to be related to the D2 deformation of the Lufilian orogeny (cf. Kampunzu and Cailteux, 1999).

Mineral zonation of the hypogene ore is recognized. Pyrite and chalcopyrite, with minor/occasional bornite, chalcocite and carrollite, are present in the upper ore body (e.g. SDS, SDB). Chalcocite, carrollite and bornite are more abundant than pyrite and chalcopyrite in the lower ore body (e.g. RSC, RSF, RAT).

Spatial distribution of grades vary from the western part (poorly mineralized), characterized by a NE-SW sinistral strike-slip fault (brittle stage 3), to the eastern part, well mineralized and affected by a NW-SE dextral strike-slip fault (brittle stage 4). Dolomite veins bearing pyrite, chalcopyrite, chalcocite, carrollite and bornite formed during the late Lufilian Cu-Co stages at Kamalondo. These late veins cross-cut all earlier generations of dolomite/quartz veins including drag folds. They are interpreted as recording the late orogenic brittle deformation (stage 5).

The supergene enrichment zone is developed until a depth of 70m. Sphero cobaltite, chrysocolla, chalcocite and malachite replace the Cu-Co sulfides. Usually the sphero cobaltite and malachite rim the carrollite and the chalcopyrite and both hypogene and supergene chalcocite are intergrown with dolomite in fractures. The chalcocite has spots of hematite/goethite indicating oxidation. Dolomite/quartz with sulfides (chalcopyrite, chalcocite, carrollite) and supergene ores (malachite, spherocobaltite) occur in fractures. The weathering processes built a leached zone and an oxide zone above the hypogene zone. The thickness of these two zones is generally dependent on the permeability of the rocks (Fig.3).
3.2 Fluid inclusion characteristics

The petrography of the fluid inclusions in the dolomite cement reveals the presence of two-phase aqueous-vapor inclusions or aqueous-gaseous inclusions with several solids (Fig. 4). The volume of the vapor bubble ranges between 5 and 20%. The solids can have a cubic (halite, sylvite) or rectangular habit (anhydrite). In all cases, the volume of the solids ranges between 5 and 10%.

Microthermometry was done only on primary fluid inclusions. The temperatures of homogenization (Th), and dissolution of halite (Ts) were measured. The Th values of the fluid inclusions in the dolomite cement are between 60° and 259°C, and Ts values between 48° and 250°C (Figs 5A, B). The latter corresponds with a salinity range between 26.5 and 35 eq. wt.% NaCl.

The Cu-Co mineralization at the Kamalondo deposit is hosted in the classical lower and upper ore bodies of the CACB. The zonation observed results in a temporal grade distribution of Cu-Co. An abundance of carrollite in the lower ore body resulted in a higher concentration of Co than in the upper ore body. The carrollite formed after the first sulfide mineral phase. The syn to late orogenic phase is interpreted to have caused the formation of the carbonate and quartz veins mineralized in chalcocite, chalcopyrite, carrollite and bornite. The Kamalondo deposit forms a stratiform/stratabound Cu-Co deposit similar to other deposits in the Katanga Supergroup (Schuh et al., 2012).

The large range of Th and Ts values requires some discussion. Although special attention has been paid to avoid analysis of deformed inclusions, it cannot be excluded that the inclusions have been stretched or slightly leaked after entrapment. Stretching results in an increase in Th values, however does not affect could have caused an increase in both the Th and Ts values. Homogenization temperature of 60°C is the minimum temperature of the mineralizing fluid at a minimum salinity of 26.5 eq. wt% NaCl. In order to obtain the actual temperature of the fluid, the homogenization temperature has to be corrected for the pressure during fluid entrapment in the inclusions. Such low minimum temperature of 60°C can also be used to determine the approximate depth during mineralization, since the pressure correction is small. Taking into account a geothermal gradient of 20°C this corresponds to a depth of ~2km. If the fluid has a higher temperature than the surrounding rocks, i.e. a hydrothermal fluid, the depth is lower. This firstly indicates that this stage of
mineralization took place after significant uplift of the area. This is in agreement with the formation of the mineralization during brittle tectonic stage 5 characterized by arc-parallel extension (Kipata et al., 2013). Alternatively, if the higher Th values are not due to stretching or leakage, the temperatures measured reflect the migration of warm fluids from the deep subsurface. The mineralizing fluid with a higher content of Na, K and Ca, as indicated by the solids present in the inclusions, is comparable to the late diagenetic to syn-orogenic mineralizing fluids studied by El Desouky et al. (2009, 2010). However, the salinity and temperature of the inclusions studied in the present study are lower in comparison with those investigated by El Desouky et al. (2009, 2010). The syn-orogenic fluids are interpreted to be related to the Kolwezian phase (brittle stages 1 and 2 of Kipata et al., 2013) and probably to the early stages of the Monwezian phase (brittle stage 3 of Kipata et al., 2013).

These results demonstrate the evolution of a high temperature and high salinity mineralizing fluid (Th ≥ 270°C, salinity: 35-45.5 eq. wt. % NaCl) present during late diagenesis and orogenesis to a late orogenic fluid with much lower temperatures (≥Th 60°) and lower salinities (≥26.5 eq. wt.% NaCl).

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Mineralization styles of the Tullacondra Cu-Ag deposit (Cork, Ireland)

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Abstract. The Tullacondra Cu-Ag deposit is located 10 km from Mallow, in Ireland, and contains an unexploited reserve of 3.6 Mt of 0.7% Cu and 27.7 g/t Ag. The deposit is hosted within Carboniferous marls of the Lower Limestone Shale (LLS) and consists of an EW-trending Cu-Ag rich orebody. Although Tullacondra is hosted within the same stratigraphic and structural context as Navan, its relationship with the metallogenic controls of the rest of the province remains poorly known. The purpose of this study is to obtain data from Tullacondra by means of petrographic and chemical analysis to understand its metallogenic controls and to further discussions on its relationship with other Zn-Pb deposits. For this purpose, six styles of mineralization were determined: disseminated chalcocite-bornite-chalcopyrite, chalcopyrite, tennantite-arsenopyrite and pyrite, vein-hosted chalcocite-bornite-chalcopyrite and vein-hosted tennantite-arsenopyrite. Disseminated and vein-hosted chalcocite-bornite-chalcopyrite is hosted through the whole LLS and in the beds with the highest Cu values, while disseminated and vein-hosted tennantite-arsenopyrite is hosted mainly in the base of the LLS, in samples with the highest Ag values. Textural and mineralogical data thus show that Cu-bearing sulfides precipitate before Sb-As-bearing sulfides and that they concentrate in two connected orebodies.

1 Introduction

The Tullacondra deposit is an Irish-type Cu-Ag mineralization located 10 km NNW of Mallow, County Cork, in Ireland, and is hosted within the Irish Midlands (Wilbur and Carter 1986). This province has some of the most important Zn-Pb deposits in the world such as Navan, Lisheen and Silvermines, with about 110 Mt at 8% Zn and 2% Pb, 22 Mt at 11.63 wt % Zn and 1.96 wt % Pb and 17 Mt at 6.4 wt % Zn, 2.5 wt %, and 23 g/t Ag, respectively (Andrew 1986; Convery 2017; Torremans 2018). Tullacondra contains unexploited resources of 3.6 Mt of 0.7% Cu and 27.7 g/t Ag characterized as an EW-trending near-vertical Cu-rich orebody and a stratabound Ag-rich orebody. The deposit is hosted within Lower Carboniferous carbonate rocks of the Lower Limestone Shale, laterally equivalent to the Navan group, at the northern limb of the Variscan Kilmaclenine anticline (Fig. 1 - Wilbur and Royall 1975; Wilbur and Carter 1986). Albeit spatially apart by several tens of kilometres, the Tullacondra deposit is hosted within the same stratigraphic intervals as other Zn-Pb deposits in the province. It is also associated with regional dolomitization and shares similar NE to ENE trending structural controls (Johnston, 1999). These similarities suggest that they are part of the same mineralizing system. However, ore formation processes which allow for the formation of a Cu-Ag deposit instead of a Zn-Pb deposit remain poorly understood.

Therefore, the aim of this study is to obtain petrographic and geochemical data of a satellite copper deposit in order to further the discussion on Cu-Ag deposit genesis and their relationship with Zn-Pb deposits. For this purpose, petrography, whole-rock chemistry and SEM-EDS analysis were carried out and interpreted, and the main styles of mineralization, their distribution and a preliminary paragenetic sequence were determined.

2 Samples and methods

The studied samples were collected from three drill holes termed M73-3, M73-11 and M73-19, located in the western, central and eastern Tullacondra orobedy, respectively (Fig. 2). Petrography of 41 samples was carried out to characterize the main host rock and sulfide mineralogy. EDS-SEM analysis were performed on 31 samples to allow for determination of poorly identified minerals whereas whole-rock chemistry of 43 samples allowed the determination of the geochemical
The Lower Shaly Calcarenite sub-unit consists of micritic dolomite and calcite matrix with trace of medium-grained quartz and muscovite; (V) Oolitic Calcarenite consists of oolitic calcarenite, also classified as packstone by Dunham (1962), containing medium-grained oolite and scattered bioclasts with subordinate medium to fine-grained quartz, feldspar and muscovite. Stylolites cutting through oolites and bioclasts are common; (VI) Silty Calcarenite is not reported in this study; (VII) The Upper Shaly Calcarenite sub-unit is defined by bioclastic calcarenite, or packstone and wackestone, interbedded with shaly beds and laminae, and dolostone in the base of the western orebody (M73-3). Calcarenite hosts calcitic bioclasts, sometimes replaced by chalcedony, disseminated medium-grained quartz and muscovite in micritic and sparry calcite matrix. Stylolite cuts bioclasts and sometimes concentrates fine- to medium grained quartz along its surface. Additionally, shaly beds and laminae consist of fine-grained quartz, muscovite, micritic calcite and dolomite and show abundant concentration of burial stylolites. Dolostone is also hosted within the base of the Upper Shaly Calcarenite in the western orebody; c) Ballyvergin Shale consists of fine calcareous shale containing mainly very fine-grained quartz, calcite and muscovite and scattered medium-grained quartz, calcite and muscovite; d) Tullacondra Limestone consists of bioclastic calcarenite medium- to coarse-grained partially fine-grained near the base, also named as grainstone and packstone according to Dunham (1962) classification. In thin section, Tullacondra limestone contains bioclasts in micritic calcite matrix. Chalcedony replaces several bioclasts and hosted veinlets.

3.2 Ag and Cu chemistry analysis

The whole-rock chemical analysis of drill holes M73-3, M73-11 and M73-19 show that the main Cu values are concentrated along the LLS (Fig. 3). In the western part of the orebody (M73-3), Cu mineralization is hosted in the Ballyvergin Shale, topmost Upper Shaly Calcarenite, through the Lower Shaly Calcarenite, Uniform Calcarenite and Lower Transition Series. In the central part (M73-11), the highest Cu content is hosted in the Upper Shaly Calcarenite, Upper and Lower Transition Series and in eastern (M73-19), in the Oolitic Calcarenite, Lower Shaly Calcarenite and Lower Transition Series. Ag mineralization occurs in the Upper and Lower Transition Series, although not limited to those beds (Fig. 3). Whereas it is lacking in the western part of the orebody, it is hosted in the Upper and Lower Shaly Calcarenite, and Transition Series the in central and eastern part.

3.3 Mineralization styles

Mineralization in Tullacondra is either disseminated or vein-hosted, but the mineral assemblage and textural relationships can vary in different sections of the orebody. Thus, we divided the Tullacondra ores into six
styles based on their cross-cutting relationships and paragenetic sequence, as follows (Fig. 4):

Figure 3. Lithological units, studied samples localization, and Cu (black line) and Ag grade (grey line) from the western (M73-3), central (M73-11) and eastern orebody (M73-19). Based on 30 years worth of drilling and whole-rock chemistry analysis. Note that the Cu-rich samples is hosted along the whole LLS and the Ag-rich samples mainly in the Transition Beds.

1. Disseminated chalcopyrite bornite-chalcopyrite: fine- to medium-grained anhedral sulfides hosted in the top of the Tullacondra Limestone and Upper Shally Calcarenite of the western orebody (M73-3) and along of the whole central and eastern orebody (M73-11 and 19). In the fine-grained parts, chalcopyrite, bornite and chalcopyrite are also elongated parallel and oriented to matrix. In addition, they replace bioclasts, are along stylolites and between the boundaries of other minerals. Bornite are mostly pinkish brown to orange, but also purple when is aggregated with chalcopyrite. Chalcopyrite is aggregated with chalcopyrite and bornite, on the border replacing them or as lamellae within bornite;

2. Disseminated Cu-As-Sb (Zn-Ni-Co) sulfide-chalcopyrite-chalcedony: fine- to medium-grained subhedral to euhedral tennantite and arsenopyrite, and traces of freibergite, arsenotennantite, cobalitite and nicolite. They are hosted in the Upper Shally Calcarenite of the western orebody (M73-3) and along of the whole LLS of the central and eastern orebody (M73-11 and 19). These sulfides overprint chalcopyrite, bornite and chalcopyrite and are also wrapped with chalcopyrite by chalcedony;

3. Disseminated chalcopyrite: anhedral fine- to medium-grained hosted along of the LLS and ORS. They replace bioclasts and are not associated with another sulfide. This is the main sulfide hosted in dolostone of the western orebody (M73-3);

4. Disseminated pyrite: fine-grained subhedral to euhedral rectangular and squared pyrite. This style occurs in the Tullacondra Limestone of the western orebody (M73-3) and in the top of the Upper Shally Calcarenite of the central orebody (M73-11);

5. Vein-hosted Cu sulfides: fine to coarse-grained anhedral to subhedral chalcopyrite, bornite and chalcopyrite within calcite vein. They are hosted in the Tullacondra Limestone of the western orebody (M73-3) and in the LLS of the central and eastern orebodies (M73-11 and 19). This style of mineralization has similar features to the disseminated Cu sulfides consisting of pink to purple bornite with chalcocite, and chalcopyrite replacing them;

6. Vein-hosted Cu-As-Sb sulfides: fine- to coarse-grained subhedral tennantite and arsenopyrite in calcitic and dolomitic vein. They are hosted in the Upper Shaly Calcarenite of the central orebody (M73-11), Upper Transition Series of the eastern orebody (M73-19) and Lower Transition Series in the western orebody (M73-3).

4 Discussion

The lithological characterization from the ORS, the Transition series and the carbonate units shows a progressive transition from a siliciclastic platform towards a carbonatic one with periodic input of siliciclastic material. This transition from siliciclastic to carbonate sequence during the Upper Devonian and Lower Carboniferous has been reported as a marine transgression (e.g. Philips and Sevastopulo 1986).

Based on the styles of mineralization previously defined, we propose that disseminated mineralization is early in the paragenetic sequence and is cut by later stage vein-hosted mineralization. The following general paragenetic sequence is suggested for Tullacondra's disseminated ore:

(1) bornite-chalcocite, (2) chalcopyrite and (3) disseminated tennantite- arsenopyrite. The paragenesis of vein-hosted sulfides and disseminated pyrite will not be covered in this work.

1. Bornite and chalcocite occur earlier than the other copper sulfides in the paragenetic sequence;

2. Chalcopyrite occurs after other copper sulfides in the paragenetic sequence. It might also include more than one generation; either as isolated grains or overprinting bornite and chalcocite. Furthermore, chalcopyrite is the unique sulfide hosted in dolostone, lithology that is described just in the western deposit (M73-3). This chalcopyrite is probably cogenetic or posterior to dolomitization, because it wraps around dolomite grains;

3. Arsenic sulfides are the last disseminated sulfides in the paragenetic sequence as they overprint chalcopyrite, bornite and chalcopyrite. Besides they are likely coeval or slightly prior to chalcedony, because chalcedony commonly occurs in their rims.

The chemistry and petrological analysis show that there are at least two stages of mineralization, as initially suggested by Wilbur and Carter (1986), a Cu-rich stage consisting of bornite, chalcocite and chalcopyrite, and an Ag-rich stage consisting of tennantite and arsenopyrite (Fig. 4). But in contrast to these authors, the Cu-rich stage is probably the first mineralization followed by Ag-rich stage. Sulfides from the Cu-rich orebody deposited prior to those hosting the Ag-rich
orebody, as per sulfide overprint relationships. These data agree partially with Wilbur and Carter (1986), who designated a Cu-rich vertical orebody along the LLS and an Ag-rich stratabound orebody along the Transition Series (Fig. 3 and 4). Ag-rich mineralization restriction to a stratabound orebody is questionable, because Ag-rich mineralization is not limited to the Transition Series.

5 Conclusion

Based on petrography, whole-rock chemistry and SEM-EDS analysis, main features of the lithological units, style of mineralization and Cu and Ag distribution were determined. We conclude that the Tullacondra deposit is comprised of at least six styles of mineralization emplaced within siliciclastic and carbonate rocks from a transgressive sedimentary basin. Chalcocite, bornite and chalcopyrite are the main copper sulfides, and their modal concentration defines the Cu-rich orebody cited by Wilbur and Carter (1986), whilst the concentration of tennantite-arsenopyrite defines the Ag-rich orebody. Additionally, our data shows that Cu-rich mineralization formed before the Ag-rich mineralization. Future work will involve grain imaging and spot major and trace elements analysis to better characterize chemical variations of sulfides. Isotope analysis (C-O in carbonates and S in sulfides) will be used to determine information about the nature of the fluids.

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In-situ Cu-isotope systematics of the Copperbelt (DRC, Zambia): variations at different scales

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Abstract. The internal zone of the Central African Copperbelt (CAC) is characterized by several mineralization stages. Cu isotope signatures from the Lumwana deposit were analyzed by secondary ion microprobe (SIMS). Chalcopyrite and bornite from the two main mineralization stages display both $\delta^{65}\text{Cu}$ values between -1.37±0.23‰ and +2.95±0.19‰. These results do not allow to determine a specific metal source.

These $\delta^{65}\text{Cu}$ signatures are compared to Cu-Co deposits of the external zone of the CAC that are characterized by several mineralization stages. The latter stages involve remobilization of an earlier mineralization during the Pan-African orogeny. Copper-sulfides of the CAC present a wide range of more than 6‰ in $\delta^{65}\text{Cu}$ values. Deposits from the external zone of the CAC have mostly negative $\delta^{65}\text{Cu}$ values, whereas the internal zone shows $\delta^{65}\text{Cu}$ enrichment. The fractionation at the grain scale can reach up to 3‰. This is significant when compared to the regional scale fractionation. This in-situ method also reveals equilibrium fractionation between the different Cu-phases. Mechanisms for such fractionations remain to be constrained.

1 Introduction

The Lufilian Pan-African orogenic belt hosts the world’s largest sediment-hosted stratiform Cu-Co province, namely the Central African Copperbelt (CAC, Fig. 1; Selley et al. 2005), which is divided in two distinct metallogenic zones: the external and internal zone.

The external zone encompasses the Congolese and the Eastern Zambian Copperbelt, where metamorphism reached $P$-$T$ conditions up to greenschists facies (Fig.2; Selley et al. 2005). Deposits of this zone are interpreted as the result of a multiphase mineralization ranging from diagenetic to syn- and post-orogenic (El Desouky et al. 2010; Muchez et al. 2015).

The internal zone is located in the Domes region, and corresponds to the Western Zambian Copperbelt (WZC). It records metamorphic $P$-$T$ conditions up to upper-amphibolite facies (Fig. 2; Eglinger et al. 2014; Turlin et al., 2016). Several mineralization stages have been documented in this internal zone and including pre-, syn- and post-orogenic phases (Bernau et al. 2013; Turlin et al. 2016). However, whether the syn-orogenic Cu was derived from remobilization of a first pre-orogenic phase remains unclear due to the high-grade metamorphic overprint (Turlin et al. 2016). In order to constrain the origin of the Cu, a Cu-isotope study could provide some useful insights. However, the size of the pre-orogenic Cu-sulfide crystals and the common bornite-chalcopyrite intergrowths (e.g. Turlin et al. 2016) do not allow bulk Cu-isotope analyses, but require an in-situ method.

The aim of this study is to determine the relationship between the different Cu mineralization stages by analyzing the Cu-isotope signatures of chalcopyrite-bornite assemblages by secondary ion microprobe (SIMS) of both the internal and external zones of the CAC. Copper-Cobalt assemblages are hosted in (i) kyanite-micaschists from the Lower Roan Group or from its pre-Katanga basement (Lumwana deposit, Turlin et al. 2016); (ii) in the siliciclastic Lower Roan Group of the Katanga series (Kambove, Luwiswi, Konkola and...
Nkana-Mindola) (Cailteux et al. 2005); and (iii) in the dolomites and sandstones of the Kundelungu Group (Dikulushi) (Haest et al. 2007). These data allow to discuss small and regional scale Cu isotope variation and fractionation, processes that could be due to differences in the source of the metal, temperatures, Eh or pH conditions of the mineralizing fluid.

3 Cu-isotopes analyzed with SIMS

SIMS Cu-isotope analyses were performed for the first time, with a Cameca IMS 1270 E7 and 1280 HR2 at CRPG, Nancy. SIMS analyses were performed by standard bracketing measurements. Chalcopyrite and bornite grains from the Copperbelt were measured by MC-ICP-MS to determine their δ65Cu values relative to NIST 976. The measured values are δ65Cu_{ccp} = -0.721±0.03‰ and δ65Cu_{n} = -0.376±0.03‰ respectively. These reference materials were analyzed with SIMS each day prior to any sample analysis.

2 Geological context

The Pan-African orogenic cycle started after intrusion, uplift and erosion of granites, which have been dated at ca. 880 Ma. It forms part of the break-up of the Rodinia supercontinent that initiated the deposition of the Katanga Supergroup in a continental rift (Hanson et al. 1994). A second rifting stage took place between ca. 750 and 720 Ma which led to the formation of an oceanic basin in the Zambezi Belt (Key et al. 2001). An inversion of the tectonic regime is recorded by eclogitic boudins between ca. 660 and 610 Ma (John et al. 2003). Subduction of the Congo craton underneath the Kalahari craton was initiated at ca. 595 Ma (John et al. 2003, 2004). A continental collision that led to the formation of the Lufilian Belt followed this subduction and is characterized by a peak of metamorphism dated at ca. 550 Ma in the internal zone (John et al. 2004; Eglinger et al. 2014b; Turlin et al. 2016). Finally, a post-orogenic exhumation between ca. 510 and 470 Ma led to the exhumation of high-grade metamorphosed rocks (Cosi et al. 1992; John et al. 2004; Eglinger et al. 2014; Turlin et al. 2016).

Figure 1. Geological map of the Central African Copperbelt hosting the investigated deposits. Dkl: Dikulushi, Kbw: Kambowe, Knk: Konkola, Lsw: Luvisi, Lwn: Lumwana, Md: Mindola, Nkn: Nkana
Figure 3. $\delta^{65}$Cu signatures covering a large part of the Copperbelt. A line represents a sample, with the exception of the Lumwana deposit where several samples are combined. Early-Lufilian = late-diagenetic mineralizing stage (ca. 590 Ma); Syn-Lufilian = syn-orogenic mineralizing stage coeval with the regional peak of metamorphis m (ca. 580-520 Ma), Late-Lufilian= a late- to post-orogenic stage (ca. 520–490 Ma). See references in the text for details on the sample age.

A primary negative oxygen beam (duoplasmatron) accelerated to 13 keV with an intensity of 10 nA was used for measurements. Secondary ions were measured with a mass resolution (M/ΔM) of 5000 in FC multicollection mode. The measured isotope ratio was converted in delta notation by using the equation:

$$\delta^{65}\text{Cu}_{\text{IMF}} = \left[\frac{R_{\text{SIMS}}}{R_{\text{NIST}}} - 1\right] \times 1000$$

where $R_{\text{SIMS}}$ is the $^{65}\text{Cu}^{63}\text{Cu}$ ratio measured by SIMS and $R_{\text{NIST}}$ is the $^{65}\text{Cu}^{63}\text{Cu}$ ratio of NIST976.

The $\delta^{65}\text{Cu}_{\text{IMF}}$ is then corrected from the instrumental mass fractionation using the equation:

$$\delta^{65}\text{Cu}_{\text{sample}} = \Delta^{65}\text{Cu}_{\text{sample}} + (X - \Delta^{65}\text{Cu}_{\text{std}})$$

where $\Delta^{65}\text{Cu}$ is equivalent to the $\delta^{65}\text{Cu}_{\text{IMF}}$ and $X$ is the true $^{65}\text{Cu}$ of the standard obtained by MC-ICP-MS.

4 Sampling

Samples analyzed with the SIMS come from deposits from the Congolese Copperbelt (Dikulushi, Kambove, and Luiswishi), the Eastern Zambian Copperbelt (Konkola, Mindola and Nkana) and the Western Zambian Copperbelt (Lumwana) (Fig.3). All these samples were taken from previous scientific studies whose ages and mineralization stages were determined based on detailed petrographic and microstructural observations coupled with geochronological analysis. (Haest et al. 2007, 2009a; Brems et al. 2009; El Desouky et al. 2010; Van Langendock et al. 2013; Torremans et al. 2013; Turlin et al., 2016 and references therein) No detailed petrography was carried out in this study. Statistically, only a few samples from the late diagenetic stage have been analyzed compared to the syn-, late- and post-orogenic stages. The reason why the earliest phases are underrepresented in the samples is due to their lower preservation potential during the Lufilian orogeny.

5 Cu-isotope signatures of the Copperbelt

The pre- and syn-orogenic mineralization stages of the Lumwana deposit present a similar range of Cu isotope values between -1.37±0.23‰ and +2.95±0.19‰, with the exception of a few outliers (Fig. 3).

Deposits from the Congolese and Zambian Copperbelt display $\delta^{65}$Cu values between -2.72±0.10‰ and +2.95±0.19‰ (Fig. 3).

6 Fractionation processes

Based on the similarities in the range of signatures, no distinct metal source could be identified for the multiple mineralization stages of the internal zone of the Copperbelt. The following sections deal with Cu-isotope fractionation processes recorded from grain-scale to regional-scale, as evidenced by the in-situ analyses.

6.1 Equilibrium fractionation

In the external zone of the CAC, bornite shows $\delta^{65}$Cu values 1‰ higher than chalcopyrite (e.g. Mindola deposit, Fig. 3). Sample measurements have been standardized to their equivalent standards in order to avoid matrix effects. Accordingly, these differences cannot be attributed to this latter effect.

Such differences are not observed in the Lumwana deposit where analysis of both sulfides yielded similar values (Fig. 3) and where chalcopyrite and bornite show intergrowth textures (Fig. 2c; Turlin et al. 2016). Such
textures are not present in deposits from the external zone where both sulfides coexist. Internal processes associated with these textures need to be investigated to understand how they influence fractionation.

6.2 Grain-scale fractionation

The grain-scale fractionation can be as important as the deposit-scale variation, as shown by a Dikulushi sample where Cu isotopes fractionate up to 2‰, i.e. as much as the deposit-scale variation measured by MC-ICP-MS (cf. Haest et al. 2009). Fractionation up to 3‰ has been recorded by a single mm-sized grain from the Nkana Central Orebody amounting to a significant fraction of the observed regional-scale variation of 6‰ (Fig. 3).

These observations demonstrate that processes that affect fractionation at a large scale could also play a significant role at the grain scale.

7 Conclusion

No specific metal source can be attributed to the different mineralization stages recognized at the Lumwana deposit in the Western Zambian Copperbelt.

The *in-situ* Cu-isotope analyses enable to investigate Cu-isotope fractionation between different phases and at different scales showing that there is as much variation in Cu isotopes within a grain as in a deposit.

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References


Anomalous metal enrichment of basin brines in the Zambian Copperbelt

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Abstract. The Central African Copperbelt is one of the most well-endowed metallogenic provinces in Africa, and the largest sediment-hosted Cu-Co-(U) district in the world. The origins, composition and relative timing of ore fluid migration in the Central African Copperbelt remain unclear, with physicochemically anomalous ore fluids potentially responsible for the unique scale of mineralization. Here, we report evidence for the passage of two temporally- and chemically-distinct brines in three deposits across the Zambian Copperbelt (Nkana-Mindola, Nchanga and Lumwana). Pre- to synkinematic veins in all three deposits host anomalously high temperature-salinity (>250°C, >35 wt % NaCl + KCl equiv) brines with unusually potassic compositions (K/Na ≥ 1) and concomitant enrichments in the principal ore-forming metals (Cu-Co).Later fluids are distinctly lower temperature (<250°C) and salinity NaCl-dominant brines with reduced base metal concentrations. We reconcile fluid compositions and base metal budgets with reported alteration assemblages from across the Central African Copperbelt and conclude that highly evaporated, ultra-potassic bittern brines with prolonged residence times in basal clastic sequences were critical to its unique metal endowment.

2 Geologic Setting

The Central African Copperbelt is located towards the southeast of the 900 km-long Lufilian Arc, which formed in response to the collision of the Congo and Kalahari cratons during the Neoproterozoic to earliest Cambrian assembly of Gondwana. The Lufilian Arc comprises Archaean to Mesoproterozoic granitic, metavolcanic and metasedimentary basement inliers, overlain by a thick succession of Neoproterozoic, Katangan Supergroup metasediments. The Katangan sediments host the majority of Cu-Co mineralization in the Zambian Copperbelt and are constrained to a maximum age of 877 ± 11 Ma (Armstrong et al. 1999) by unconformably underlying granites. Katangan sediments were deposited during two main rift phases, with the Lower Roan sediments deposited in predominantly terrestrial and shallow marine environments during the earliest stages of rifting. The basin was inverted and metamorphosed, typically to greenschist facies, during the Lufilian Orogeny which peaked at 545 to 530 Ma (John et al. 2004; Turlin et al. 2016).

The Nkana-Mindola and Nchanga deposits comprise Lower Roan-hosted orebodies located on the western flank of the Kafue Anticline. Mineralization is primarily hosted by reduced argillaceous units, along with footwall arkosic and arenaceous lithologies, with different orebodies characterized by variable Cu:Co ratios. Lumwana represents an atypical style of Cu-Co-(U) mineralization in the Zambian Copperbelt and is hosted by relatively high metamorphic grade schists (± gneisses) of the Mwombezhi Dome, west of the Kafue Anticline (Bernau et al. 2013). The Chimiwungu and Malundwe orebodies at Lumwana represent a mineralized basement shear zone, stratigraphically below the ‘classic’ prospective stratigraphy of the Lower Roan.

All three deposits display finely disseminated mineralization as well as a range of temporally distinct vein sets, some of which are mineralized. The abundance of veins spanning the pre-orogenic and Lufilian stages of basin evolution at all three deposits provides an excellent opportunity to assess the compositional and temporal evolution of fluids involved in at least some of the mineralizing events in the CACB.
3 Paleofluids in the Zambian Copperbelt

Based on their kinematics relative to peak orogenesis, we divide the veins into two end-member generations. Approximately bedding-parallel, quartz-carbonate-sulphide veins are present at all three deposits and often host significant mineralization. These veins typically occur as planar, or folded and boudinaged arrays (Fig. 1B), implying formation prior to peak orogenic conditions. Temporally distinct, discordant, massive quartz veins with lesser carbonate and rare sulphides typically cross-cut ore horizons, as well as hangingwall/footwall units and Lufilian fabrics (Fig. 1C), indicating post-orogenic emplacement.

Bulk crush-leach analysis of paleofluids hosted by the two end-member vein sets display markedly different Cl/Br ratios, indicating distinct fluid origins (Fig. 1A) (Nowecki 2014; Selley et al. 2018). Fluids hosted by pre- to syn-kinematic veins show molar Cl/Br values below that of modern day seawater, indicating the presence of highly evolved bittern brines. Post-kinematic veins display distinctly higher Cl/Br ratios, indicative of a seawater-derived brine that has dissolved in situ halite.

3.1 Microthermometry

Microthermometric analyses of ~1000 fluid inclusions hosted by pre- to syn-kinematic, or post-kinematic veins from Nkana-Mindola, Nchanga and Lumwana show clear distinctions in total homogenization temperatures (T<sub>h</sub>) and total salinities (wt % NaCl + KCl equiv.) (Fig. 2). Primary inclusions spatially associated with base metal sulphides and hosted by kinematically early veins represent anomalously high temperature-salinity KCl-enriched brines (>250°C and >35 wt % NaCl + KCl equiv.). Primary inclusions in discordant, post-kinematic veins represent distinctly lower temperature-salinity NaCl-dominant solutions, more typical of fluids recovered from other sedimentary basin environments elsewhere in the world (Fig. 2). These fluids also occur as ubiquitous secondary fluid inclusions in all vein types.

3.2 Elemental analysis of fluid inclusions

Laser ablation inductively coupled plasma mass spectrometry (ICP-MS) analysis of individual, texturally-constrained inclusions indicate that pre- to syn-kinematic potassic brines are geochemically distinct from later, lower temperature NaCl-dominant solutions (Fig. 3). Early fluids are characterized by K/Na ≥1 and 1-2 orders-of-magnitude enrichments in the principal ore-forming metals (Cu + Co) relative to later, lower temperature fluids which typically show K/Na <1. Additionally, high-temperature metal-rich potassic brines display distinct enrichments in Fe, Mn, Pb, Zn, Ba and Li.
Fluid inclusion phase proportions, homogenization temperatures and major and trace element chemistry indicate a clear compositional distinction between pre- to syn-kinematic fluids associated with mineralization and post-orogenic fluids in mostly barren vein sets. Early ore fluids are confirmed as amongst the most Cu-Co-rich brines recovered from any sedimentary basin environment and across all three deposits studied here, display a unique, ultra-potassic signature (K/Na ≈1).

4.1 Evaporitic ore fluid origins?

Anomalously high-temperature, potassic brines associated with mineralization at Nkana-Mindola, Nchanga and Lumwana correlate with brines shown to possess distinctly low Cl/Br and Na/Br ratios characteristic of highly evaporated bittern brines (Nowecki 2014; Selley et al. 2018). Development of such brines requires extended periods of evaporation in a restricted marine setting, where the conservative nature of K serves to elevate fluid K/Na ratios as NaCl becomes saturated and drops out of solution.

Although estimates of secular variations of Precambrian seawater chemistry, based on a combination of numeric modelling and interpretations of seafloor carbonate precipitate mineralogy, suggest the prevalence of Mg- and SO₄-rich seas during the middle Neoproterozoic (Hardie, 2003), direct measurements of halite-hosted fluid inclusions from the Amadeus and Officer Basins in Australia indicate that during the proposed time period that early, ultra-potassic bittern brines were sourced in the Zambian Basin (ca. 800 Ma), marine sulfate concentrations were as low as ~10% of modern seawater values. Both theoretical and observed evaporite crystallization sequences indicate that elevated fluid K/Na ratios can be developed at lower degrees of evaporation from such seawater, where an initially low sulfate budget is largely consumed through gypsum precipitation during the earliest stages of evaporation (Valyashko 1962).

Elevated Ba concentrations measured in ore fluids from all three Zambian deposits, combined with a paucity of BaSO₄ daughter phases within brine inclusions supports a sulfate-deficient, Neoproterozoic seawater origin (Kovalevych et al. 2006; Spear et al. 2014).

4.2 Fluid-rock interaction and mineralization

Elevated fluid K/Na ratios of ≥1 likely necessitate further K-enrichment of paleofluids within the Lower Roan clastic sequences of the Katangan Basin. Burial depths of up to 11 km, along with the presence of up to 30% detrital potassium feldspar in these rocks provides a viable source, and mechanism, to further supplement the K-(Ba) contents of fertile ore fluids. Petrographic studies of Lower Roan rocks provide evidence of the pervasive breakdown and replacement of detrital (primary) potassic phases in footwall clastic sequences (Sutton and Maynard 2005; Selley et al. 2005).
Subsequent interaction between fertile ore fluids and reduced argillaceous units is indicated by a strong association between mineralization and secondary potassic alteration assemblages (K-feldspar-phlogopite) (Sutton and Maynard 2005; Selley et al. 2005; Selley et al. 2018).

4.3 Development of halite dissolution fluids

Primary fluid inclusions from largely barren, post-kinematic veins at Nkana-Mindola and Lumwana are characterized by moderate salinities and homogenization temperatures, as well as distinctly low base metal concentrations and K/Na ratios. Similar fluids have been reported from demonstrably post-kinematic deposits such as Kansanshi and Kipushi, ranging in age from ~512 to 451 Ma and appear to have been capable of mobilizing relatively low quantities of Cu (<10^2 ppm) (Heijlen et al. 2008; Nowecki 2014; Selley et al. 2018). In all cases, these fluids have returned halogen ratios typical of solutions having undergone a component of halite dissolution. Widespread dissolution breccias in the Upper Roan stratigraphy (Selley et al. 2005, 2018) indicate pervasive breakdown of salt by halite-undersaturated fluids originating at supra-salt levels. The progressive penetration of these fluids into the Lower Roan stratigraphy during, and after Lufilian orogenesis is demonstrated by their presence as primary inclusions in barren, discordant veins, and by structurally-controlled sodic (albite ± scapolite) alteration that commonly overprints stratiform mineralization and earlier potassic alteration assemblages (Sweeney and Binda 1989; Selley et al. 2005).

5 Implications

Quantification of base metal concentrations and major salt chemistries of paleofluids interpreted to be responsible for vein-hosted mineralization at three Cu-Co deposits in the Zambian Copperbelt suggests that ore fluids acquired unique physicochemical characteristics from a series of favorable conditions. Generation of anomalously high temperature-salinity brines was aided by extremely high degrees of evaporation in a restricted marine environment, followed by deep burial within a fertile, hydrologically closed system. Significant degrees of fluid-rock interaction, along with high Cl concentrations in ore fluids promoted the leaching and transport of anomalously elevated base metal concentrations. Few other systems appear to have produced the requisite geologic and physicochemical conditions over sufficient time periods to generate similarly fertile basin brines.

Acknowledgements

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References


Variability of ore mineralization in the vicinity of fault zones in the Radwanice-Gaworzyce copper-silver deposit (Lubin-Sieroszowice mining district, SW Poland)

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Abstract. The characteristics of ore mineralization in the immediate vicinity of fault zones in the Lower Zechstein-related Kupferschiefer deposits are shown. All presented outcomes were obtained on the basis of rock material taken from mining profiles in the Radwanice-Gaworzyce deposit (SW part of the Lubin-Sieroszowice mining district). In all of the analyzed profiles, hematite-enriched Rote Fäule oxidized zone was found, which occurs at various levels of the Kupferschiefer series below the ore-bearing reduced rocks. The redox front cuts across the boundaries of lithostratigraphic units, moving from the Weissliegend to the uppermost parts of the Zechstein Limestone. The primary ore mineralization in the reduced zone is the chalcocite-digenite association with subordinate bornite and covellite. The secondary sulphide mineralization, superimposed on primary ore mineralization and hematitized rocks, is represented by chalcopyrite, bornite, tennantite, tetrahedrite and pyrite. Secondary mineralization is preferentially located in the direct vicinity of fault zones and associated tectonic deformations.

1 Introduction

Previous research conducted on the Fore-Sudetic Monocline revealed a number of regularities in the distribution of the ore mineralization hosted by Lower Zechstein rocks (e.g. Oszczepalski 1999; Speczik 1995), including the mineral zonation pattern in relation to the Rote Fäule oxidized zone (Figs. 1 & 2) and the presence of relict mineralization in profiles with oxidized rocks (Rydzewski 1978; Oszczepalski 1994, 1999; Oszczepalski et al. 2002; Chmielewski 2014, 2016; Chmielewski et al. 2015; Oszczepalski and Chmielewski 2015) that are locally enriched in gold and PGE (e.g. Oszczepalski 2007). Much less attention has been given to the role of tectonic deformation in the mineralization processes (Salski 1975, 1977; Markiewicz 2007).

Samples of the Kupferschiefer series were collected from underground workings in the G-32 section located in the Polkowice-Sieroszowice mine (Fig. 3), which operates in the westernmost part of the Radwanice-Gaworzyce deposit. The analyzed area is located in the SW part of the Fore-Sudetic Monocline, approximately 5 km north-east of the Middle Odra Fault Zone that separate the Fore-Sudetic Monocline from the Fore-Sudetic Block. As a result of the location close to the border of the Fore-Sudetic Block, this region is characterized by intense tectonic deformations within the deposit series (Salski 1975, 1977; Markiewicz 2007).

Figure 1. Stratigraphic position of the Kupferschiefer series and the distribution chart of geochemical zones

2 Characteristics of ore mineralization

During studies of the investigated mine profiles, both reduced and oxidized intervals were examined. The following ore minerals have been identified: chalcocite Cu2S, djurleite Cu1.93-1.95S, digenite Cu1.8S, roxbyite Cu1.78S, anilite Cu1.75S, geerite Cu1.6S, spionkopite Cu1.4S, covellite CuS, bornite Cu5FeS4, chalcocyprite CuFeS2, sphalerite ZnS, galena PbS, electrum (Au,Ag), native gold, native silver, silver amalgam Ag2Hg3,
stromeyerite AgCuS, naumannite Ag₂Se, tennantite Cu₆(Cu(Fe,Zn))₄As₄S₁₃, tetrahedrite (Cu₆Fe₂Sb₄S₁₃, rammelsbergite NiAs₂, gersdorffite NiAsS, clausthalite PbSe, tiemannite HgSe, pyrite FeS₂ and iron oxide minerals: hematite Fe₂O₃ and goethite FeO(OH). Current data on the Kupferschiefer mineralization in SW Poland reveals a number of regularities in spatial distribution patterns of geochemical zones (Figs. 1 & 2).

Figure 2. Map showing location of the research area in relation to Rote Fäule areas and metal zoning patterns in the Zechstein copper-bearing series of SW Poland (after Oszczepalski and Chmielewski 2015). A-B Schematic section through the Lubin-Sieroszowice Copper District (after Klapiński et al. 1984)

The profiles of the Kupferschiefer series within reduced rocks are characterized by the predominance of copper sulphides from the Cu-S group, mainly chalcocite with subordinate digenite and bornite. The richest Cu mineralization is confined to the reduced zone that occurs above the oxidized rocks, transecting lithostratigraphic units. The predominant forms of ore minerals are: disseminations, tiny aggregates, accumulations of microlites and fine crystals (Fig. 5A). Lenses and nests of ore minerals are also common. Individual specimens of the ores usually take on the subhedral and anhedral (Fig. 5B), rarely euhedral textures. Cu sulphides occur primarily as fine-grained crystals dispersed within the rock matrix (Fig. 5C & D). They also occur as replacements of carbonate and detrital minerals by sulphides, chalcocite, digenite, bornite and galena pseudomorphs after pyrite framboids, and the pyrite framboids cemented by chalcocite, bornite or galena. Polymetallic aggregates composed of bornite, digenite and chalcocite are also common. Complex intergrowth textures are characteristic and take the form of invasive replacement of bornite by covellite, digenite by bornite or chalcocite by digenite and bornite. Microprobe examination showed elevated concentrations of silver in chalcocite, digenite and bornite. The highest concentrations of silver were found in chalcocite, up to 4% by weight, while the silver substitution in digenite and bornite reaches up to 0.59 wt.% and 1.16 wt.%, respectively. The concentration of silver in the ore minerals decreases towards the top of the mineralized interval.

Veinlets and fillings of pores, open spaces and stylolites are sparse.

Oxidized profiles are characterized by the occurrence of iron oxides mainly in the form of hematite. Goethite is rarely found. Iron oxides occur in several forms, as red pigment, clumps, irregular small grains dispersed in the rock background (so-called “hematite dust”), earthy masses with lenticular shapes of brown to red colors. Copper sulphides are rare. Very fine hematite grains often replace carbonate minerals and detrital grains and form inclinations in copper sulphides. Noteworthy are complex hematite intergrowths with covellite, digenite and chalcopyrite as well as native gold inclusions in ore minerals (Fig. 5E). Particularly important for the interpretation of the origin of ore mineralization are partial or total replacement of covellite, digenite, bornite and chalcopyrite by hematite (Fig. 5F). Sulphide relicts resulting from partial replacement of copper sulphides are most common in the transition zone from oxidized to reduced rocks, which form the highest part of oxidation zone. Evidently, this substitution of copper sulphides by iron oxides and hydroxides often takes on an invasive character, which indicates extensive alteration and leaching of Cu sulphides. In areas where the oxidation front of oxidizing solutions has significantly exceeded the Kupferschiefer horizon, ore mineralization in the Zechstein Limestone is poorer than when the oxidation front has stopped at the boundary of the Kupferschiefer with the Weissliegend.

Figure 3. Location of selected profiles of the Kupferschiefer series across the SW part of the Lubin-Sieroszowice deposit (the depth contours are the base of the Kupferschiefer)

An important phenomenon is the presence of secondary sulphide mineralization that includes copper sulphides and sulphosalts, such as: chalcopyrite, bornite, tennantite, tetrahedrite and euhedral pyrite. Secondary mineralization is superimposed on the primary ore mineralization in reduced rocks and
overprinted also hematitized rocks. Occasionally, inclusions of tiemannite and naumannite in chalcopyrite are recorded. Secondary mineralization is strongly associated with fault zones and accompanying tectonic deformations (Fig. 4). This late-stage mineralization occurs in the form of brecciated crystals, irregular nests, fillings of cataclastic fractures in primary ore minerals (Fig. 5G), as well as rims and overgrowths of chalcopyrite (Fig. 5H) and pyrite around hematite accumulations. In addition, replacements and impregnations of Cu-S-type minerals by chalcopyrite, tennantite and bornite are also observed. Very often the faults are partly filled by chalcopyrite and bornite, mainly in the form of encrustations on the fault surfaces. Numerous fractures adjoining to fault zones are commonly filled with irregular sockets and lenses of chalcopyrite and bornite accompanied by tennantite and tetrahedrite with minor pyrite.

Figure 4. Examples of tectonic structures observed in the mine galleries in the Weissliegend sandstone (Ws), the Kupferschiefer shale (T1) and the Zechstein Limestone (Ca1). A. Juxtaposition of the Zechstein Limestone and the Weissliegend sandstone through fault surface, the Kupferschiefer is smeared along the fault plane. B. Lower part of the Zechstein Limestone (striped dolomite) juxtaposed with upper part of Ca1 carbonates (calcareous dolomite) through fault zone, near the fault zone the Ca1 carbonates are intensely folded, and the thrust is cutting the vein. C. The Kupferschiefer shale tectonically deformed (folded and faulted) D. Rock material from the Kupferschiefer shale injected into fractures in the Zechstein Limestone.

Locally, in the uppermost part of the Weissliegend tectonic engagement is visible in the form of extensive and irregular network of veins filled with chalcopyrite, bornite and euhedral pyrite. In some areas, the Kupferschiefer took the form of a pitchy shale, highly deformed and folded, with chalcopyrite and bornite veinlets and irregular nests, both concordant and diagonal relative to lamination (Fig. 5D). In the Zechstein Limestone, small fractures filled with anhydrite, gypsum, bornite, chalcopyrite and tennantite on their surfaces are common. In addition, displacements of thin-skinned-style in the form of slip surfaces and tectonic breccia impregnated and incrusted with chalcopyrite and bornite have been recorded. Furthermore, in some areas a tectonic increase in the thickness of copper-bearing beds was noted due to intraformational thrusting within the Kupferschiefer and the Zechstein Limestone (Fig. 4C). Characteristically, the intensity of the secondary mineralization decreases with distance from the fault zones.

Figure 5. Photomicrographs of the Lower Zechstein mineralization (reflected light; A-D - primary mineralization, E-F - relict mineralization, G-H - secondary mineralization superimposed on primary mineralization) A. Digenite (Dg) with tiny inclusions of chalcocite (Cc), bornite (Bn), chalcopyrite (Ccp) and silver amalgam (Ag-Hg), U profile, Zechstein Limestone. B. Fusinite (Fus) cells filled with chalcocite (Cc), C profile, Zechstein Limestone. C. Rich disseminated bornite (Bn) - digenite (Dg) - chalcocite (Cc) mineralization, K profile, Kupferschiefer. D. Chalcocite (Cc) dispersed between folded laminae, with some laminae partly broken by chalcocite crystals, H profile, Kupferschiefer. E. Mineral aggregate composed of digenite (Dg), bornite (Bn), chalcocite (Ccp) and covellite (Cv) with native gold (Au), profile 1, Kupferschiefer. F. Relicts of bornite (Bn) in replacing hematite (Hem), profile A, Zechstein Limestone. G. Cataclastic fractures in digenite (Dg), partly filled by bornite (Bn) and filled with chalcopyrite (Ccp), profile A, Zechstein Limestone. H. Hematite (Hem) partly invaded with chalcopyrite (Ccp), profile F, Weissliegend.

3 Discussion

The obtained outcomes of petrographic and tectonic research lead to the conclusion that the change in the mineral composition near the redox zone is a result of
the evolution of ore system, as evidenced by progressive alteration of the earliest formed ore minerals, until their oxidation and replacement by hematite. The components of the reduced intervals underwent advanced alteration, leading to the conversion of ore-enriched reduced rocks into oxidized rocks with relict copper mineralization represented by replacement remnants of sulphides in hematite. The expansion of oxidative alteration is clearly marked by the appearance of red color of the altered rocks and remnants of Cu sulphides. The occurrence of hematite mineralization in the highest parts of the Kupferschiefer series indicates the centers of the most intense activity of ascending hydrothermal solutions. Therefore, it should be considered that the current position of the oxidized zone and sulphide mineralization concentrated in the ore bodies results from preservation of the products of the last phase related to the propagation of flow of mineralizing solutions and their interactions with rocks through which these solutions were moving, consistently with the direction of spreading.

4 Conclusions

The ore mineralization in the reduced zone represents primary mineralization that was transformed by an advancing flow of the same mineralizing fluids which formed the Rote Fäule. Secondary mineralization overprinted primary mineralization and is also present in fault zones and associated tectonic deformations that cut through the mineralization of the first stage. Secondary mineralization in fault zones occurs in the form of microbreccia, impregnations, fillings of cataclastic fractures of the primary ore minerals, irregular nests, lenticular bodies, aggregates and veinlets. Close relationships with tectonic deformation imply that the secondary mineralization is a result of tectonically-controlled late-stage fluid action. Established faults and fractures formed due to extensional stage strain developed in the Permian-Mesozoic basin (presumably during middle Triassic-Lower Cretaceous tectonics), which then were compressively reactivated between Upper Cretaceous and Paleogene during inversion of the basin (Dumicz and Don 1977; Salski 1975, 1977; Jowett 1987; Markiewicz 2007). It is constrained by a tectonic increase in the thickness of the strata in zones of compressional deformations such as thin-skinned thrusts and folds. Following their formation, the ore bodies underwent tectonic deformation and, as a result, became a source of metals for the formation of secondary mineralization, occurring in the immediate vicinity of fault zones and other tectonic structures.

In summary, the distribution of oxidized zones determines the position of the ore body, both vertically and laterally, while the tectonic deformations did not have a significant impact on the formation of primary ore mineralization, but caused its partial remobilization and precipitation in the form of secondary mineral phases. Fluids which mineralized faults and fractures did not carry only remobilized metals from the primary mineralization, but also could carry elements from extrinsic sources, which is indicated by the supply of As and Sb in the form of a tennantite and tetrahedrite enrichments.

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New gold amalgams from a Kupferschiefer type deposit, Sieroszowice Mine, Poland

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Abstract. Several gold-silver amalgams were identified within the zone characterized by the secondary oxidation profile in sandstone (Weissliegend) and elevated gold concentration. Tetra-auricupride, native gold of high purity, bornite, Se-bearing chalcopyrite and coffinite have been identified in intergrowths with the amalgams. WDS analyses show variable content of major elements in amalgams. The Ag content ranges from 20.79 to 37.90 wt%, gold: from 41.69 to 66.80 wt% and Hg: 10.29 to 19.93 wt%. This data does not fit to the described literature phases.

1 Introduction

The Kupferschiefer copper-silver deposit was described in over 600 papers and books (e.g. Kucha and Pawlikowski 1986; Vaughan et al. 1989; Piestrzyński et al. 1996; Piestrzyński 2008; Borg et al. 2012). The mineralogy of this deposit was described in detail by Pieczonka and Piestrzyński, (2000, 2006), Pieczonka et al. (2006, 2007), Pieczonka (2011). In general, sulfide copper mineralization transgresses all sediments close to the Lower-Upper Permian border. The Kupferschiefer organic shale contains the highest metal concentrations, however the Permian Weissliegende sandstone, that overlies Rotliegende sandstone, hosts the biggest Cu-Ag reserves.

The first discovery of gold in the Lubin deposit took place in 1973 (Kucha 1974). Therefore, gold deposit was discovered in 1994 during routine mineralogical study (Piestrzyński et al. 1996, 2002). Ag-amalgams are very common in the ore horizon. Gold amalgams are discovered for the first time in this deposit, and are related to the barren sections.

2 Geological setting

The gold deposit is located in a continuous, thin horizon with an average thickness of 0.22 m (0.05 to 2 m), showing an average content of 2.25 ppm Au, 0.14 ppm Pt and 0.08 ppm Pd and characterized by low copper and organic matter contents (Piestrzyński et al. 2002). Pt and Pd also occur out of the gold horizon.

Gold deposit was found in secondary oxidized sections of the copper deposit (Piestrzyński et al. 1996, 2002; Piestrzyński and Pieczonka 1998; Pieczonka et al. 2008; Speczik et al. 1997). In the literature exists several common opinions about the genesis of the oxidation facies, but only a secondary oxidation system (SOS) is related to the gold deposit. The horizontal shape of the SOS is a paraconformity (Fig. 1) to the sedimentary strata and it was classified as epigenetic (Pieczonka and Piestrzyński 2000, 2008; Piestrzyński et al. 2002; Pieczonka et al. 2008). An average content of gold in the Kupferschiefer horizon is 5.78 ppb only. It is not enough to be a source for the gold deposit.

Figure 1. Oxidized profile in the Sieroszowice mine, black layer – Kupferschiefer, vertical scale 1 m. White dash line show position of SOS.

Typical black Kupferschiefer is discolored in the contact with the SOS and becomes a maroon variety. The maroon type of the Kupferschiefer is characterized by a high content of Fe₂O₃ presence of coarse-grained hydrothermal hematite and gold (Piestrzyński et al. 2002).

Two factors control the position of the gold horizon: the redox barrier, which is usually independent of sedimentary textures, and the micro tectonic system (Fig. 2), that is not easy for documentation, especially within the sandstone sections (Pieczonka, Piestrzyński 2011).

The copper mineralization is oxidized and transported away to the more reducing surrounding environment. Copper-enriched zones surround the areas affected with the SOS.

Gold was transported in thiosulphate complexes \(\{Au(S_2O_3)_{2-3}\}\) (Piestrzyński 2008; Piestrzyński and Wodzicki 2000). The system is enriched in trivalent iron. It also suggests that gold was transported in complexes of \((FeAu)(S_2O_3)_{2-1}\) (Pieczonka et al. 2008).
3 Analytical methods

Quantitative WDS analyses were carried out in the Critical Elements Laboratory of the Faculty of Geology, Geophysics and Environmental Protection, AGH-UST Cracow using a JEOL JSM-78200 microprobe (EMP).

The analyses were carried out at an accelerating voltage of 20 kV, and a probe current of 40 nA, with a focused beam diameter of 1 μm. The following standards and measurement lines have been used: SKα, FeKα (Pyrite), AgLα (100 %), CuKα (CuFeS₂), SbLα (Sb₂S₃), AuMα (100%), HgMα (HgSe), AsLα (As₂S₃), SeLα (PbSe) Counting times peak/background (in sec) were as follow 10/5. Original Jeol ZAF procedures were used for a final correction of all measured elements.

4 Gold – mercury mineralogy

Several small grains of amalgams intergrowing with tetra-auricupride (AuCu), native gold of high purity and copper sulphides were identified (Fig. 3). Au-Ag amalgams have been recognized in the uppermost part of Weissliegend sandstone (Fig. 1). Aggregates are up to 100 μm in size and are located in sandstone cement. Au-Ag-Hg alloys formed complicated intergrowths, which can be well recognized on the WDS BSE image (Fig. 4) Major element distributions in amalgams are easily visible in WDS contour maps (Fig. 5, 6, 7, 8, 9, 10). EDS observation revealed also uranium silicate (coffinite) which is occurring in form of thin, aroun 3-5 μm thick bands well visible on contour map (Fig. 9). The position of coffinite suggests its early precipitation from the solution containing silica.

WDS composition confirmed presence of tetra-auricupride and mineral phases characterized with different grey colors well visible on Figure 4. Quantitative WDS measurement (Tab. 1) showed variation in chemical composition all analyzed points. Only tetra-auricupride show stoichiometric composition. Within the Au-Ag amalgams at least three different phases can be recognized. Gold varies from 41.69 wt% up to 66.80 wt%. Silver varies from 20.79 wt% up to 37.90 wt%. Finally mercury concentration varies from 7.90 up to 37.90 wt% (Tab. 1). One analytical point shows also 11.00 wt% of copper (Tab. 1). Almost all points reveal small admixtures of iron. Whole investigated area shows also contamination with selenium (Fig. 10). Some visible hot spots on Se map (Fig. 10) belongs to selenides.

Table 1. WDS composition of amalgams and tetra-auricupride in wt%, analytical points (in red) are mark on figure 4

<table>
<thead>
<tr>
<th>No.</th>
<th>Ag</th>
<th>Hg</th>
<th>Fe</th>
<th>Au</th>
<th>Cu</th>
<th>Total</th>
<th>Mineral</th>
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<tr>
<td>1</td>
<td>1.01</td>
<td>0.51</td>
<td>0.06</td>
<td>75.43</td>
<td>24.09</td>
<td>101.3</td>
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<tr>
<td>2</td>
<td>20.79</td>
<td>10.85</td>
<td>0.00</td>
<td>66.80</td>
<td>0.91</td>
<td>99.4</td>
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<td>3</td>
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<td>0.26</td>
<td>0.05</td>
<td>76.18</td>
<td>24.33</td>
<td>100.9</td>
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<tr>
<td>4</td>
<td>34.92</td>
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<tr>
<td>5</td>
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<td>0.07</td>
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<td></td>
<td></td>
<td>Pb, Se- sought but not detected</td>
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</table>
In the zone with Au-Ag amalgams the analyzed sulfides show elevated amounts of selenium, reaching a maximum 10 wt%. This problem, as well as the presence of uranium, requires further investigation.

5 Discussion and conclusions

From the group of amalgams presence of three different alloys can be pointed out. To the first group belongs phases containing low amounts of silver. Their atomic proportions are as follow: \( \text{Au}_{1.000} \text{Ag}_{0.568-0.810} \text{Cu}_{0.042-0.082} \text{Hg}_{0.159-0.173} \). The next group is representing by a phase containing high amounts of silver: \( \text{Au}_{1.000} \text{Ag}_{1.166-1.367} \text{Cu}_{0.060-0.093} \text{Hg}_{0.301-0.470} \). Finally one point has high copper content. Its atomic proportions are as follow: \( \text{Au}_{1.000} (\text{Ag}_{0.596} \text{Cu}_{0.540})_{1.137} \text{Hg}_{0.122} \). Taking into account concentration of major elements and atomic proportions it can be concluded that a new line of Au-Ag-Cu-Hg alloys have been documented. These minerals are related to the secondary oxidation system developed on the redox low temperature barrier. Ag-amalgams are very common in the ore horizon and together with native Ag and silver substitutions in the major copper sulphides give high Ag content in the ore, copper concentrate and SX-EW products. Gold and Au-amalgams are occurring in the foot wall of the economic copper zone, mostly in the uppermost of the secondary oxidized section. During the intensive copper ores production only a small
volume of rocks containing enrichments in gold are mined out together with copper ores. Usually so called transition zone containing low grade copper ore and elevated amounts of gold (Piestrzyński et al. 1996; Piestrzyński and Wodzicki 2000) is extracted. Dilution of the copper ores is on the level of 7 – 15%.

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New insights into growth history of chimney conduits and local native gold enrichment from a hydrothermal chimney (Manus Basin, PNG)

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Abstract. Seafloor hydrothermal chimneys from back-arc basins are important hosts for metals, e.g. Cu, Zn, Pb, Ag and Au, and bear potential for deep-sea mining. A solid understanding of the distribution of metals requires an appreciation of detailed mineralogy and chimney growth histories. This study reports the first submicron scale investigation of mineralogy and microstructures of a chalcopyrite-lined conduit wall of a multi-conduit hydrothermal chimney from the PACMANUS hydrothermal field (eastern Manus basin, Papua New Guinea). New observations reveal that the conduits are dominated by thick chalcopyrite walls with bi-directional growth (towards and away from the conduit) which is bounded by a thin layer dominated by fine-grained (< 1 µm) sphalerite. Clustered pyrite grows outwards from the sphalerite substrate. The mineralogy reflects a detailed process of the early growth of chimneys during the initial mixing between hydrothermal fluids and seawater. Late-stage sphalerite and barite then overgrew the conduits at the waning stage. Four types of native gold are observed within the conduit walls, three of which are associated with the sphalerite-rich layer and have not previously been reported. Native gold is interpreted to have precipitated from various mechanisms. This study bears important potential for searching for native gold in fossil hydrothermal chimneys.

1 Introduction

Modern hydrothermal sulfide chimneys, formed due to the rapid mixing between hot hydrothermal fluids and cold seawater (Haymon 1983), have been discovered on the seafloor in various geologic settings, including oceanic spreading ridges in a number of oceanic basins (German and Seyfried 2014). Those from back-arc basins are important hosts for precious metals, such as Au and Ag, as well as other commodities, such as Cu, Zn and Pb (Binns and Scott 1993; Herzig et al. 1993; Herzig and Hannington 1995). The hydrothermal fields in the Manus Basin in particular have attracted interest as potential targets for deep sea mining (Gena 2013). Previous studies have shown that the mineralogy of chimneys at micron-scale is complex; individual minerals within the same zone present various morphologies and were formed under variable physicochemical conditions (Kristall et al. 2011; Berkenbosch et al. 2012). However, so far, there have been relatively few studies investigating the micron to submicron scale mineralogy of sulfide chimneys (e.g. Hu et al. 2019). The characterization of minerals at such small scale is essential to provide detailed information about the microenvironments and a basis for understanding the role of sulfides in controlling the enrichment of precious metals (Kristall et al. 2011).

In this study, we performed the first detailed microstructural investigations of Au-rich chalcopyrite-lined conduits from mm to nm scale to decipher the mineral associations and deposition sequence in the conduits, re-construct the detailed growth processes of conduits and assess their roles in facilitating native gold deposition.

2 Geological setting and studied chimney

The Manus Basin is an extensional back-arc basin, located in the Bismarck Sea, Papua New Guinea (Fig. 1). A series of spreading centers and transform faults are developed in the basin due to the subduction of the Solomon plate under the Bismarck plate along the New Britain Trench. The back-arc extension in the eastern Manus basin (EMB) is developed in the remnant island-arc crust which has formed during the previous subduction along the Manus Trench (Binns and Scott 1993). The volcanic zone in the EMB is located between the Djual and Weitin transform faults, and develops east-west en echelon neovolcanic ridges and domes (Binns et al. 2007). The volcanic edifices are aligned in a northeast direction, normal to the extension direction,
and the composition varies from basalt to dacite-rhyodacite. The active volcanic activity has resulted in the occurrence of numerous hydrothermal fields, i.e. PACMANUS (Binns 2014), Desmos (Seewald et al. 2015) and SuSu Knolls (Yeats et al. 2014), and has produced a large number of Cu-Zn-Pb-Ag-Au rich seafloor deposits (Binns and Scott 1993; Yeats et al. 2014).

The analyzed sample is part of a polymetallic chimney fragment with multiple conduits (CSIRO ID: 118584) which has been described in detail by Hu et al. (2019) and in the PACMANUS Memoir (P2+) (Binns et al. 2002). This sample is characterized by multiple sub-parallel chalcopyrite-lined conduits which are surrounded by a chalcopyrite-sphalerite transition zone and further rimmed by a sphalerite-dominated outer zone with variable barite (Fig. 2) (Hu et al. 2019). A cm-scale sub-sample was taken from a part of the chimney containing multiple chalcopyrite-lined channels.

### 3 Mineralogy and paragenesis

This sub-sample includes four small conduits. Each conduit has its wall lined with coarse-grained chalcopyrite, completely or partly overgrown by late-stage coarse-grained sphalerite (as Sp 1). Chalcopyrite can be separated into two groups (Ccp 1 and Ccp 2), which are characterized by inward-directed growth into the conduit, and outward-directed growth in opposite directions, respectively.

Conduit 1 is described in detail as it includes all types of observed native gold and exemplifies the critical features of all other conduits. To better illustrate these features, conduit 1 is further divided into region 1, 2, and 3 based on the various distribution of clustered pyrite and late-stage Sp 1. From higher magnification observations, the conduit can be also divided into four distinguishable zones from the inner to the outer part of the conduit. The detailed associations are illustrated in figure 4 and table 1.

Based on the petrographic observations, the chimney conduits are proposed to grow in four stages (Fig. 5): 1) the development of an initial sphalerite thin wall, then 2) the accumulation of disseminated euhedral pyrite, followed by 3) the bi-directional overgrowth of chalcopyrite and 4) the late-stage precipitation of sphalerite and barite.
4 Native gold

Four types of native gold are observed within the conduit walls, three of which are associated with the sphalerite-rich layer in zone 2. Type 1 gold is associated with tennantite-tetrahedrite solid solution series within chalcopyrite, an association which is likely due to high sulfur activity when hydrothermal fluids mixed with seawater. Type 2 gold occurs at the contacts between early stage sphalerite-chalcopyrite transitions. This enrichment in native gold is attributed to the replacement of Au-rich sphalerite by chalcopyrite. Pyrite is rimmed by type 3 gold, probably resulting from the temperature decreasing during hydrothermal fluid-seawater mixing. Type 4 gold occurs in the cavities which are in the vicinity of dissolution-re-precipitation boundaries of chalcopyrite and is proposed to have re-precipitated from the dissolution of Au-bearing sphalerite.

5 Comparison to fossil chimney conduits

A similar chimney conduit has been found in the Silurian volcanic-host massive sulfide deposit, reported by Maslennikov et al. (2009). It is a well preserved fossil conduit, dominated by chalcopyrite and pyrite. From the inner to outer zone, the conduit includes coarse-grained Ccp 2, drusy chalcopyrite with sphalerite inclusions, and euhedral pyrite cemented by Ccp 1 (see Maslennikov et al. 2009), which are thought to correspond to zone 1, 2 and 3 in this study, respectively. Native gold was not observed by Maslennikov et al. (2009), and this might be due to the optical observations being conducted at ~ 100 microns scale. However, LA-ICP-MS data in that study has shown that the sphalerite layer includes high Au contents, an association which was interpreted to result from a fast precipitation of Au with sulfides directly from hydrothermal fluids. Due to the striking similarity in sulfide distributions between the fossil chimney and the studied modern chimney, we propose that the high content of Au associated with sphalerite could be attributed to the occurrence of native Au nanoparticles, and either due to the high sulfur activity of hydrothermal fluids or the temperature decrease during hydrothermal fluid-seawater mixing, or dissolution and re-precipitation. Therefore, the comparison between similar conduits in fossil and modern chimneys provides new insights into the deposition mechanism of gold in sea-floor chimneys.

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Accumulation of uranium in fossil and modern Fe-oxyhydroxide sediments of massive sulfide deposits

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Abstract. The ferruginous gossanites of the Yubileynoe VHMS deposit (South Urals) and Fe-oxyhydroxide gossans of the Ashadze-2 hydrothermal sulfide field (Mid-Atlantic Ridge) have high U contents (up to 73 ppm and 352 ppm, respectively). In gossanites, small (1–2 μm in size) round inclusions of uraninite, which locally coalesce to large grains up to 5 μm in size, are observed in authigenic chalcopyrite, as well as numerous fine uraninite particles (<2 μm in size) associated with apatite, V-rich Mg-chlorite and micronodules of pyrite and galena in a hematite–carbonate–quartz matrix. In gossans, isometric anhedral zonal uraninite grains (up to 2 μm in size) associated with pyrite, isocubanite, chalcopyrite, atacamite, and galena occur in Fe-hydroxides and sepiolite and are characterized by outer P-rich rim. It is suggested that similar processes of accumulation of uranium in ancient and modern Fe-rich sediments are caused by fixation of seawater-derived U during oxidation of sulfide minerals. Uraninite in gossanites was mostly deposited from pore diagenetic fluids, which circulated in hyaloclast–carbonate–quartz sediments during Fe-oxide evolution and formation of authigenic sulfide mineralization via oxidation–reduction reactions.

1 Introduction

Despite a wealth of research on modern hydrothermal seafloor massive sulfide deposits and their ancient equivalents (volcanic-hosted massive sulfide/VHMS deposits), little attention has been paid to radioactive elements such as uranium. It is considered that hydrothermal fluids venting at the seafloor are depleted in U and consequently sulfides derived from these fluids are also U-poor (Hegner and Tatsumoto, 1987; Butler, Nesbitt, 1999; German et al., 2002). However Fe-oxyhydroxide sediments from modern massive sulfide hydrothermal field (gossans, cf. Hannington et al., 1988) are characterized by higher U concentrations (up to 20–30 ppm) (Hrischeva and Scott, 2007; Mills et al., 2004). The enrichment of U in these sediments has therefore been attributed to the fixation of seawater derived U during the oxidation of iron sulfides, possibly through microbial mediation (Mills et al., 1994).

The high U concentration (up to 9.08 ppm) are revealed in the Fe-oxide products of submarine oxidation of sulfide ores (gossanites, cf. Maslennikov et al., 2012) in the Uralian VHMS deposits (Maslennikov et al., 2012) and this enrichment is related to the U-bearing (up to 22.59 ppm) pseudomorphic hematite after sulfide clasts and tube microfossils (Ayupova et al., 2017). In this paper, we describe the anomaly contents of U and find of uranium minerals in gossanites in the well preserved Yubileynoe VMS deposit from the South Urals and in gossans (precursor of ancient gossanites) of the Ashadze-2 hydrothermal field of the Mid-Atlantic Ridge. We have revealed the source of U for these rocks and the reasons for U enrichment and track its evolution from seawater to precipitation as a solid phase and further remobilization during postsedimentation processes.

The samples of gossanites and gossans were studied on an Olympus BX51 optical microscope and a VegaTescan SEM equipped with an EDAX (a 1-micron electron beam, 15 nA beam current, 20 kV accelerating voltage, and a counting time of 120 s for peak). The contents of elements were analyzed with classical chemical methods (major oxides) and on an Agilent HP4500 quadrupole ICP MS (trace elements).

2 Geological background

2.1 The Yubileynoe VMS deposit

The Yubileynoe VHMS deposit is situated in the Buribai VHMS region of the West Magnitogorsk zone, which is interpreted as a fore-arc region of incipient oceanic island arc (Herrington et al., 2005) (Fig. 1a). The host rocks are related to the basalt-boninite basement of bimodal mafic Baimak-Buribai succession. It hosts six ore bodies (Fig. 1b), which interpreted as a strongly eroded sulfide mounds (Maslennikov et al., 2013). The ores of the deposit contain 1.5 % Cu, 1 % Zn, and 44 % S. Total ore resources are more than 106 Mt.

Samples of gossanites were collected from the top of the ore body no. 2, which is being exploited by an open pit (Fig. 1c). In the lower part of the mound core, massive pyrite and disseminated chalcopyrite are major minerals. Locally, colloform pyrite ores with carbonates contain numerous fragments of pyritized tube worms. The pyrite-chalcopyrite-sphalerite- and pyrite-chalcopyrite clastic ores (coarse breccias cemented by carbonates and quartz and sulfide turbidites with fragments of paleohydrothermal smoker chimneys) occur at the top and flanks of the ore body (Maslennikov et al., 2013). Gossanites (hematite–carbonate–quartz rocks developed after clastic sulfides) form a discontinuous layer (up to 2–5 cm) at the top of clastic ores. Usually, there is a rhythm alternation of gossanite with sulfide breccias and fine clastic pyrite-chalcopyrite layers exhibiting asymmetric load casts typical of gravitational mass flows. The gossanites show high contents (ppm, up to) of Cu (9666), Zn (1165), Pb (285), V (120), Ti (487), Se (40), and Te (146). The U
contents are 0.04–0.64 ppm in black smoker chimneys, 1.03–3.18 ppm in sulfide turbidites, and extremely variable from very low (1.77–7.28 ppm) to high (up to 73 ppm) contents in gossanites.

Figure 1. Location of the Yubileynoe VHMS deposit in paleotectonic zone of the South Urals (a), schematic position of ore bodies (b), and geological cross-section of the sulfide ore body no. 2 (c).

2.2 The Achadze-2 hydrothermal sulfide field

The Achadze-2 hydrothermal field (12°99´ N, 44°91´ W) of the Mid-Atlantic Ridge is part of the Achadze hydrothermal cluster, which consists of four hydrothermal fields located between the Fifteen Twenty and Marathon fracture zones (Fig. 2a). The Achadze-2 hydrothermal field (discovered in 2003 by the Polar Marine Geosurvey Expedition, St. Petersburg, Russia) is located in the western wall of a rift valley, at a depth of 3100–3350 m (unpublished report of PGME, 2007; Cherkashev et al., 2013) and is associated with gabbros and ultramafic rocks (Beltenev et al., 2003). A high resolution (up to 30 cm) topographic survey in the Achadze-2 field revealed a chain of hydrothermal mounds and a crater shaped structure 20–25 m in diameter and 1–3 m deep (Fouquet et al., 2008). Subsequent visual observations revealed black smokers on the crater bottom, indicating recent hydrothermal activity.

Five massive sulfide bodies were found within the Achadze-2 hydrothermal field (Fig. 2b), most of which is covered by sediments (unpublished report of PMGE, 2007). The largest orebody (number I) is approximately 125 by 335 m in size. Massive sulfide bodies in the south (numbers III and IV) are mostly composed of Fe-sulfides (pyrite and marcasite), whereas those in the centre and far north (numbers I, II, and V) contain significant amounts of Cu and Zn sulfides.

Figure 2. Location of the Ashadze hydrothermal cluster in the Central Atlantic (Mid Atlantic Ridge (a) and the schematic structure of the Ashadze-2 hydrothermal field (b), simplified after an unpublished report by PMGE (2007) (b).

3 Results

3.1 The Yubileynoe deposit

Samples of ferruginous gossanites (Fe₂O₃ 12.31–34.23 wt. %) from the Yubileynoe deposit consist of partly or fully oxidized sulfides, which are mixed with carbonates and detrital hyaloclastic material (Fig. 3a). In addition to oxidized sulfides, gossanites host abundant authigenic chalcopyrite (after pyrite) and sphalerite and minor amounts of radial microlodes (10–15 μm across) of pyrite and galena (Fig. 3b). The microinclusions of galena, Ag-rich native gold, cerussite, hessite, tellurolbismuthite, cobaltite, acanthite, apatite and V-rich (up to 1.2 wt. %) Mg-chlorite are present in authigenic chalcopyrite and hematite–carbonate–quartz matrix (Ayupova et al., 2018; Maslennikov et al., 2019).

Numerous finest uraninite particles (<2 μm in size) were found in hematite–quartz–carbonate matrix (Fig. 3c). Small (1–2 μm in size) round inclusions of uraninite, which locally coalesce to larger grains up to 5 μm in size, are observed in authigenic chalcopyrite with inclusions of galena–hessite intergrowths (Fig. 3d). In some cases, the ED spectra of the uraninite particles (except of U and O peaks) demonstrate peaks of V and P.
3.2 The Ashadze-2 hydrothermal field

Samples of gossans (Fe$_2$O$_3$ 14.28–73.64 wt.%) from the Ashadze-2 hydrothermal field are composed of amorphous iron hydroxides, crystalline goethite, sepiolite, atacamite, halite, calcite, quartz, and sulfide minerals (Ayupova et al., 2018). The Cu–Fe sulfides sulfides are partly to completely pseudomorphed by Fe-hydroxides (Fig. 3e). The Fe-rich samples are mostly composed of ochreous to reddish brown cryptocrystalline Fe-oxyhydroxides, which completely replace primary sulfide clasts mixed with sepiolite, which makes a cement for oxidized sulfide clasts. Pyrite occurs as euhedral crystals 2–3 μm in size in sepiolite and at the contacts between sepiolite and Fe-oxyhydroxides.

Fe-hydroxides host numerous uraninite particles (2–3 μm) and small particles of Cu–Fe sulfides (isocubanite and chalcopyrite), pyrite, galena, and apatite (Fig. 3f). Isometric anhedral zonal uraninite grains (up to 2 μm in size) occur in sepiolite, are intergrown with pyrite, and are characterized by outer P-rich rim (Fig. 3g and Fig. 3h). ED spectra containing U and O are characteristic of uraninite. Some grains of uraninite are surrounded by fine (<1 μm) rims, which are characterized by much lower brightness in BSE images (Fig. 4h) and peaks of P and Ca (possibly a P- and Ca-rich uraninite), and replaces uraninite.

In spite of extremely low Th contents (max 1.59 ppm) in gossans, Fe-hydroxides locally contain microinclusions of Th–Zr-bearing minerals 1.5 μm in size.

4 Discussion

In oxidizing environments, uranium is most soluble and mobile in the hexavalent oxidation state (Langmuir, 1978). U has been shown to be elevated on the surface of altered hydrothermal sulfide minerals (Mills et al., 1994) and in sulfidic plume particles (German et al., 2002), reflecting efficient U reduction and removal onto Fe-sulfide particles in modern Fe-oxyhydroxide sediments. The presence of discrete (smaller 100 nm in diameter) U minerals with P association were found here (e.g., Mills et al., 1994). The average Th/U ratio of the Ashadze-2 gossans and Yubileynoe gossanites is 0.009 and 0.003, respectively, similar to the average Th/U ratio of seawater (0.003) indicated the major source of U for these sediments is related to seawater. The high contents of “hydrogenic” V (up to 458 ppm) and Mo (up to 54) in Fe-oxyhydroxide sediments, as well as U, are due to extraction from seawater during to redox mechanism (Emerson and Huested, 1991; Butler and Nesbitt, 1999). The association of P and U suggests the presence of P–U complex compounds (Langmuir, 1978).

The U distribution in gossans from the Ashadze-2 hydrothermal field and gossanites from the Yubileynoe deposit is extremely heterogeneous. Recently, it was found that U in low-U (<10 ppm) gossanites is hosted in pseudomorphic hematite after sulfide clasts and tube.
worms (Ayupova et al., 2017). It is known that U(VI) is co-precipitated or adsorbed onto ferricydrite may be reduced during the transformation of the iron oxyhydroxide to goethite or hematite, which incorporates reduced U into its mineral structure, where it is readily preserved (Boland et al., 2011). However, unstable sulfide-derived sediments in oxidizing seawater may undergo oxidation after burial. It is suggested that uraninite was deposited predominantly from pure diagenetic fluids, which circulated in hyaloclast–carbonate–sulfide sediments during Fe-oxide evolution and formation of authigenic sulfide mineralization via oxidation–reduction reactions.

Uraninite in gossanites from the Yubileynoe deposit, as well as in gossans of the Ashadze-2 hydrothermal field, is associated with galena, V-rich Mg-chlorite (sepiolite in gossans), and apatite. In addition to Fe-oxyhydroxides, U may also be absorbed by smectite from seawater (a product derived from the decomposition of hyaloclastic material). High U sorption from seawater (a product derived from the oxyhydroxides, U may also be absorbed by smectite (sepiolite in gossans), and apatite. In addition to Fe-


Uraninite in gossanites from the Yubileynoe deposit, as well as in gossans of the Ashadze-2 hydrothermal field, is associated with galena, V-rich Mg-chlorite (sepiolite in gossans), and apatite. In addition to Fe-


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References


Accessory diagenetic minerals in clastic ores of the Novy Shemur massive sulfide deposit, North Urals

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Abstract. The features of mineral composition are considered for clastic ores composing the main part of rich Cu–Zn ores of the Novy Shemur massive sulfide deposit. Most abundant ore types include sulfide breccias, which are composed of pyrite and sphalerite clasts, enclosed in chalcopyrite–sphalerite–pyrite matrix, and sulfide turbidites with rhythmic alternation of sphalerite and pyrite layers. The amount of newly formed pyrite, sphalerite and magnetite increases and the amount of clasts of primary ores decreases in a range from breccias to sandstones. In the same direction, the Zn, Cd, Ag, Pb and Ga contents increase, while the Cu, Au, As, Co, and Mn contents decrease. The indicative accessory minerals of sulfide breccias include electrum, utenbogaardite, tennantite (up to 3.52 wt. % Ag), Ag- and Se-galena (up to 1.7 wt. % Se) and enargite. The sulfide turbidites contain Ag-rich galena, magnetite, arsenopyrite, tetrahedrite, and cassiterite hosted by newly formed sulfides. The matrix of clastic ores contains Ga-bearing chlorite, mica, epidote and albite (1.24–4.88 wt. % Ga2O3).

1 Introduction

As a result of ore facial mapping of the Novy Shemur massive sulfide deposit it was found that the deposit is composed of rich clastic Cu–Zn ores. Among them, the most common are sulfide breccias with fragments of pyrite and sphalerite, enclosed in chalcopyrite–sphalerite–pyrite matrix, and sulfide silty sandstones, which represent a rhythmic alternation of sphalerite and pyrite layers with a thickness of few centimeters. Unlike breccias, the pyrite–sphalerite silty sandstones contain extremely high contents of Zn (up to 40%) and Ga (up to 604 ppm), elevated average contents of Pb (up to 0.4%), Cd (0.3%), and Ag (64 g/t) and low contents of Cu (0.46%) and Au (0.2 g/t). The presence of sulfide chimneys fragments enriched in chalcopyrite and sphalerite in clastic ores is responsible for specific position of rich Cu–Zn ores and strongly variable Cu and Zn contents of ores. Therefore, a detailed study of mineral composition of various granulometric clastic ores is necessary to enhance the extraction of useful components from ores minimizing the cost of Cu and Zn concentrates. The identification of higher Ga contents is relevant because of the growing use of Ga in high-tech economic areas and its classification as a critical material (Erdmann and Graedel 2011).

2 Geological background

The Novy Shemur massive sulfide deposit is located in the North Urals within the northern part of the Tagil rift-paleoisland arc system (Prokin et al. 1988). It is confined to the central part of the Shemur tectonic-volcanic structure, filled with Ordovician-Silurian rhylolite-basaltic rocks (Kuskov 1983; Prokin et al. 1988; Kontar 2013) (Fig. 1).

A lenticular ore body 1050x500 m in size extends in longitudinal direction and dips to the west at an angle of 40–50°. Numerous post-ore dikes of diabases and plagioclase rhylolites divide the deposit into small fragments and ore layers are characterized by sharp flanks. The "core" of the deposit is dominated by massive pyrite ores. The upper horizons and flanks of northern, southwestern and southeastern directions are composed of rich Cu, Cu–Zn clastic ores, dominated by sulfide breccias and layered and banded pyrite–sphalerite ores (Fig. 2). The various clastic ores are frequently intercalated at the deposit.

The ore samples were studied macroscopically at the Institute of Mineralogy (IMin UB RAS), Miass (Russia). The chemical composition of ores was analyzed using ICP MS analysis on a Agilent 7700Х mass spectrometer at the IMin UB RAS (analyst K.A. Filippova). The chemical composition of minerals was analyzed on a Tescan Vega 3sbu SEM equipped with an Oxford Link EDS (IMin UB RAS, analyst I.A. Blinov) and on an Agilent 7700Х mass spectrometer equipped with a LA-ICP-MS device (IMin UB RAS, analyst D.A. Artemyev).

3 Results

In sulfide breccias of the Novy Shemur deposit, the high Zn (up to 10%) and Cu (up to 6%) contents are typical of ores with chalcopyrite–sphalerite and sphalerite chimney fragments, as well as with authigenic sphalerite, which occurs in small-clastic matrix (up to 20%). The higher contents of Co (827 ppm), Mn (153 ppm) and As (401 ppm) are characteristic of breccias with dominant pyrite fragments. In contrast to breccias, sulfide turbidites contain extremely high contents of Zn (up to 40%) and Ga (up to 604 ppm), elevated average contents of Pb (0.4%), Cu (0.3%), and Ag (64 g/t) and low contents of Cu (0.46%) and Au (0.2 g/t). Indicative accessory minerals of sulfide breccias are electrum, utenbogaardite, tennantite (up to 3.52 wt %
Figure 1. Geographical (a) and geological (b) setting of the Novy Shemur massive sulfide deposit (Figure b is based on unpublished materials of the Severnaya copper-zinc mine). 1 – basaltic andesites and basalts; 2 – plagioclase and dacitic andesites; 3 – plagiorthydacites; 4 – diabases, gabbrodiabases; 5 – volcaniclastic basaltic andesites and basalts; 6 – sericite-chlorite-quartz metasomites; 7 – ore body; 8 – faults.

Figure 2. Sulfide breccias (a, b) and sulfide turbidites (c, d) of the Novy Shemur massive sulfide deposit: a. sphalerite and pyrite clasts enclosed in pyrite-sphalerite cement; b. chalcopyrite-pyrite clasts enclosed in pyrite-sphalerite cement; c. gradational layering of fine-clastic sulfide turbidite; d. layers of thin-bedded pyrite–sphalerite ores in coarse-clastic breccias. Scale bar is 1 cm.
Figure 3. Au and Ag minerals of colluvial breccias of the Novy Shemur deposit: a. electrum (Au) in chalcopyrite (Chp); b. inclusions of electrum, galena (Gln) and Ga-bearing minerals (Ga) in sphalerite (Sph); c. intergrowth of electrum and utenbogaardite (Ut) with quartz (Qtz), chalcopyrite and sphalerite; d. electrum and utenbogaardite at the contact of sulfides and quartz. Reflected light.

Figure 4. Ga-bearing minerals of sulfide breccias (a–c) and layered ores (d–f) of the Novy Shemur massive sulfide deposit: a. lamellar aggregates of Ga-bearing chlorite (j), quartz (Qtz) and fractured pyrite (Py) crystals in chalcopyrite (Chp); b. Ga-bearing chlorite (point b) and Ga-bearing epidote (a) in sulfides (gray); c. Ga-bearing epidote (x) with inclusions of quartz (Qu) at the contact of pyrite and sphalerite grains; d. inclusions of Ga-bearing mica (j, i), Ga-bearing chlorite (h) and galena (Gln) in sphalerite; e. inclusion of Ga-bearing chlorite (y) at the contact of pyrite and sphalerite, inclusions of Ta-bearing cassiterite (Cas) in sphalerite; f. inclusions of Ga-bearing mica (Ga) and galena.
in sphalerite between pyrite grains

Ag), Ag- and Se-bearing galena (Se up to 1.7 wt %), and enargite (Fig. 3). Sulfide turbidites host Ag-galena, magnetite, arsenopyrite, tetrahedrite and Ta-bearing cassiterite (0.51–1.03 wt % Ta_2O_5) as inclusions in newly formed sulfides. The presence of these accessory minerals has resulted in higher contents of Au, Ag, As, Pb, Sb, and other elements of ores. These elements derived from fragments of hydrothermal ores, e.g., sulfide chimneys. According to LA-ICP-MS data, in fragments of pyrite–sphalerite–chalcopyrite chimneys, pyrite is enriched in (mean, ppm) Co (567), As (1360), Ag (316), Se (170), and Bi (182); chalcopyrite has higher contents of Co (16), Ga (30), As (up to 70), Sb (up to 1%), Pb (up to 80) and Bi (up to 20); and sphalerite has higher contents of Mn (185), Co (22), Se (130) and Hg (145) and high contents of Ga (up to 500).

In contrast to Cu–Zn ores of other massive sulfide deposits of the Urals, the Cu–Zn ores of the Novy Shemur deposit are characterized by high contents of Ga and the presence of Ga-bearing minerals (Fig. 4). The high contents of Ga, along with Zn, Cd, In, and Sb, are characteristic of breccias, whereas banded pyrite–sphalerite ores exhibit extremely high Ga contents (up to 600 ppm).

It is suggested that the decomposition of sulfide chimneys fragments, enriched in Ga, during the formation of fine-clastic sulfide ores, has released this element leading to its accumulation in sphalerite, chalcopyrite and other minerals. Gallium was also absorbed by primary clay material, which cemented the ore clasts and which were later transformed into Ga-bearing chlorites (1.24–2.89 wt % Ga_2O_3) and mica (1.56 wt % Ga_2O_3). Albite and epidote also host Ga: 0.45–1.52 and 1.11–4.88 wt % Ga_2O_3, respectively.

The higher Ga content of newly formed sphalerite (33–364 ppm) and chalcopyrite (67–363 ppm), as well as of mica (up to 13 wt % Ga_2O_3), chlorite (to 14 wt % Ga_2O_3) and magnetite (5–7 wt % Ga_2O_3), is also typical of chalcopyrite and sphalerite of sulfide breccias of the Shemur massive sulfide deposit (Safina et al., 2018), located in 15 km from the deposit studied.

4 Conclusions

Thus, the variable contents of Cu, Zn and other elements of rich Cu–Zn ores of the Novy Shemur deposit are related to the variable mineral composition of clastic ores. Various granulometric types of clastic ores are characterized by specific textural, structural, mineralogical and geochemical features. The diagenetic transformation of clasts of primary hydrothermal ores changes the mineral and chemical composition of ores leading to local accumulation of valuable and toxic elements within the sulfide massive deposit. Small- and fine-clastic ores, as a rule, are enriched in most trace elements, including precious and rare metals. These ores occur mainly in the slopes of the sulfide deposits and cannot be mined, because they form thin layers of few tens of centimeters thick (rarely, few meters thick inside the ore bodies). The flanks of many massive sulfide deposits (e.g., Yubileynoe, Yaman Kasy, Molodezhnoe, Valentorskoe, Aleksandrinskoe, Saf'yanovskoe) in the Urals are enriched in trace elements (Au, Ag, Sb, Te, Bi, Se, In, U) (Maslennikov et al., 2019). The mode of occurrence of these elements and their associations are atypical of primary hydrothermal ores of the deposits. Thus, our results should be taken into account during processing of ores to enhance the efficient use of the deposit.

Acknowledgements

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Petrographic and mineralogical study of the Kilmacoo gold occurrence, Avoca District, Southeast Ireland

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Abstract. Petrographic investigation of the quartz vein hosted Kilmacoo gold occurrence spatially associated with the copper rich Avoca massive sulphide ore body evidenced a close association between gold and sulphides. Visible electrum grains are frequently observed within chalcopyrite, and more rarely as minute inclusions in both arsenopyrite and pyrite. Mineralogical investigations also revealed complex sulphide paragenetic succession from framboidal pyrite to colloform and idiomorphic cements with overall a low arsenopyrite content. We also documented the presence of hydrothermal phosphates (apatite and monazite) subsequently altered in aluminum phosphate sulphate minerals, as well as a broad diversity of phyllosilicates. These observations as well as the cross cutting relationships tend to indicate a brittle deformation event involving possible remobilization of some of the copper mineralization from the main VMS ore body. At the present time the source of gold is still under investigation to determine the possible contribution from both local and distal sources.

1 Geological context

Background

The Avoca Belt in Co. Wicklow, southeast Ireland has been host to base-metal production for over 300 years (Fig. 1). Volcanogenic massive sulphide (VMS) mineralization at Avoca consists of semi-massive to massive sulphides (Cu-Zn-Pb) exhibiting both epigenetic stockwork and syngenetic exhalative features, and hosted by Middle to Upper Ordovician volcanic and sedimentary rocks of the Duncannon Group (McConnell et al. 1991). Mineralization covers a strike length of approximately 15 km and is punctuated by the Avoca Mine which produced over 16 Mt of chalcopyrite-rich sulphide ore with a grade of 0.6% Cu (Sheppard 1980; Williams et al. 1986; McArdle 1993). The gold-rich Kilmacoo zone at the northeast end of the Avoca Mine property was identified by Mianrai Teoranta in the 1950’s, intersecting 19 meters of quartz veined schist with 2.88 g/t Au and 16.6 g/t Ag (Milner and McArdle 1986). The site was the focus of further exploration in the 1980’s by Riofinex defining a resource of at least 300,000 tons at 1.5 g/t Au.
out by IMC Exploration Group and Koza Gold as part of a JV agreement.

1.2 Regional geology

Sulphide mineralization in the Avoca District is hosted by Ordovician volcano-sedimentary rocks of the Duncannon Group. These felsic volcanoclastic rocks were generated in an active continental margin above a southeast facing subduction zone (Iapetus Ocean), with volcanism initiated during a period of extension within a volcanic arc (Stillman and Williams 1979; McConnell et al. 1991). The volcanic pile sits conformably to unconformably on a continentally-derived turbidite sequence of Cambro-Ordovician carbonaceous (graphitic) sediments (Ribband Group), which were derived from a Peri-Gondwana margin of Ganderia. Closure of the Iapetus Ocean (Late Ordovician to Late Silurian) and westward-directed subduction resulted in the development of an accretionary wedge, with subsequent obduction onto the continental margin and associated polyphase deformation accompanied by lower to middle-greenschist metamorphism.

1.3 Massive sulphides

Avoca mineralization can be found between two distinct felsic volcanic packages and occurs along a 15 km-long zone (McArdle 1993). Although disseminated sulphide and vein mineralization is common throughout the region, sulphide tonnage is largely concentrated in the Cronebane, East Avoca and West Avoca orebodies. Here, sulphides form vein stockwork replacement and stratiform pyritic lenses that are roughly coeval with their host volcanoclastic and sedimentary rocks. The lenticular shape of the stratiform sulphide zones can, in part be attributed to exhalative processes (i.e., buoyant plumes); however, their aspect ratio has also been affected by post-depositional poly-phase deformation.

Mineralization consists of pyrite, chalcopyrite, sphalerite, and galena, as well as a wide range of trace accessory phases including pyrrhotite, arsenopyrite, native bismuth, bismuthinite, bournonite, tetrahedrite-tennantite, magnetite and hematite. Three hydrothermal facies have been recognized: 1) Stockwork pyrite-chalcopyrite (Siliceous); 2) Sub-massive to massive pyrite-chalcopyrite; and 3) banded pyrite-sphalerite-galena (Platt 1977), consistent with other VMS deposits along the Appalachian-Caledonian Orogen (McClenaghan et al. 2003; 2009).

1.4 Quartz veining and gold mineralization at Kilmacoo

Gold mineralization at Kilmacoo has to-date only been recognized in silicified chloritic sulphide-rich tuffs and one of the main feature of the occurrence is the common quartz veining, as foliation parallel banded veins, foliation-parallel lensoid veins and discordant veins, name respectively QV1, 2, and 3 according to Milner and McArdle (1992). According to these authors, the QV-1 formed of white to grey semi-translucent laminated quartz veins are the main host to the Kilmacoo gold mineralization. According to Milner and McArdle (1992) structural study QV1 are foliation (D1) parallel and postdate the D1 cleavage. They are considered to be syn to late D2 in age. QV2 are foliation parallel lensoid veins associated with chalcopyrite and pyrite. They are similar to the veins miner for copper at Avoca (Platt 1977; Williams et al. 1986). QV3 are sulphide poor and discordant to the main D1 cleavage.

Petrology and mineralogy

2.1 Sulphides and sulfosalts in gold bearing quartz veins

At Kilmacoo gold occurrences were mostly documented macroscopically in relation to silicified chloritic tuffs with high pyrite, sphalerite and galena content in foliation-parallel banded quartz veins (Milner and McArdle 1991). One of the main results of our new observations of the veins resides in the close spatial relationship between electrum and sulphide, primarily chalcopyrite hosted in quartz veins (Fig. 2).

Figure 2. a. Thin section reflected light image of a gold bearing quartz sulphide vein sample from the Kilmacoo occurrence, a cropped image of the electrum grain hosted in chalcopyrite is presented at the bottom right. b. coincident scanning electron microscope energy dispersive X-ray spectrometry (SEM-EDS) element map. Abbreviations: Ap (apatite), Apy (arsenopyrite), Cpy (chalcopyrite), Py (pyrite) Qtz (quartz), Sp (sphalerite)
Electrum is commonly present as round anhedral inclusions in chalcopyrite ranging from 10 to 150 microns in diameter. In contrast euhedral pyrite and arsenopyrite hosted electrum is significantly more fine-grained, from small micron-sized rounded inclusions to micro fracture fillings or along the dislocated boundaries of large pyrite porphyroblasts. In places, euhedral crystals of electrum have been found in association with native Bi, Pb-sulfsalts (nuffieldite, Pb₂Cu(Pb,Bi)Bi₂S₇) and rare cassiterite; the sulfsalts partially replace chalcopyrite filled fractures. Electrum is also present as a single phase fracture filling in iron sulphides. Irrespective of the type of electrum occurrence and relationship with the host sulphides, electrum has a consistent gold fineness averaging 750‰, (Fig. 3).

Pyrite textures allow for the identification of at least six generations: 1) an early framboidal pyrite (Py₁), isolated or occurring in clusters following the main planar fabric (S₁/S₂ penetrative cleavage), 2) colloform pyrite overgrowths radiating from the framboids (Py₂), and 3) euhedral pyrite overgrowth (Py₃) on Py₂. Py₁-3 occur in relative variable abundance and exhibit the effects of recrystallization forming large porphyroblasts in places (Py₄). Porphyroblast are later partially replaced by a fifth generation of porous pyrite (Py₅). Finally, a late generation of pyrite (Py₆) occurs as euhedral isolated pyrite grains cogenetic with arsenopyrite, in places, both host minute electrum inclusions that postdate the pyrite porphyroblasts.

2.2 Accessory and alteration minerals

A wide range of minerals were identified in samples from Kilmacoo including hydrothermal apatite and monazite associated with the quartz veins (Fig. 2) as well as their alteration to hinsdalite (PbAl₃(PO₄/SO₄)(OH)₆) a lead end member of the woodhouseite series of aluminum phosphates sulfates (APS) minerals. Occurrence of such minerals provide important Eh/pH constraints on fluid rock interactions during regional metamorphism as well as a possible later phase alteration.

The present work focuses on phyllosilicates associated within rocks hosting gold bearing quartz veins. The most common phyllosilicates are of a Fe-Mg chlorite composition followed by the potassic phyllosilicates. The latter present a broad range of compositions from phengite plotting on the muscovite-celadonite line to illite and interstratified illite/smectite to possible beidellite according to their compositions (Fig. 4). This represents a record of the metamorphic/hydrothermal and late alteration events across the region. Both laths of phengite and chlorite are ubiquitous in the host strata and are well developed in the pressure shadows of pyrite porphyroblasts; these growths most likely coincide with peak metamorphic conditions and define the penetrative S₁/S₂ Caledonian fabric. Temperature estimates using the ³⁷Al occupancy of chlorite from Cathelineau (1988) indicates temperatures of c. 400°C, consistent with widespread greenschist conditions. In masses of Fe-Mg chlorite an indicator of the high pressure and low temperature conditions is present in the form of partially dislocated ferrocarnpholite (Fe,Mg)Al₂Si₂O₆(OH)₄, to our knowledge described for the first time in the Avoca area.

Figure 3. Composition of electrum grains from inclusions hosted in chalcopyrite, arsenopyrite and pyrite from the Kilmacoo gold occurrence.

Figure 4. Composition of phyllosilicates from Ribband Group metasediments hosting the Kilmacoo Au occurrence, plotted in the 2R₃-3R₂-MR₃ coordinates. Abbreviations: Chm (chamosite), Cel (celadonite), Mus (muscovite).

Genetic implications for gold occurrence in the Avoca VMS

The new petrographic and mineralogical knowledge gathered on the Kilmacoo gold occurrence reveal a link between brittle fractures developed in sulphide porphyroblasts as well as euhedral pyrite and...
arsenopyrite formed during metamorphic/hydrothermal events and the gold deposition. The main host of gold is chalcopyrite in fracture-fills hosting electrum. Previous studies solely focused on the structural setting without detailed paragenetic constrain (Milner and McArdle 1992) nevertheless documented free gold in quartz in the banded quartz units, however such occurrence were not present in the sample set (n=30 thin sections) from the present study.

A cross-cutting relationship between the auriferous banded quartz units and the early penetrative S1/S2 Caledonian fabric indicates late gold emplacement in the region, postdating regional prograde metamorphism and associated ductile deformation (Fig. 5). Petrographic observations also indicate a late paragenesis for gold at Kilmacoo postdating Py4.

This late event is coincident with growth of Py4 and arsenopyrite and may be linked to late brittle deformation during the retrograde path as indicated by the chlorite temperature estimate from pyrite porphyroblast pressure shadows. In addition the presence of ferrocarpholite could help to refine the pressure and temperature conditions as the mineral is the marker of LT HP metamorphism (Goffé 1982; Pourteau et al. 2014). This would support that lower greenschist metamorphic condition generally identified for the area would have an affinity toward a low grade blueschist facies.

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Rare metal mobility in a metamorphosed base metal deposit: the Schneeberg / Monte Neve Zn-Pb-(Ag-Cu) SHMS

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Abstract. We present element abundances and evidence for rare metal (Ga, In, Co, Ag) mobility in the metamorphosed sedimentary massive sulphide (SHMS) deposit Schneeberg / Monte Neve, Italy. Within the main stratiform ore body, elements that are predominantly hosted in solid solution within sphalerite include (in order of decreasing median abundances) Fe, Cd, Mn, Cu, Hg, Co (20 - 440 ppm), In (3 - 250 ppm), Ga (1 - 18 ppm), Ag (1 - 10 ppm). Secondary ore lenses caused by intra-metamorphic, hydrothermal sulphide remobilisation, are depleted in Fe, Cu, In, Ga, Co, and enriched in Ag, relative to main ore. During subsequent static recrystallisation Fe and Cu partition into exsolution trails along grain boundaries, without capturing mobile In, Ga, and Co. Late stage shearing form dynamic recrystallised textures and lead to further depletion of In and Co. Low temperature-induced ejection of coupled one-, two, and three-valent cations triggered coeval (fluid-assisted) mobilisation from sphalerite. Evidence for complex mobility of rare metals from sphalerite ore in metamorphic/-hydrothermal modification has significance for ore genetic studies and also for metallurgy.

1 Introduction

Sphalerite, (Zn,Fe)S, occurs as a dominant ore mineral in many types of base metal sulphide deposits. A number of elements can substitute for Zn and Fe and because of this, sphalerite is an economically important carrier of rare metal by-products Ga, Ge, In, Co, Sn, Sb, or Ag (Cook et al. 2009; Sinclair 2014). Metamorphism and deformation as partitioning processes for trace metals in sphalerite are not thoroughly investigated, even though a good understanding of mobility and partitioning of rare metals will advance our knowledge on metal cycling in nature and impact on ore genesis and metallurgy.

We are beginning to understand how metamorphic processes control trace metal concentrations: Lockington et al. (2014) showed that Mn, Fe, Cd, In and Hg in various metamorphosed SEDEX and VHMS ores are not correlated with metamorphic grade, hence primary signatures prevail. On the other hand, Frenzel et al. (2016) revealed a statistical dependence of trace metal concentrations with peak metamorphic grade up to 400 °C. George et al. (2015) showed that Ga, In, and Sn change their preferred host in recrystallised sulphaides at high metamorphic grades from sphalerite to chalcopyrite. Besides these recent advances, there is still a lack of robust models for the mobility of minor and trace metals under (wet) deformation. Here we investigate the significance of element mobility in an amphibolite facies metamorphosed SHMS system, namely the Schneeberg / Monte Neve deposit in the Austroalpine Ötzal-Stubai crystalline (OSC) complex. At the microscale we employ laser ablation ICPMS and EMPA to understand the relationship of element budgets with sulphide remobilisation and sulphide deformation.

2 Geological framework

2.1 The Ötztal-Stubai crystalline complex

The polymetallic ore district ÖSC includes numerous occurrences of stratiform sulphide mineralisations hosted mainly in paragneisses and mica schists. There are two regionally distinct metal associations: the northern Cu-Fe dominated with chalcopyrite – pyrite – pyrrhotite ± arsenopyrite ± sphalerite parageneses and the southern Pb-Zn dominated with sphalerite – galena ± chalcopyrite ± pyrite – pyrrhotite parageneses (Vavtar 1988). The overall lithostratigraphic context suggests an Late Neoproterozoic or early Palaeozoic, clastic dominated sedimentary exhalative (CD-SEDEX) genesis of ore. The ÖSC region experienced a mining boom in the 15th and 16th century with silver-rich galena being a sought-after ore. Emerging Zn production rejuvenated mining in the 19th century, and the Schneeberg-St. Martin mine grew to one of Central Europe’s major Pb-Zn producers. In the 1960ies, annular productions reached a climax with ~50,000 t @ ~7 wt.% Pb and ~1.5 wt.% Zn. Mining activity terminated in 1989.

2.2 The Schneeberg deposit

The Schneeberg district in the eastern part of the ÖSC hosts the largest Pb-Zn ore deposit in the ÖSC. Schneeberg is located in an amphibolite facies (kyanite zone) metamorphic zone (Mair et al. 2007, and references therein). Country rocks are mainly paragneisses with minor mica schists and amphibole-garnet schists.
Within the Schneeberg mine, three orebodies were exploited. They are mostly concordant with the moderately steep, NNW dipping lithostratigraphy and metamorphic foliation. Main mineralisation style is massive layers of sphalerite - galena ± pyrrhotite ± chalcopyrite ± sulfosalts with variable quantities of the gangue minerals quartz - calcite - siderite - dolomite - garnet - tremolite/ferroactinolite - antophyllite. Distal concordant ore lenses and discordant remobilised ore are present at the meter scale.

2.3 Paragenetic sequence of mineralisation

The framework of the paragenetic sequence follows the established tectonometamorphic evolution of the OSC. Primary massive sulphide mineralisation style during basin evolution was most likely a sedimentary exhalative or shallow bedded vein replacement (Vavtar 1988). However, genesis remains ambiguous without primary phases being preserved. The earliest preserved sulphide texture is a coarse grained type, interpreted as peak-metamorphic stage. At the Schneeberg area Variscan and Eoalpidic orogeny caused similar overprint, which makes a clear age determination impossible. However, this texture is preserved in main ore and in distal remobilised ore, thus remobilisation took place prior to, presumably Eoalpidic, peak metamorphism. Two retrograde metamorphic sphalerite types overprinted the coarse peak-metamorphic textures, an earlier annealed recrystallisation textures, and a latter fine grained dynamic shear texture.

3 Petrography

Massive sphalerite - galena - chalcopyrite ± sulfosalts ± (arseno-) pyrite textures are typical for the Schneeberg ore. Gangue is variably present and always interlocked in the massive sulphide matrix, forming a weak layering, concordant with wall rock foliation.

3.1 Sphalerite textural types

Peak-metamorphic sphalerite: Earliest preserved sphalerite is relatively coarse with grain sizes ranging from 180 to 2100 µm. Growth and deformation twinning is common (Figure 1a). Grain boundaries are serrate or bulged without showing annealing textures.

Annealed sphalerite: This sphalerite type is characterised by a foamy, massive, fabric produced by straight boundaries and 120°-triple points. Grain sizes range from 50 to 550 µm. Recrystallisation replaced larger stage 1 grains (Figure 1a). Typical for stage 4 are pyrrhotite and chalcopyrite trails along the straight grain boundaries. Evidence for progressive deformation of annealed stage 4 sphalerite are deformation twinning, flattening of polygons and associated pyrrhotite/ chalcopyrite trails, bulging along polygon-boundaries, subgrain formation and recrystallization to a fine grained sheared sphalerite.

Sheared Sphalerite: Plastic shearing of sphalerite locally produced fines grained shear bands (Figure 1b). Grain sizes range from 10 to 100 µm. Shearing took place as a progressive deformation within shear zones.

4 Sphalerite mineral chemistry

4.1 Gross element abundances in sphalerite

The following elements are present in sphalerites of the Schneeberg deposit (inclusion-related concentrations being rejected): Fe (7 - 9.6 wt.%), Cd (2800 - 5200 ppm), Mn (155 - 790), Cu (88 - 350), Hg (14 - 420), Co (20 - 440), In (3 - 250), Ga (1 - 10), Pb (1 - 4), Sn, Sb (<3), As, Ni, Ge, Bi, Cr (<1).

Fe, Zn, Cd, Hg, In, show smooth and horizontal spectra, suggesting that these elements are hosted in sphalerite solid solution. Inclusions that affect these elements have not been identified in the samples.

Heterogeneous distributed sulphides and sulphosalts affect Pb, Cu, Sb, Ag, As, Ni, Bi, Ge, and Sn. Carbonates and silicates locally change Mn, Ga and Cr abundances. Common chalcopyrite disease shows extreme effects on Cu abundances (up to >>1000 ppm),
while pyrrhotite "diseases" affect Fe to a lesser extent, because of the generally high content in sphalerite.

When comparing main ore with a distal (remobilised) ore, the trace element abundances in sphalerite vary: Fe, Cu, In, Co, and Ga show lower abundances in distal ore (Figure 2). Only Ag shows elevated abundances in distal ore, all other elements do not show clear trends.

A comparison of the three sphalerite types shows that there are some significant variations: While most elements do not show significant differences, the trace metals In, Co, and Ga are depleted in recrystallised sphalerite (Figure 2).

### 4.2 Spatial distribution in sphalerite types

In EPMA element maps the main elements Fe, Zn, Cu have been mapped. It is shown in various examples that Fe mobility took place at the grain scale in response to deformation: annealed sphalerite has characteristic pyrrhotite trails along the straight grain boundaries, mainly located at 120 triple points. Fe depletion in the vicinity of grain boundaries is shown (Figure 3a). Complete Cu depletion near annealed grain boundaries is revealed, leaving remnant chalcopyrite only in the crystallite cores. Similarly, Cu is depleted in sheared sphalerite (Figure 3b), while disseminated pyrrhotite grains remain in the sheared texture between sphalerite.

### 5 Discussion and Conclusions

#### 5.1 Controlling mineral hosts

Elements are categorised into three groups with respect to their predominant mineral hosts: (1) *in solid solution* are Zn, Cd, Hg, In, Se. (2) *predominantly in sphalerite solid solution and minor inclusions* are Mn, Co, Ga, Cr, while Fe and Cu are heavily effected by diseases, (3) *predominantly in inclusions and minor presences in solid solution* are Pb, Sb, Ag, As, Ni, Sn, Ge, Bi.

#### 5.2 Processes of element mobilisation

Elements are subject to remobilisation during ore modification at various scales. At the decameter scale inter-metamorphic mobilisation of sulphides is evident by distal, partly discordant vein-type mineralisation. Fe, Cu, In, Ga, Co are depleted in remobilised ore. This depletion may be related to lower fluid temperatures, and/or variations in the travelling distances, thus solubility of elements. Silver is enriched in distal or, indicating highest solubility at the given alteration temperatures.

Pyrrhotite and chalcopyrite diseases are evidence of local Fe and Cu mobilisation during sphalerite annealing. Here no depletion of trace elements is recorded. Pyrrhotite exsolution (Mizuta 1988; Mizuta and Scott 1997) is evident by Fe depletion in the vicinity of grain boundaries. Whether Cu was primarily within the sphalerite structure (c.f., Barton Jr and Bethke 1987) is unlikely, considering that average concentrations of up to 5000 ppm exceed the Cu dissolution capacity in sphalerite (Bortnikov et al. 1991).

Further Cu mobility took place during dynamic recrystallisation. Here, In, Ga and Co are also depleted. A combined mobilisation of mono-valent Cu⁺ and tri-valent In³⁺, Ga³⁺, and (Co²⁺³⁺) are explained by their coupled presence in and hence ejection from the ZnS structure.
Dynamic recrystallisation-induced Cu, In, Ga, and Co, mobilisation was at larger scale than Fe, which locally re-precipitated in pyrrhotite. This suggests a fluid-assisted deformation process.

These outcomes indicate a high complexity of modifications of rare metal budgets in metamorphosed stratiform massive sulphide deposits. In future we aim to map trace elements by Nano-SIMS. Implications to metamorphic ore genesis / modification and geometallurgy of high-tech metal are evident.

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Figure 3. EMPA backscatter, Cu and Fe maps of sphalerite textures. (a) annealed sphalerite polygon with pyrrhotite exsolution trails along grain boundaries and Fe depletion. See the remnants of chalcopyrite (cpy) in the core and absence of cpy close to the grain boundaries. (b) sheared sphalerite matrix showing partial absence of cpy in a clast and complete vanishing within the shear zone.
Stacked VHMS potential at Erayinia in the Eastern Goldfields Superterrane, Western Australia?

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Abstract. Despite decades of interest, few significant VHMS resources have been delineated in the Archean Yilgarn Craton of Western Australia. At Erayinia in the southern Eastern Goldfields, a small Zn-(Cu) VHMS deposit (King; 2.15Mt at 3.47% Zn) occurs in an overturned and metamorphosed volcanic sequence. Here we present the first results of an exploration target 2.5km to the north, where recent drilling has intercepted zones of Zn-Cu-Au mineralization over a multi-element soil and VTEM anomaly. Combining core logging, detailed petrography of rock chips, SEM imaging, XRD analysis, and high quality fusion lithogeochemistry, the King North stratigraphy has been characterized and correlations made with the King area. Furthermore, hydrothermal signatures have been recognized that are consistent with an overturned VHMS system. The presence of HFSE enriched (FIII-affinity) rhyolites is significant, in addition to a unit of BIF identified higher in the stratigraphy (associated with quartz-sericite-pyrite altered felsic volcanic rocks). The latter suggests there is stacked VHMS potential in the King/King North regional stratigraphy.

1 VHMS mineralization at Erayinia

Volcanic-hosted massive sulfide (VHMS) deposits occur throughout Earth’s history and are an important source of base and precious metals (Galley et al. 2007). Despite decades of interest, few significant VHMS resources have been delineated in the Archean Yilgarn Craton of Western Australia. Exploration is hampered by a combination of a paucity of outcrop, deep weathering, and saline groundwater in geologically complex greenstone belts (Hollis et al. 2005).

At Erayinia in the southern Kurnalpi Terrane (Fig. 1), geophysical methods have had limited success in identifying and locating mineral deposits. Geophysical responses from conventional airborne VTEM surveys in the region are strongly affected by conductive sediments, hypersaline groundwater, and units of black shale within the host stratigraphy. Furthermore, relics of an Eocene marine transgression are scattered throughout the region, and several large salt/playa lakes drain the local area. Consequently, the current landscape is characterized by limited outcrop, and bedrock obscured by deep and variable cover.

In the far south of the Edjudina Domain at King, a small base metal deposit has been recognized (~2.15 Mt at 3.47% Zn, non-compliant at 1% cut-off) in a metamorphosed (lower amphibolite), overturned and east-dipping volcanic rock dominated sequence (Hollis et al. 2019). The local stratigraphy is dominated by garnet-amphibolite, intermediate to felsic banded schist, and rare zones of graphitic schist and talc schist (Hollis et al. 2019). Massive sulfide mineralization (1-7m thick) is characterized by stratiform pyrite–pyrrhotite– sphalerite. Locally intense zones of pyrite-(sphalerite) and pyrrhotite–pyrite–(chalcopyrite) veining occurs throughout footwall lithologies, coincident with a feeder zone characterized by quartz-chlorite±magnetite schist, and cordierite-anthophyllite bearing banded schist. The deposit has a confirmed strike length of ~600m, depth of >500m, and remains open in three directions.

Figure 1. Base metal occurrences in the Yilgarn Craton of Western Australia (modified after Hollis et al. 2015). Significant VHMS deposits and mineral occurrences are labelled.

2 King North

In recent years (2012-2019) Black Raven Mining have
conducted an extensive program of soil and rock-chip geochemistry across the Erayinia area. A heliborne VTEM (Versatile Time Domain EM) geophysical survey was also flown in 2013 identifying 24 targets. In this paper we focus on the King North area, ~2.5km along strike north from the King deposit. A transect of seven west-dipping Reverse Circulation (RC) holes were drilled in 2015-2016 (Fig. 2) over a multi-element soil (Zn-Cu-Pb-Tl-Bi-W-Mo) and VTEM anomaly. An additional RC hole dipping 60°E (EC179) was also drilled in this transect, and in 2018 a diamond extension to RC hole EC173 (from ~125 to 360m). Drilling was in part funded by an Exploration Incentive Scheme grant from the Department of Mines and Petroleum (DMP), Western Australia. Several zones of base and precious metal mineralization have been intersected to date, including:

- EC164: 1m at 4.66% Zn, 2.14% Pb, 0.69g/t Au.
- EC175: 11m at 0.34% Cu, 0.52g/t Au, including 1m at 0.11% Zn and 3.21g/t Au.
- EC179: 13m at 0.2% Cu, 0.16g/t Au.

Through detailed petrography, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) analysis of rock chips, extensive lithogeochemistry, and logging of recently drilled diamond core, we have characterized the King North stratigraphy and established clear correlations to units farther south at King. Geochemical signatures are consistent with an overturned VHMS system with the main feeder zone not yet identified.

### 3 Methodology

Rock chips derived from RC drilling were collected from two holes at King North (EC164 and EC175) for detailed petrography and SEM analysis. Four acid digest geochemical data was also supplied by Black Raven Mining for all RC holes along this transect. This was used to correlate identified lithologies between drillholes. From these data, 26 samples were selected for high-quality fusion lithogeochemistry at ALS Laboratories, Ireland. Precision and accuracy for lithogeochemistry was monitored using a suite of laboratory blind standards. X-ray diffraction (XRD) analysis was performed at the University of Southampton on 22 samples to complement the existing lithogeochemical dataset. Samples were chosen based on depth and a variety of geochemical parameters in order to provide a representative analysis of each hole.

### 4 Stratigraphy

Based on the extensive petrological and geochemical observations, three broad stratigraphic sequences were defined and correlated across the main area of RC drilling (Fig. 2). Logging of the diamond extension EC173D is summarized in Figure 3, with key lithologies shown in Figure 4. Metamorphic grade appears to increase slightly to the east from lower to upper greenschist facies. This is significantly lower than at King (amphibolite facies) which is closer to a large, late-stage granitic pluton.

![Figure 2. Simplified cross section of the King North drilling after Kelly (2018).](image)

**Figure 2.** Simplified cross section of the King North drilling after Kelly (2018).

**Figure 3.** Geological Log of the King North diamond tail (EC173D).

Felsic volcanic and volcanioclastic rocks dominate the upper portions of the RC drillholes. These rocks are dominated by quartz, chlorite and muscovite, with lesser illite, rutile, apatite, zircon and monazite. Immobile element characteristics include high Zr/Ti ratios, FII characteristics (Lesher et al. 1986; Hart et al. 2004) and steeply dipping, LREE-enriched trace element profiles. Pronounced negative Eu anomalies are consistent with plagioclase fractionation at depth. These rocks can be classified as quartz-muscovite-chlorite phyllites or schists.

A relatively thin (~50m thick) package of rocks (of intermediate geochemical composition) occur between
the felsic rocks (near surface) and those of mafic composition at depth. Examined rock chips are either sedimentary or volcaniclastic in origin, and have a highly variable mineralogy (quartz, epidote, amphibole, chlorite, muscovite). Perhaps the most significant finding is the recognition of FIII-affinity (Lesher et al. 1986; Hart et al. 2004) rhyolites at several depths in drillhole EC179 near the top of the ‘intermediate sequence’ (assuming an overturned stratigraphy – see Section 4). These high field strength element (HFSE) enriched rhyolites have very high Zr/Ti ratios, and Y concentrations exceeding 25ppm. Such rocks are indicative of shallow crustal melting (Lesher et al. 1986; Hart et al. 2004), and are a common host to VHMS mineralization across the Yilgarn and other Archaean cratons (references in Hollis et al. 2015). The base of the ‘intermediate sequence’ includes the most significant base metal intercepts (VHMS target horizon 1; Fig. 2).

Mafic rocks at depth are dominated by amphibolite, epidote (clinozoisite), chlorite and quartz. Minor muscovite and plagioclase (albite) was noted in the matrix, along with titanite and apatite. These rocks can be classified as amphibolites and actinolite-chlorite schists. Immobile element ratios are subalkaline and samples plot predominantly within the calc-alkaline fields of Pearce (1996) and Hastie et al. (2007). Chondrite normalized REE profiles are typically flat, as at King (Hollis et al. 2019).

Rocks logged from the diamond tail of drillhole EC173 (Fig. 3) can be divided into three broad sequences:

1. A thick sequence of silica-epidote altered amphibolite (Fig. 3a,b) - a likely continuation of the above mafic stratigraphy. Rare horizons of graphitic schist (Fig. 3c) and mafic tuff also occur. Garnet porphyroblasts are absent, but are abundant in similar rocks from King.

2. A mixed sequence dominated by argillaceous metasedimentary rocks (Fig. 3i). Rare units of altered ‘quartz-eye’ felsic volcanlastic rocks (of unknown F- affinity; Fig. 3d,f,g), talcose high-Mg basalt (Fig. 3e), and mafic tuff (Fig. 3h) also occur.

3. A sequence of amphibolite, with a narrow zone of intensely altered (quartz-sericite-pyrite) felsic volcanlastic rocks and banded iron formation (BIF). The latter resembles a unit from the immediate hanging-wall of the King deposit.

5 Implications for VHMS mineralization

The presence of normative corundum from CIPW calculations is a useful tool for indicating intense alkali leaching in footwall strata associated with VHMS deposits (Grunsky 2013). At King, normative corundum values are highest in the chloritic chalcopyrite-rich feeder zone, and directly below massive sulfides (Hollis et al. 2018). Values are always >0 wt.% in altered footwall rocks due to alkali leaching. By contrast, all hanging-wall units have normative corundum values of 0 wt.% (Hollis et al. 2018).

At King North, samples from holes EC164 yield high values until 73m depth where they drop to zero. A similar situation occurs in EC175 at the shallower depth of 59m (dropping from 6.9-5.5 to 0 wt.%). These depths correlate with the top contact of the felsic rocks assuming an overturned stratigraphy, and corresponds to a zone of highest Zn grades. From this, we infer the stratigraphy is likely inverted (as at King), and that these depths can be inferred to represent the contact between the footwall and hanging-wall to a VHMS target horizon (target horizon 1; Fig. 2). This is also consistent with major element variations (see following), the distribution of pathfinder elements (e.g. Bi, Sb, Ag; Kelly, 2018), and a lack of significant alteration in the mafic sequence.

Felsic rocks from RC drilling at King North are characterized by high SiO₂ (>70 wt.%), generally low Fe₂O₃ (2.35-4.37 wt.%) and low CaO (<1.46 wt.%). Variable Na₂O and K₂O in combination with the above points to intense silicification and sericitic alteration prior to metamorphism. This is consistent with our
petrographic observations of rocks classified as quartz-muscovite±chlorite phyllites/schists. Alteration in the felsic rocks is most intense, plotting towards the chlorite-pyrite node (or ‘ore corner’) on the Alteration Box Plot of Large et al. (2001; Fig. 5). Mafic and intermediate samples are ‘least altered’ (Fig. 5). The geochemistry of samples collected from the EC173D diamond tail is in progress.

Based on the above correlation, it is anticipated that further into the hanging-wall at King a second BIF horizon will occur. At King North this horizon is associated with hydrothermally altered (and weakly mineralized) felsic rocks. If our correlation is correct, there is the potential for additional VHMS deposits stacked higher (farther west) in the regional King stratigraphy.

Acknowledgements
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References
Mineralogical and geochemical characterisation study of Perkoa Zn mine, Burkina Faso, West Africa

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Abstract. This study focuses on the Perkoa Zn deposit, Western Burkina Faso, currently operated by Trevali Mining Corporation. Previous works have not conclusively established the style of mineralization at Perkoa suggesting either VMS or skarn origins. The deposit is located in the Boromo belt of Leo-Man Shield, within the West African Craton. The N-S trending Boromo belt is composed of mafic and intermediate volcanics at its margins, and volcano-sedimentary and sedimentary units in the central portion. This package underwent polyphase deformation during the Eburnean orogeny. The aims of this project are to address the following areas regarding the deposits origin and formation: Determine if the deposit is a VMS or Skarn (debated in the previous study); characterise the lithologies in and around the deposit; propose a formation process for the deposit; and to characterise the alteration geochemistry, developing exploration vectors.

1 Introduction

The Perkoa Zn deposit is located in the Sanguie region of western Burkina Faso. The deposit is hosted within the Boromo Belt of the Birimian Supergroup (Leube et al. 1990), formed during a period of arc-volcanism in the Paleoproterozoic dated to ~2190-2160 Ma (Baratoux et al. 2015). The Birimian Supergroup is comprised of greenstone-granitoid assemblage which are made up of volcano-sedimentary belts separated by extensive tonalite-trondhjemite-granodiorite (TTG)/granitoid provinces or comparatively younger sedimentary basins (Fig. 1).

The Zn mineralisation at Perkoa occurs as a series of stacked, northeast-southwest striking massive sulphide lenses sitting subparallel to foliation. These are hosted within greenschist metamorphosed andesitic tuffs, interpreted as being overturned and dipping at ~70° towards the NW. A granodioritic body (dated 2175 ± 1Ma, U-Pb zircon; Schwartz & Melcher 2003) has intruded the area to the SE and field relationships described, suggest that it post-dates the initial mineralisation. The massive sulphide mineralisation is dominated by coarse sphalerite (30%), pyrite (25%), barite (10%), pyrrhotite (5%), magnetite (5%) and white mica (Schwartz & Melcher 2003). The deposit is a high-grade zinc deposit (averaging 14% Zn) but contains significantly less copper and lead (averaging 60ppm Cu and 0.1% Pb), elements commonly associated with other Zn rich massive sulphide deposits (Torben et al. 2018). The remaining measured and indicated resource of 4.85Mt current at a grade of 13.73% Zn with mineralisation still open at depth.

2 Methodology
A suite of 16 samples were selected from drill core, the open pit and the underground workings representing the key lithologies and mineralization styles. The spatial distribution of the samples reflected distance from the mineralization and the intrusive margin.

Polished sections were prepared for petrological description and mineral chemistry analysis by EDS by analytical-SEM. Whole rock geochemistry was determined at ALS using the propriety Complete Characterisation Package.

3 Results

3.1 Lithological observations

The study represents the first optical petrography description of the Perkoa lithologies. The main lithotypes identified are:

An andesitic lapilli tuff, characterised by a predominantly massive fine to medium grained rock with occasional lapilli sized clasts of two feldspar porphyritic material. The mineralogy is dominated by quartz, feldspar, biotite and chlorite and has been metamorphosed to approximately greenschist facies.

An andesitic-volcanoclastic characterised by a strong pervasive foliation and weaker crenulation with a pronounced banding. The bands are formed of quartz + plagioclase + mica + epidote + titanite + ilmenite and chlorite + quartz + epidote. Overall the mineralogy and fabric suggest a metamorphic grade of greenschist facies.

The most felsic volcanic lithology observed is the quartz eye rhyolite, which is characterised by the presence of large quartz phenocrysts in quartz-rich + plagioclase + white mica ground mass. This lithology maybe representative of a cryptodome facies/subvolcanic intrusion.

The most enigmatic lithology is described at site as a quartz exhalative, in hand specimen is typified by an absence of foliation, however under the microscope the textures and mineralogy suggest a re-worked felsic rock.

The late intrusion, which cross-cuts all the other lithologies, is a coarse grained equigranular leucocratic rock composed of plagioclase + quartz + biotite and Fe-oxides. In places the rock mass is overprinted by a haematitic alteration. This granitoid body shows no obvious deformation features.

The skarn-rocks, are characterised by a high magnetite content and frequent euhedral garnets which have undergone significant alteration to chlorite, possibly as a consequence of retrograde metamorphism.

A key texture observed is the differing fabrics of chlorite. Chlorite is ubiquitous through the more mafic members of the volcanic succession as foliation ‘controlled’ chlorite (Figure 2A). However, when approaching mineralization chlorite is observed to form a ‘parquet-like’ texture (Figure 2B). The massive sulphides in the observed intercepts are variable in texture at the macroscopic and microscopic scale. The lenses vary from massive sulphide (sulphide >90%) to a strongly layered sulphide dominated rock, to a clastic semi-massive sulphide containing clasts of host rock. Both lenses are dominated by sphalerite at the stratigraphic top of the lenses with increasing amounts of pyrite and pyrrhotite towards the stratigraphic base of the lenses. Minor chalcopyrite is observed at the base of the lens.

Figure 2. Transmitted light microscopy images of the two chlorite phases seen in the deposit. A) Elongate pervasive chlorite aligning with chlorite B) Chlorite concentrated into bands displaying a parquet-like appearance and located proximal to ore

3.2 Whole rock geochemistry results

Major element distributions suggest that there has been significant elemental mobilization due to both hydrothermal alteration and metamorphism (regional and contact). However, initial use of conventional major element classification plots, such as TAS (Maitre 1989), R1-R2 (De La Roche et al 1980) and the Jenson Cation plot (Rollinson 1993) show the data to form coherent trends from basaltic andesites to anodesites to rhyolites.

Using trace element based classifications diagrams (the Th-Co plot, the modified Winchester-Floyd plot and the (Zr/TiO2)/SiO2 the samples consistently plotted in the basalt-basaltic andesite fields with the high silica samples plotting as rhyolites. In the Y/Zr plot of MacLean and Barret 1993 the suite of samples show a coherent trend within the calc-alkaline field. Overall the REE patterns when normalized show elevated light REE compared to the heavy REE with a flat to positive Eu
anomaly. This steep LREE, flat HREE pattern is consistent with those expected from a volcanic-to-back arc environment.

The effects of hydrothermal alteration were further evaluated using the Alteration Box Plots (Large et al 2001) which showed that where the majority of the samples plotted within the least altered andesite basalt box, some samples, including those rich in sulphide trended towards a chlorite-carbonate-pyrite index (CCPI) = 100. When elements are plotted for the same lithology on the basis of distance to mineralization, some elemental mobility is evident. However, this appears to be largely a consequence of dilution due to increasing sulphide content in the footwall.

3.3 Mineral chemistry results

Chlorite compositional data collected by EDS shows clear variation with distance from ore. As described above chlorite is observed as being related to the metamorphic fabric and as the parquet-like texture related to a hydrothermal event. The chlorites of hydrothermal origin are Fe-rich chamosites whereas the chlorites related to the regional metamorphism are more Mg-rich towards the clinochlore end member (Fig. 3).

EDS analysis of the garnets from the skarn-rocks of the open pit showed that the skarn is typified by Mn-rich garnets close to the spessartine end member; whereas garnets, where present, away from the contact aureole are typically closer to the almandine end member composition.

Fig. 3: Plot of iron and magnesium content in individual chlorite crystals from throughout the deposit. Insets: S.E.M spectra for end compositions of the two chlorite phases

4 Discussion

4.1 Ore formation

The following characteristics support a VMS origin for the Perkoa sulphide bodies: Massive to semi-massive sulphide lenses with variable textures, the intimate spatial and temporal relationship of the sulphide lenses with a sea floor deposited rhyolitic to basaltic composition volcanic succession.

The two lenses, although formed by the same hydrothermal system are proposed to have formed in different environments. The stratigraphically lower lens is interpreted as having formed in the paleo-subseafloor, while the stratigraphically higher lens is thought to be exhalative and to have formed on the paleo-seafloor.

Field observations from the open pit suggest that the main conduit to the hydrothermal, with at least two stages of activity causing for the separate lenses and environments. The ‘quartz exhalative’ lithology, which is located stratigraphically above the lenses, is suggested to have acted as a cap facilitating preservation of the sulphide lenses.

4.2 Implications of skarn formation

Field and geochemical observations suggest that the skarn event, related to the emplacement of the late granite, overprints the altered HW rocks of the deposit, redistributing mobile elements such as manganese which was previously concentrated during the VMS-style mineralizing event. The main effects skarn formation has on the lenses are: The recrystallisation of sphalerite to marmatite; deflection of the lenses to follow the geometry of the intrusion boundary and; the re-mobilisation and recrystallization of the barite and sulphide mineralization in the overprinting skarn facies.

4.3 Alteration

Three main alteration assemblages/products are observed throughout the deposit, varying with distance from ore. These are summarised below in Table 1.

<table>
<thead>
<tr>
<th>Alteration</th>
<th>Spatial Distribution (footwall)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorite-Quartz-Magnetite</td>
<td>Proximal</td>
<td>Large, interlocking euhedral Quartz crystals with intergranular chlorite and magnetite. Bands of concentrated chlorite observed with a parquet-like texture with minor sulphides and magnetite.</td>
</tr>
<tr>
<td>Amphibole-Chlorite-Epidote</td>
<td>Intermediate</td>
<td>Vein controlled alteration with elongate amphiboles seen wrapping round clasts composed of chlorite + epidote + sulphides (minor)</td>
</tr>
<tr>
<td>Sericite</td>
<td>Intermediate-Distal</td>
<td>Destruction of plagioclase crystals forming needle-shaped crystal of sericite. Seen intergrowing with chlorite.</td>
</tr>
</tbody>
</table>

These are interpreted as being related to the fluid-rock ratio in different areas of the system. Proximal to mineralisation the fluid-rock ratio is thought to be high causing all elements to be stripped and only quartz being able to crystallise into large interlocking crystals and chamosite from the iron rich fluids. Further from the mineralisation the fluid-rock ratio is assumed to be lower and constrained to fractures within the rock resulting in the formation of iron rich amphibole veins which have incorporated clasts of chlorite and epidote. Classic sericitic alteration is seen and linked to the destruction
of plagioclase, the intensity of sericitization increases as you move further from mineralisation.

5 Implications for ongoing exploration

The below results from this study can be applied in exploration vectoring both at Perkoa and regionally:

- Distinguishing the two different chlorite end members in order to identify the presence of a hydrothermal system. This can be achieved using a combination of analytical field techniques such as XRF, FT-IR-based techniques and “Field portable” XRD.

- The identification of Eu anomalies within the majority of massive sulphide samples and the quartz exhalative sample. This shows Eu anomalies are related to exhalative material so a relative enrichment in Eu could identify exhalative horizons through the succession which ore could have formed on.

- Depletion of elements is a broad scale feature that can act as a vector towards mineralisation. Many major oxides (Na₂O, P₂O₅, TiO₂, CaO) show depletion with increased proximity to ore, allowing for interval core sampling to show relative position in FW alteration and indicate if mineralisation is becoming closer or further downhole.

- LREE in the hydrothermal fluid are slightly mobile and are identified as being depleted with increased proximity to the centre of the system. Therefore the ΣLREE can be used to show proximity to ore.

- An enrichment of Ba and Mn in the HW rocks can be used to identify potential hydrothermal systems from the HW side.

6 Conclusions

The mineralisation is hosted within a bimodal felsic volcanic succession comprised of a coherent volcanic andesite with periodic pyroclastic flows at the base and less coherent andesitic clastic tuffs at the top of the sequence. The majority of the mineralization is hosted by the upper andesitic clastic tuff. mineralisation formed within stratigraphically above.

Post mineralisation, the succession was affected by two metamorphic events. A regional metamorphism occurred first, followed by a contact metamorphic event associated with granotoid intrusion.

Four main hydrothermal alteration features are identified:

1. Proximal to ore: Chlorite + magnetite + quartz
2. Intermediate to ore: Amphibole-rich veins surrounding clasts of chlorite and epidote are observed crosscutting foliation.
3. Intermediate-distal to ore: Destruction of plagioclase to form sericite observed with increasing amounts of sericite seen as distance to mineralisation increases.
4. Throughout succession: replacement of titanite by ilmenite as an accessory phase.

Combining the above results with field observations it is concluded that the Perkoa Zn resource is a regionally metamorphosed bimodal felsic VMS-style deposit which has then been affected by a later contact metamorphic and metasomatic event associated with the intrusion of the cross-cutting granotoid.

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References


Rare earth elements in ferriferous crusts of the Semenov modern submarine hydrothermal massive sulfide cluster (13°31´N, Mid-Atlantic Ridge)

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Abstract. The Semenov modern submarine hydrothermal massive sulfide cluster, associated with peridotites and basalts, was discovered on the 32nd scientific cruise (2009) of the Russian R/V Professor Logachev by the Polar Marine Geosurvey Expedition (PMGE) in collaboration with VNIIOkeangeologia, Saint Petersburg. This work presents the results of mineralogical and chemical investigation of ferriferous crusts of the Semenos-2, -4 and -5 modern submarine sulfide fields (Mid-Atlantic ridge). The total REE content in the ferriferous crusts of the Semenov-2, -4, -5 (ΣРЗЭ – 16.16 – 103.11 ppm) is higher than the total content of REE in sulfides from the hydrothermal fields of the Mid-Atlantic Ridge and lower than in the ferromanganese deposits of Atlantic and Pacific oceans. The ferriferous crusts of the Semenov cluster are similar in the chondrite-normalized REE distribution patterns of sulfides and hydrothermal fluids from modern submarine hydrothermal fields of the MAR (positive Eu anomaly, Eu_an – 1.27-15.98), and the ferromanganese deposits of Atlantic and Pacific oceans (negative Ce anomaly, Cean – 0.18–0.89). The negative Ce anomalies testify to the formation of crusts during the sub-oxidative diagenesis.

1 Introduction

The ferriferous deposits (crusts) associated with modern submarine hydrothermal systems, formed as a result of underwater transformations of sulfide ores, characterized by increased or decreased contents of REE from sulfides and seawater. The study of the chemical composition of ferriferous crusts allows us to characterize the conditions of their formation and to answer the question of what type of sediment they are: hydrothermal, hydrogenic, or is it the oxidation product of sulfide ores. For this purpose, we studied the contents of rare earth elements in the ferriferous crusts of the Semenov-2, -4, -5 at Mid-Atlantic Ridge (MAR).

2 General description

The Semenof sulfide edifice cluster is related to an Oceanic core complex (OCC) at 13°30´N on the Mid-Atlantic Ridge (MAR) (Cherkashev et al. 2013; McLeod et al. 2009). The sulfide cluster (Semenov-1, -2, -3, -4, and -5) are located on the hydrothermally altered (serpentinized and talc-replaced) peridotite and basalt, including fresh pillow lavas with well-preserved quenched glasses, with rare gabbroids, plagiogranite, tonalite, and diorite (Beltenev et al. 2009, Pertsev et al. 2012), composing a rise (OCC massif) with a height of 850 m above the seafloor on the western side of a rift valley at a depth of 2500–2800 m below sea level (bsl). The active Semenov-2 field is associated with the hydrothermally altered basalts at a depth of 2480–2750 m bsl. The Semenov-2 is located along a ridge-parallel fault scarp bounding a local depression. This field shows several hydrothermal mounds, three of which are actively venting (Michaelangelo, Ash Lighthouse, and Yellow Submarine). The Semenov-4 site is located on the eastern slope of the OCC massif at depths from 2560 to 3020 bsl. This field is associated with basalt. The field size is 2700 x 1600 m. The Semenov-5 site is located on the central part of the OCC massifs at depths from 2160 to 2340 m bsl. The field size is 700 x 500 m. The Semenov-5 is associated with serpenitized peridotite and basalt (Escartin et al. 2017).

Chalcopyrite, isocubanite, wurtzite are major sulfides in the edifices of the Semenov-2; sphalerite pyrite, marcasite, and covellite are minor minerals. Galena, pyrrhotite, native gold are rare. Opal, barite, and aragonite were found as well (Melekestseva et al. 2010). Pyrite and marcasite are major sulfides in the edifices of the Semenov-4 and -5 fields; chalcopyrite and hematite are minor minerals. Sphalerite, isocubanite, bornite, and pyrrhotite Barite, quartz, anhydrite, and aragonite were found as well (Bortnikov et al. 2014).

Ferriferous deposits of the Semenov-2, -4 and -5 modern submarine sulfide fields are composed of irregularly porous reddish- or brown-dark, orange-brown, buffy aggregates. Goethite and hematite are major minerals, atacamite, barite, quartz are less abundant. Rhodochrosite, cristoballite, aragonite, siderite, calcite, kaolinite, ilite, chlorite nontronite, pyrite, chalcopyrite are rare. Hematite occurs as thin veinlets in crusts. In places, atacamite overlie, as 0.5- to 1-mm layer, ferriferous crust fragments. Atacamite occurs as zonal veinlets as well. An outer zone of these veinlets consists of finely-crystalline atacamite, aggregates of atacamite crystals (1 – 2 mm) occur in an inner zone. Dark-green atacamite crystals (0.5 – 1 mm) line the surface of cavities in porous ferriferous crust.
3 Samples studied

Sample 32L323 was taken from Semenov-2. Samples 32L373/1 and 32L355/3b were taken from Semenov-5. Samples 32L349/2; 32L353/1; 32L354/2; 32L358/1; 32L358/2, 32L359/1 and 32L357/4 were taken from Semenov-4. All samples were collected during the 32nd (2009) cruise of the R/V Professor Logachev.

4 Analytical procedure

Concentrations of rare earth elements were determined by ICP-MS. Measurements were performed at the VIMS (Moscow, Russia) on a Inductively Coupled Plasma Mass Spectrometer ICP Elan-6100 («Perkin-Elmer», USA) with techniques HCAM № 499-А3С/МС and HCAM № 509-МС.

5 Results

The total REE content in the ferriferous crusts of the Semenov-2, -4, -5 is $\Sigma$REE = 16.16 – 103.11 ppm. Contents of REE in the ferriferous crusts are presented in the chondrite-normalized REE distribution patterns in figure 1. The maximum concentrations of REE ($\Sigma$REE = 103.11 ppm) were established in the ferriferous crusts of Semenov-4. The ferriferous crusts of the Semenov cluster are enriched in LREEs ($\Sigma$LREE/$\Sigma$HREE = 2.46 – 5.05). The REE content in the ferriferous crusts of the Semenov cluster is higher than in the sulfides of the Broken-Spur, TAG, Rainbow and Irinovskoe hydrothermal fields and lower or closer with the total REE contents in the ferromanganese deposits (FMD) of the Ashadze-1, Logachev-2 and the Fersman seamount. The REE distribution patterns for all samples from the Semenov cluster show a positive Eu anomalies. Sample 32L323 from the Semenov-2 field demonstrates the smallest Eu anomaly.

The Chondrite normalized REE distribution patterns (Taylor and McLennan 1988) for the sulfides and the hydrothermal fluids of the Broken-Spur, TAG, Rainbow and Irinovskoe hydrothermal fields and lower or closer with the total REE contents in the ferromanganese deposits (FMD) of the Ashadze-1, Logachev-2 and the Fersman seamount. The REE distribution patterns for all samples from the Semenov cluster show a positive Eu anomalies. Sample 32L323 from the Semenov-2 field demonstrates the smallest Eu anomaly.

Distinctive characteristics of the samples of the Semenov cluster are a low negative Ce anomaly and positive Yb anomaly. It is interesting that the REE distribution patterns for the ferromanganese deposits in the Atlantic and Pacific oceans show a negative Ce anomaly, whereas the Eu anomaly is marked by virtually neutral values in the ferromanganese deposits Atlantic and Pacific oceans (Fig. 1).

6 Conclusions

The ferriferous crusts of the Semenov cluster are similar in the total REE content and chondrite-normalized REE distribution patterns to sulfides and hydrothermal fluids from modern submarine hydrothermal fields of the MAR, and the ferromanganese deposits of Atlantic and Pacific oceans. The samples of the ferriferous crusts of the Semenov cluster are characterized by more or less prominent negative Ce anomalies. In the case of low total REE content, the above property can testify to the formation of crusts during the sub-oxidative diagenesis (Usui et al. 1997).

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References


Mineralogical zoning within the Freiberg epithermal Ag-(Au)-Pb-Zn-Cu system, Germany

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Abstract. The Freiberg epithermal system comprises numerous hydrothermal veins with rich Ag-(Au)-Pb-Zn-Cu mineralisation. Even after more than 800 years of extensive mining, substantial resources remain in the northern sub-districts. This area is subject to recent exploration activity. Preliminary petrographic data of two vertical profiles from the northern part of the district are presented and a new model for the district-scale zoning is proposed. The highest Ag grades occur in Ag-Sb-S-quartz veins and seem to systematically occur above an Ag-Sb-S-Carbonate stage and below Sb-S-quartz mineralisation. This high-grade Ag mineralisation is relatively distal, shallow, and abundant in the northwest sector of the Freiberg district. This, and similar insights may be used to develop new exploration vectors for the Freiberg district.

1 Introduction

The Freiberg district in the eastern part of the Erzgebirge (Germany) hosts one of the largest epithermal Ag-Zn-Pb-Cu-(Au) systems in Europe. In excess of 5600 t of Ag (~180 Moz) were extracted during more than 800 years of active mining. Historical mining focused mainly on the central district (Halsbrücke, Freiberg and Brand-Erbisdorf), while most of the mines in the peripheral sectors (Bräunsdorf, Kleinvoigtsberg, and Siebenlehn) were significantly smaller but richer in Ag (Müller 1901). Mining ceased in 1969 due to political, technological and economic reasons, leaving substantial resources unexploited.

Epithermal veins of the Freiberg district are polystadial with distinct spatial variations within each stage, resulting in an overall increase of Ag at the expense of base metals from the centre to the peripheral sectors. Silver grades reported from veins of the peripheral sectors reach up to 2000 g/t (Müller 1901; Seifert and Sandmann 2006), and are therefore the prime target of recent exploration. During the last century, only few scientific studies on the Freiberg district were carried out, which is why the genesis of these hydrothermal veins remains poorly understood.

Recent studies (Bauer et al. 2019; Burisch et al. 2019; Ostendorf et al. 2019) on a limited number of samples from the Freiberg district provide valuable insights into the genesis of the epithermal system. However, the processes causing the district-scale variations in mineralogy remain unclear. Understanding these ore-forming processes on the scale of the entire district is key to efficient exploration targeting.

Consequently, this study focuses on the historical mining camps of Kleinvoigtsberg and Reinsberg in the northern sub-district. The silver grades are relatively high (100 to 2000 g/t), and recently, up to 2.27 g/t of gold was reported from a hydrothermal quartz vein near Reinsberg (Globex Mining Enterprises 2018), generating further interest in this particular sub-district.

Petrographic investigation of 25 polished thick sections was carried out to characterize the zonation of the vein mineralisation. This detailed petrographic investigation will be complemented by whole-rock geochemistry, electron microprobe analyses, microthermometry and LA-ICP-MS analysis in order to understand district-scale spatial and temporal mineralogical and geochemical zonation (vertically and horizontally) of the Freiberg epithermal system.

2 Geological setting

The Erzgebirge extends about 145 km in a NE-SW direction along the Czech-German border and is bound by the Elbe zone in the Northeast, the Gera-Jachymov zone in the Southwest, and the Eger Graben in the southeast. The Erzgebirge formed as part of the Saxo-Thuringian zone during the Variscan orogeny following the collision between Gondwana and Laurussia (Kroner et al. 2007; Kroner and Romer 2013). It is an erosional window exposing a stack of Cadomian and Palaeozoic units, which were metamorphosed during the Variscan orogeny (Romer et al. 2010). Peak metamorphism (c. 340 Ma) was followed by wide-spread late-collisional granitic magmatism (Kroner et al. 2007). Subsequently, the break-up of Pangea led to Permian rifting (c. 310 to 275 Ma) and the intrusion of rhyolite dykes and small granitic intrusions (Förster et al. 2007). The most recent period of exhumation and erosion of the area is related to the Eger Graben rifting (~15-13 Ma; Ziegler and Dézes 2005; Pächen and Walter 2011).

The Freiberg district is located in the eastern part of the Erzgebirge and largely consists of a lens-shaped unit of para- and orthogneisses (Fig. 1). In the northwest, the dome is overlain by mica schists and phyllites forming a structurally more complex area (Baumann et al. 2000). The units in the Freiberg district are cross-cut by numerous epithermal veins with a preferred N-S to NE-SW orientation (Baumann et al. 2000).
3 Hydrothermal veins of the Freiberg district

The epithermal system of the Freiberg district comprises two major stages of vein mineralisation. Stage 1 consists of polymetallic sulphides with quartz. Stage 2 is dominated by Ag-Sb sulphides and sulfosalts accompanied by carbonates and quartz. (Müller 1901; Baumann et al. 2000; Bauer et al. 2019; Burisch et al. 2019).

The veins exhibit a systematic vertical zonation and lateral variability with respect to mineralogy, geochemistry, and fluid inclusion characteristics. In general, stage 1 is most dominant in the deepest parts of the veins and the modal abundance of stage 2 gradually increases upwards (Müller 1901; Bauer et al. 2019; Burisch et al. 2019).

The centre is dominated by stage 1 Fe-Zn-Cu-quartz mineralisation. Fluid inclusion studies of stage 1 yield homogenisation temperatures ($T_h$) from 300 to 340°C and salinities up to 6 wt.% eq. (NaCl). Heterogeneously trapped fluid inclusions and distinctive quartz textures (bladed calcite, lattice textures) indicate fluid boiling. CO2 was only detected in the oldest fluid inclusion assemblages with relatively high homogenisation temperatures indicating CO2 loss in the early stages of mineral precipitation (Bauer et al. 2019).

The peripheral sub-districts are characterized by a significantly higher amount of stage 2, which continues to a greater depth than in the centre (Müller 1901; Baumann et al. 2000). In Bräunsdorf, the abundance of carbonates decreases upwards. Furthermore, in the shallower sections of the veins the amount of Sb-sulphides strongly increases at the expense of Ag- and Ag-Sb-sulphides. Fluid inclusion data from the Bräunsdorf sector show that stage 1 formed at ~300°C and stage 2 formed at temperatures from 275 to 180°C. Both stages are associated with low- to intermediate sulphidation, low salinity fluids with 0.6-4.0 wt.% eq. (NaCl). Evidence for boiling is not reported, most likely because initial boiling occurred earlier at deeper levels. The main mineral precipitation mechanism is assumed to be cooling (Burisch et al. 2019).

4 Sampling

60 samples were selected from the scientific collections of the TU Freiberg and from the field. Two veins were studied, 1) Peter Stehender, Kleinvoigtsberg, and 2) Reinsberger Glück Morgengang, Reinsberg, since samples over a large vertical profile were available. A Carl Zeiss Axio Imager M1m light microscope was used to investigate the age relationships between minerals and to characterize textures.

5 Results and discussion

The vertical profiles of Kleinvoigtsberg and Reinsberg are very similar, regarding both textures and mineralogy. The investigated samples include different mineralisation stages which can be classified according to their mineral assemblages: Stage 1 comprises base metal sulphides, including arsenopyrite, pyrite, sphalerite, and galena, with quartz as the main gangue mineral (Fig. 2a). Stage 1 is followed (and partly replaced) by base metal sulphides accompanied by Ag-sulfosalts, carbonate and quartz (Fig. 2b). In several samples containing stage 2, quartz is dominant and carbonate is completely absent or occurs subordinately (Fig. 2c). Well-developed textures like crustiform and lattice bladed quartz can be recognized in various samples (Fig. 2d and e). Ivory-coloured carbonate is often present as cavity infill on flamboyant or euhedral quartz (Fig. 2f). Brecciated vein quartz exhibiting pronounced lattice bladed textures have been
documented. Sulphide minerals are absent in these samples. This mineralisation style is outcropping near Reinsberg and has not previously been recognised in the Freiberg district. It is interpreted as the latest vein infill.

Both stage 1 and 2 are present at all levels of the sampled profile. Hydrothermal breccias consisting of hydrothermal quartz, altered host-rock and fragments of older vein infill can be observed in the upper levels of the veins.

Based on petrographic observations and data from Burisch et al. (2019), stage 2 can be divided in 4 substages. Stage 2A is the most carbonate-rich and contains high amounts of galena and sphalerite as well as tetrahedrite and freibergite (Fig. 2b). Stage 2B is characterised by Ag-Sb sulfosalts with fine-grained quartz and only minor amounts of carbonate, galena, and sphalerite (Fig. 2c). Besides Ag, stage 2B is also associated with elevated Au contents (up to ~9 g/t; Seifert and Sandmann 2006). Stage 2C is dominated by berthierite and stibnite, accompanied by quartz. Stage 2C has not been identified in Reinsberg and Kleinvoigtsberg. Stage 2D is characterised by late-stage quartz with lattice textures. Preliminary results show that these quartz veins contain up to ~2.5 g/t Au.

5.1 Lateral zonation

The previously introduced paragenetic stages show a distinct and systematic zoning (Fig. 3). Stage 1 with base metal-rich sulphides (Fe, Sn, Cu, Zn) is most prominent in the centre of the district (Müller 1901; Bauer et al. 2019). Shallow and more distal, the modal abundance of stage 2 generally increases. Stage 2A is most prominent in Brand-Erbisdorf near Freiberg (in-between the centre and the peripheral sectors), but also exists in Reinsberg, Kleiinoigtgsberg and Bräunsdorf. Subsequently, Ag-sulfosalts with only minor amounts of carbonate prevail (Stage 2B). Even more distal and shallower, the mineralogy of the vein changes to stage 2C dominated by Sb-sulphides (Burisch et al. 2019). The shallowest and most distal part of the epithermal system is marked by Stage 2D.

The formation of the Eger Graben during the Cenozoic resulted in asymmetric uplift and erosion of the Freiberg district (Pälchen and Walter 2011). The zonation pattern at the surface is most likely a direct result of asymmetric erosion caused by increasing uplift towards the southeast combined with the primary mineral zonation. Units exposed at the surface in the centre of the district formed at deeper crustal levels than the units in the northwest. As a consequence, the majority of the shallow mineralisation is preserved in the north and northwest, with the most shallow parts of the epithermal system near Reinsberg (Fig. 3).

5.2 Fluid evolution

Temporal and spatial changes in the mineralogy indicate a distinct physical and chemical evolution of the associated ore fluid. Decreasing T_s in fluid inclusions from the central district to the peripheral sectors, both related to stage 1 indicates an overall spatial cooling trend (Bauer et al. 2019; Burisch et al. 2019). Furthermore, a systematic decrease in T_s from stage1 to stage 2C (290 to 200°C; Burisch et al. 2019) indicates not only a spatial but also a temporal cooling trend. Besides cooling, the presence of CO_2 in pre-boiling and its absence in post-boiling fluid inclusion assemblages (Bauer et al. 2019) as well as the sudden occurrence of carbonates in stage 2A is evidence for CO_2 degassing. CO_2 degassing has a major effect on the ore fluid’s pH (White and Hedenquist 1995), and most likely initiated Ag deposition, although highest grades occur more
distal than the major degassing horizon. In those Ag-rich parts, cooling is most likely the major ore-forming mechanism (Burisch et al. 2019). Gold occurs late and distal in the paragenetic sequence, however the controlling factors for Au precipitation in the Freiberg district are not yet understood.

5.3 Implications for exploration

Understanding processes which cause the distinct mineral zoning facilitates the development of robust exploration vectors by translating the mineral system analysis approach to mappable criteria. From the preliminary data we can assume that the highest silver grades (stage 2B) are spatially confined by the shallow/more distal Sb-sulphide assemblage (stage 2C) and deeper/more proximal Ag-Sb-carbonate assemblages (stage 2A).

6 Conclusion

The Freiberg district represents a large low- to intermediate-sulphidation epithermal system with a resource potential for Ag, Au, and base metals. The mineral zonation exposed in the Freiberg district is a consequence of a physical and chemical evolution of the ore forming fluid and differences in the present-day erosional level.

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References


Figure 3. Schematic cross section showing the district-scale zoning and possible mineral precipitation mechanisms. The relative positions of localities are indicated with abbreviations: Freiberg (FG), Bräunsdorf (BD), Kleinvoigtsberg (KVB), and Reinsberg (RB).
Genesis of the vein-type Niederschlag fluorite deposit in the Erzgebirge, Germany

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Abstract. The Niederschlag fluorite vein deposit in the western part of the Erzgebirge has been actively mined since 2013. In order to approximate constraints on the hydrothermal mineralisation, a comprehensive study on the mineralogy, mineral paragenesis, fluid inclusion compositions and the geochemistry of the two identified hydrothermal fluorite stages was carried out. These two stages constitute the bulk of resources of the Niederschlag deposit. The older fluorite I mineralisation is associated with abundant quartz and forms complex breccia textures. Fluorite II – and closely associated barite and occurs as coarse crystalline and massively-textured or banded open space infill. Microthermometric analyses of fluorite II suggests fluid mixing as the main ore-forming process. Due to obvious similarities to many other fluorite-barite-Pb-Zn-Cu vein deposits in Central and Western Europe we relate the origin of fluorite II to rifting associated with the Mesozoic opening of the northern Atlantic.

1 Introduction

The Erzgebirge/Krušné hory metallogenic province hosts numerous ore deposits, which have been mined since medieval times (Baumann et al. 2000). The fluorite-barite deposit of Niederschlag in the Erzgebirge/eastern Germany is actively mined for fluorite and barite since 2013 and is operated by Erzgebirgische Fluß- und Schwertschmelztiegel GmbH (EFS).

The Niederschlag deposit was first discovered during uranium exploration by the SDAG Wismut in 1954 (Kuschka 2002). Despite extensive exploration and active mining, modern geochemical data for this deposit is entirely missing. To fill this gap, we carried out petrographic, microthermometric and geochemical studies on samples from two distinct fluorite stages of the Niederschlag deposit. Both mineralisation stages are economically mined and constitute the bulk of the resources of the mine. Based on this data a preliminary genetic model is proposed.

2 Geological Setting

2.1 Regional Geology

The Niederschlag deposit is hosted by metamorphic Variscan basement units of the western Erzgebirge, which formed at 400-340 Ma due to the collision of Gondwana and Laurussia (Kroner and Romer 2013). The metamorphic basement units of the Erzgebirge were subsequently intruded by post-collisional granitoids (320-280 Ma), as well as rhyolite and lamprophyre dikes (Romer et al. 2010; Seifert 2008).

The host rocks of the Niederschlag fluorite deposit (Fig. 1) comprise gneisses, mica schists and other meta-sedimentary units. Besides the metamorphic units, the F-Li enriched Eibenstock granite (~320 Ma intrusion age) (Fürster et al. 1999; Tichomirowa and Leonhardt 2010) is present in the vicinity of the deposit; it has been estimated to also occur ~1000 m below the present-day surface (Kuschka 2002).

Apatite fission track thermochronology suggests a 2-3 km thick marine sedimentary cover was present above the metamorphic host units of the Niederschlag deposit during early Mesozoic times (Wolff et al. 2015).

Uplift and erosion related to the Eger-rift (starting during the Cenozoic) led to a deep excavation of the previously buried basement units (Pälchen and Walter 2012). This event is also associated with the intrusion of phonolite dikes and plugs that crosscut both host rocks and fluorite veins. Intrusions of phonolite dykes at the Niederschlag mine are known to extensively modify hydrothermal vein-type fluorite mineralisation. Relative age relations thus suggest that all fluorite mineralisation postdates peak metamorphism, but predates the intrusion of phonolite dykes.

2.2 Hydrothermal mineralisation

Polystadial hydrothermal mineralisation is bound to the Scheibenberg-Niederschlag-Kovářská-fault, an NNW-SSE striking fault system, which extends in strike direction across the German-Czech border.

The thickness of the sub-vertical vein is discontinuous (pinch-and-swell) and varies between 4 and 12 m (Baumann et al. 2000).

The shallow part of the deposit hosts uranium and five-element mineralisation associated with carbon-rich horizons (Guilcher et al. 2019). At greater depths those are absent and the same vein structure comprises multiple generations of fluorite, barite, quartz and minor base metal sulphides. Two distinct fluorite generations are recognised. One is accompanied with quartz (fluorite I), the other one (fluorite II) is associated with barite and sulphides (Kuschka 2002).
Figure 1. Simplified geological map of the area around of the Niederschlag fluorite-barite mine. Mineralisation occurs mainly on the Scheibenberg-Niederschlag-Kovářská-fault zone (SNK) (modified after Baumann et al. 2000).

3 Methodology

Fluorite samples were selected from underground workings (5.1 level south; 650 m a.s.l) and from drill cores of a historical exploration program. Double-polished thick sections (~250 µm) were prepared for fluid inclusion analyses.

Microthermometric analyses were carried out with a Linkam THSMG600 fluid inclusion stage combined with an Olympus BX53 microscope. Synthetic standards of CO₂-H₂O- and H₂O inclusions were used for calibration. Petrographic descriptions are classified as primary, secondary, pseudo secondary or isolated fluid inclusions (van den Kerkhof and Hein 2001). Liquid-vapour ratios were estimated by image analysis. To ensure reproducibility each phase transition of each inclusion was measured three times. Fluid inclusions with signs of post entrapment processes were excluded from the data. Based on the presence of hydrohalite, salinities were calculated according to Steele- MacInnis et al. (2011) for the Na-Ca-Cl-H₂O-System.

4 Results

4.1 Petrographic investigations

Fluorite occurs in two distinct generations (Fig. 2). The older fluorite generation (fluorite I) occurs predominantly along the selvages of the vein structure; it is accompanied by quartz and chalcedony. Besides fluorite and quartz/chalcedony, no other associated minerals were identified. Stage 1 mineralisation (Fig. 3) typically forms multiple sequences of thin, irregularly shaped bands of fluorite and quartz that comprise irregular masses of up to several m thickness. Host rock-brecciation, mostly as cockade breccia (Frenzel and Woodcock 2014), is commonly observed. Fluorite often forms botryoidal or radiating aggregates; prismatic crystal shapes are also observed. Crystal sizes range from very fine-grained to a few cm in size. The bulk of fluorite exhibits green and purple colours, accompanied by subordinate yellow to whitish fluorite.

The second fluorite generation (fluorite II) is developed on the same fault structure where it cross cuts fluorite I and is thus distinctly younger. Fluorite II is accompanied by barite, base metal sulphides and quartz. Barite is often intimately inter-grown with minor amounts of fluorite II and quartz pseudomorphs after barite occur. Chalcopyrite, galena and tetrahedrite are the most abundant sulphides. The fluorite is mostly blue and green in colour and of cubic shape. Vugs and druses abound within the massive fluorite II.

Figure 2. Exposure of fluorite I with quartz (Fl I+ Qz) and fluorite II (Fl II) and barite (Ba) mineralisation, level 6.1 south, Niederschlag mine. Note crosscutting phonolite (Ph) dyke.

Figure 3. a. Typical Stage I assemblage with fluorite I breciated and cemented by chalcedony in contact with strongly silicified and altered host rock (SHFB-Nds-01). b. Fluorite II accompanied by barite (SHNds P8).

4.2 Fluid inclusion investigations

Fluorite I and quartz of the first mineralisation stage did not host any fluid inclusions suitable for investigation. Fluorite II, in contrast, shows abundant fluid inclusion assemblages; these are of primary, pseudo-secondary and secondary origin with inclusions up to 100 µm in
size. Some inclusions showed evidence for post-entrapment modification; these were excluded from the data set. Two phase liquid-vapour inclusions dominate, but three phase liquid-vapour-solid inclusions are also observed. The solid phase appears greenish with irregular crystals shapes. The phase does not melt upon heating. The fluids show first melting (eutectic) temperatures around -50 °C typical for Na-Ca-Cl dominant fluids. Homogenisation temperatures are between 80 °C and 120 °C with salinities varying greatly between 19 and 27 % eq. w(NaCl+CaCl₂).

![Figure 4. Homogenisation temperature (in °C) versus total salinity (% eq. w(NaCl+CaCl₂)) including 54 analyses of two-phase inclusions in fluorite II. Data is summarized as fluid inclusion assemblages (FIA). The whiskers indicate the range not the error of the FIAs.](image)

5 Discussion and Conclusions

Preliminary petrographic and microthermometric data suggest that the two different fluorite generations are formed in contrasting fluid regimes.

Fluorite I is not accompanied by any sulphides/sulphates. This indicates that associated fluids were nominally S-free. Furthermore, intense host-rock alteration related to stage I suggests that water-rock interaction could have been an important ore-forming process. Comparable fluorite mineralisation is not reported from other fluorite districts in Europe and its relationship to late-variscan ore forming processes in the northern Atlantic ~140-40 Ma (Golonka and Bocharova 2000); an analogue to other hydrothermal rocks and the accompanied documents. This study is funded by the European social fund (ESF) and the Sächsische Aufbaubank (SAB).

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**References**


Ore-forming processes and mineral zoning in Ag-Bi-Co-Ni-As±U (five-element) veins of the Erzgebirge, Germany: new observations from the Annaberg district

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Abstract. Native metal Ag-Bi-Co-Ni-As±U (five-element) veins in the Erzgebirge host valuable resources of Co, Ni, and Ag. In recent times, these were primarily exploited for U closely associated with Co-Ni-Fe-arsenides. Today, the focus of exploration has shifted to Co, Ni, and Ag. For political and environmental reasons, the identification of Co-, Ni-, and Ag-rich zones with low concentrations of U will be of major importance. High-grade ore shoots in the Annaberg district are restricted to carbon-rich horizons within the gneissic host rock. Furthermore, a distinct vertical zonation is observed along the veins: U-rich mineralisation dominates the shallowest parts of the veins whereas Co-Ni-arsenides prevail below the U-rich zone. With increasing depth, the mineralogy of the veins changes to fluorite, barite, and small amounts of base metal sulphides. These geological observations provide important constraints for the five-element vein system in the Erzgebirge. Complemented by fluid inclusion analyses and thermodynamic computations, they can be used to understand the separation of arsenides and U minerals during ore formation.

1 Introduction

Hydrothermal Ag-Bi-Co-Ni-As±U veins are widespread in the Erzgebirge. Schneeberg, Annaberg, Marienberg, Schlema-Alberoda, Niederschlag, and Hartenstein are some examples of historical mining districts where such mineralisation occurs. In these districts, five-element veins were mined for Bi, Co, Ni, Ag between the 16th and the 20th century.

These so-called “five-element” veins are characterized by the presence of dendritic native Ag, Bi, and/or As followed by a succession of Fe, Co, and Ni arsenides (Burisch et al. 2017; Kissin 1992; Markl et al. 2016). Many five-element vein systems, especially those in the Erzgebirge, are also associated with substantial amounts of U mineralisation.

In the Erzgebirge, five-element veins have been extensively mined for Ag and Co from the 16th to the 19th century and were one of the major sources for U from 1945 to 1991 in the former GDR. Besides Co, Ag, and U, they contain significant amounts of Ni. Co and Ni are increasingly required for renewable energy technologies, in particular for energy storage (rechargeable lithium ion batteries; Crundwell et al. 2011).

The intimate association of Co and U significantly deteriorates the economic potential of five-element veins in the Erzgebirge for obvious environmental reasons. Therefore, exploration would have to target zones of Co-Ni mineralisation with no or negligible U content. In the Annaberg district, a distinct vertical zoning of U minerals and Co-Ni arsenides is observed. It is an example where the five-element association is spatially related to carbon-rich horizons in the host-rock. Understanding this mineral zoning may be used to identify preferred zones in five-element systems, which are rich in Co, Ni, and Ag, but poor in U.

In this study, we present preliminary petrographic observations of samples from the Annaberg district. Petrographic investigations will be complemented by fluid inclusion studies, geochemical analyses and thermodynamic computations. The ultimate goal is to understand how U, Ni, Co, and As fractionate in hydrothermal five-element systems.

2 The Annaberg district

2.1 Geological setting

The Annaberg district is located in the central part of the Erzgebirge. The Erzgebirge is an erosional window which comprises metamorphic and igneous rocks associated with the Variscan Orogeny (Kroner and Romer 2013). The district is situated in the ENE-WSW striking Annaberg-Marienberg anticline (Baumann et al. 2000). The predominant lithology is a muscovite-biotite paragneiss (“Annaberg-Marienberg” gneiss; Tichomirowa et al. 2012). Smaller lenses of orthogneiss (locally referred to as “Rogneiss”) are present in the NW of the district (Fig. 1). Both gneiss units were intruded by microgranites and Li-F granites occurring in the northwestern and central parts of the district. Tertiary basalts are locally present.
2.2 Hydrothermal mineralisation

Styles of hydrothermal vein-type mineralisation in the Annaberg district include Sn-quartz, polymetallic-sulphide-quartz, uraninite, fluorite-barite-Pb-Zn and five-element assemblages (Baumann et al. 2000). The past production of Co, Ag and U in the Annaberg district was 8700 t, 350 t, and 496 t respectively (Baumann et al. 2000). Here, we focus only on the younger (post-Variscan) types of mineralisation, which are all predominantly hosted by NW-SE to N-S trending fault systems (parallel to the Schlettau Fault System; Fig. 1). Although relative ages of the mineralisation stages can be inferred from cross-cutting relations, absolute ages of the different mineralisation styles are poorly constrained (Baumann et al. 2000).

The oldest post-Variscan stage of hydrothermal mineralisation (stage 1) comprises carbonate and pitchblende. This stage is preferentially present in the vicinity of carbon-rich horizons (Fig. 2). The timing of the mineralisation is vaguely constrained between 220 and 100 Ma by U-Pb geochronology of pitchblende (Baumann et al. 2000). Examples of major veins with carbonate-pitchblende mineralisation are “Uranus Flacher”, “Sina Flacher”, “Himmelsch Heer Stehender”, and “Merkur Stehender”. Stage 1 is followed by a younger fluorite-quartz stage, typically occurring on the same structures. Hematite, chaledony, and barite are even younger and mark stage 3. Stage 4 of mineralisation consists of fluorite, barite as well as subordinate quartz and base metal sulphides. “Glück Flacher” and “Gründonnerstag Spatgang” are the major veins that comprise abundant stage 3 and 4 mineralisation (Baumann et al. 2000).

The age and paragenetic position of Ag-Bi-Co-Ni-As-U mineralisation (stage 5) is not entirely clear. It is either younger or of the same age as stage 4. Approximately 160 veins with Ag-Bi-Co-Ni-As-U mineralisation are known in the Annaberg district. Some of the major veins in the district are “Erst Neu Glück”, “Heynitz Flacher”, “Himmelsch Heer Stehender”, and “Krönung Flacher”. The thickness of the five-element association is highly variable, ranging from 0.1 to 1m (Baumann et al. 2000). These veins are currently difficult to access.

3 Sampling and methodology

Approximately 50 samples were selected from the geoscientific collections of the TU Bergakademie Freiberg. The samples are from the Markus Röhling, Bäuerin, Altväter, Uranus, and Himmelsch Heer mines and cover a vertical profile of about 200m (Fig. 1). This vertical profile includes samples from 346m, 420m, 462m, 485m, 510m and 540m (depth given in meters above sea level). The petrographic description was done based on optical microscopy and scanning electron microscopy (SEM).

4 Vertical zoning

Historical mine records reveal that rich five-element mineralisation occurs in ore shoots where veins intersect carbon-rich horizons (locally referred to as “Schwebende” or “Schwarze Flöze”). These carbon-rich horizons, partly composed of graphite, occur erratically in the paragneisses, but are mostly present in the central and shallow parts of the district (Baumann et al. 2000).

Vein 303 is a well-documented example, which hosts U, Ag-Bi-Co-Ni-As, and fluorite-barite mineralisation and exhibits a distinct vertical mineral zoning. Carbon-rich horizons are restricted to the uppermost part of the vein and are slightly dipping towards SSE (Fig. 2). These carbon-rich horizons are hosting most of the U and five-element associations. In the upper horizon of the vein (around 50m) U minerals dominate with little irregular Co-Ni arsenide mineralisation whereas Co-Ni-arsenides prevail in the lower part of the carbon-rich horizons. Fluorite-barite veins with minor base metal sulphides are present over the entire structure, even below 300m above sea level where five-element mineralisation does not occur.

Uranium mineralisation occurs as veins and stockwork; pitchblende is the most common ore mineral. Ag-Bi-Co-Ni-As mineralisation occurs as veins and forms irregularly-shaped lenses and ore shoots in the vicinity of the carbon-rich horizons.

Very similar observations have been made at the Marienberg and the Niederschlag districts, located farther to the north-east and to the south of the Annaberg district, respectively (Baumann et al. 2000 and references therein).
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5 Results – Petrographic observations

Ag-Bi-Co-Ni-As associations occur late in the paragenetic sequence of the Annaberg district (stage 5). In the studied samples, the mineralisation consists of native Bi, Ag, As associated with Ni-Co-Fe arsenides, base metal sulphides, and Ag-bearing sulphides (Fig. 3). Gangue minerals are quartz and carbonates (mostly dolomite and calcite) as well as occasional fluorite.

Native metals (Ag and Bi) typically form dendritic textures, which are encapsulated by different types of arsenides (Fig. 4A). In most cases, earliest arsenide minerals consist of nickeline, rammelsbergite, and skutterudite (Fig. 4B and 5), which are followed by safflorite, loellingite, and gersdorffite. The arsenide stage is followed by sulphides namely proustite, pearceite, acanthite, sphalerite, chalcopyrite, and pyrite (Fig. 4C and 5). Late stage sulphides often replace native metals or overgrow the arsenides. U-bearing minerals (coffinite and uraninite) occur only subordinately and are coeval with loellingite and late stage sulphides (Fig. 4D and 5). Coeval gangue minerals are quartz and carbonates.

These observations are in agreement with petrographic observations of previous studies in well-documented districts such as Schlema-Alberoda, Niederschlag and Schneeberg where five-element veins occur (Hiller et al. 2008; Kuschka et al. 2002; Lipp 2003).
Figure 5. Paragenetic sequence of ore and gangue minerals observed in the samples of the Annaberg district.

6 Discussion and conclusions

As and U are both redox-sensitive elements (Markl et al. 2016). This is the apparent reason for the close spatial link between the carbon-rich horizons, that acted as redox barriers, and the U, and five-element mineralisation (Hösel et al. 1997). Although both elements are highly redox-sensitive, U- and arsenide-minerals seem to precipitate at different $\Delta$O2 – they fractionate – thus resulting in the observed spatial separation of U-dominated and As-dominated five-element-vein assemblages. A profound geochemical understanding of this fractionation process is key to the identification of Co-rich and U-poor zones within a given vein system.

Major questions that still remain unclear are: 1.) Is the trend from deeper arsenides to shallower U minerals a result of increasing or decreasing $\Delta$O2? 2.) Is the mineral zoning a consequence of a temperature gradient or the implication of different types of fluid? 3.) Is the ore fluid related to the U- and arsenide-minerals the same fluid that formed fluorite- and barite-rich assemblages at depth? 4.) Is the reducing agent actually graphite or methane hosted by the carbon-rich horizons?

We are planning to solve these questions with further petrographic studies, careful fluid inclusion work, and geochemical analyses (on Ag-Bi-Co-Ni-As mineralisation, and samples from the carbon-rich horizons) as well as thermodynamic computations.

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Micas $^{40}\text{Ar}^{39}\text{Ar}$ dating of hydrothermal events related with the post-orogenic W ($\pm$Sn), (Cu, Mo) mineralization from Borralha, Northern Portugal

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Abstract. Secondary mica minerals collected from the Santa Helena (W - (Cu) mineralization) and Venise (W-Mo mineralization) endogenic breccia structures were $^{40}\text{Ar}^{39}\text{Ar}$ dated. The muscovite $^{40}\text{Ar}^{39}\text{Ar}$ data yielded 286.8 ± 1.2 (±1σ) Ma (samples 6Ha and 11Ha) which reflect the age of secondary muscovite formation probably from magmatic biotite or feldspar alteration. Sericite $^{40}\text{Ar}^{39}\text{Ar}$ data yielded 280.9 ± 1.2 (±1σ) Ma to 279.0 ± 1.1 (±1σ) Ma (samples 6Hb and 11Hb) reflecting the age of greisen alteration (T~300ºC) where the W-disseminated mineralization occurs. The muscovite $^{40}\text{Ar}^{39}\text{Ar}$ data of 277.3 ±1.3 (±1σ) Ma and 281.3 ± 1.2 (±1σ) Ma (samples 5 and 6) also reflect the age of muscovite (selvage) crystallized adjacent to molybdenite veins within the Venise breccia. Geochronological data obtained confirmed that the W mineralization at Santa Helena breccia is older than Mo-mineralization at Venise breccia. Also, the timing of hydrothermal circulation and the cooling history for the W-stage deposition was no longer than 7 Ma and 4 Ma for Mo-deposition.

1 Introduction

The W ± Sn ore deposits in Europe are spatially associated to granites emplaced during syn-orogenic compression and post-orogenic extension of the European Variscan belt (EVC). The timing of W-mineralization geochronology across the EVC evolution is still poorly constrained due to the presence of multiple fluids with distinct origins and to a lack of integrated data combining mineralogical, chemical and isotope geochemistry either on tungstate or silicate neoformation from the hydrothermal alteration.

The main aim of this work is the $^{40}\text{Ar}^{39}\text{Ar}$ dating of mica specimens collected from the different locations and hydrothermal stages related to W- and Mo-mineralizations from the Borralha ore deposit, in order to estimate the age of alteration-mineralization event and the time of breccia structure formation.

2 Geology

The Variscan orogeny in the Iberian Peninsula was explained by an obduction–collision orogenic model (Ribeiro et al. 1990, 2007; Matte 1991). The final stages of the continental collision process occurred during the D3 deformation phase (316-310 Ma), where most of the granite intrusions and the associated thermal metamorphic peak are coeval with the D3 phase in the Central Iberian zone (e.g. Ferreira et al. 1987; Dias and Ribeiro 1995; Ribeiro et al. 2007). The magmatic activity generated voluminous granitoid batholiths, where the emplacement was, in most cases, controlled by major Variscan structures.

Figure 1. Geological map of the northern part of Portugal (Ferreira et al. 1987) and location of the W ($\pm$Sn), (Cu, Mo) ore deposit of Borralha, Gerês Mountains

The W ($\pm$Sn) (Cu, Mo) deposit of Borralha is located at the Northwest of the Iberian Peninsula near to the boundary between the Central Iberian Zone and Galicia Trás-os-Montes Zone, where different syn-orogenic Variscan granite-types intruding Paleozoic metasedimentary rocks were assigned: two-mica peraluminous (syn-D3) granites and biotite-rich (syn-D3) granites.

The ore deposit occurs at the contact between
metasedimentary formations and the syn-D3 porphyritic biotite granite (~315 Ma) known as the Borralha granite, and syn-D3 two-mica granites (~310 Ma) (Fig. 1).

Four evolving metallogenic stages associated with a magmatic - hydrothermal evolution of the post-D3 Gerês granite were recognized (Noronha 1988): (i) Mo, (W) at Bouzadrago (Galicia-Spain); (ii) W, Sn (Cu,Mo,Bi) at Las Sombras (Galicia-Spain), Carris and Borrageiro; (iii) W, (Cu,Mo,Bi,Sn) at Penedos; and (iv) W (± Sn), (Cu,Mo,Bi) at Borralha.

Assumed to be related to the concealed Gerês granite, the Borralha ore deposit is the second most important W deposit of Portugal after Panasqueira. The ore was exploited from 1903 to 1985 for wolframite, scheelite, and argentiferous chalcopyrite. The mineralization occurs in quartz veins and also in the two breccia pipe structures of Santa Helena (SHB) and Venise (VB).

The mineral ore assemblage in quartz veins consists of tungstates (wolframite and scheelite), sulfide minerals (chalcopyrite + molybdenite and pyrite, pyrrhotite, sphalerite, galena, bismuthinite, marcasite), Pb-Bi-Ag sulfosalts, and native bismuth. Fluid inclusion studies were carried out on quartz veins identified aqueous-carbonic fluids (300 ºC < T < 400 ºC and 50 MPa < P < 100 MPa) related to the W mineralization and aqueous fluids (250 ºC < T < 300 ºC and 30 MPa < P < 50 MPa) with sulfide mineralization (Noronha 1984; Noronha et al. 1999). The discrimination of different mineralization events in the magmatic-hydrothermal system of Borralha was discussed on the basis of textural relationships, crystal chemistry and stable isotopic data obtained between chlorite minerals and the W, (Cu, Mo) mineralization (Bobos et al. 2018; Gonçalves et al. 2017), such as: i) early tungsten stage: formation of scheelite (I) and Fe,Mn-chlorite at temperatures from 400 to 500ºC; ii) tungsten - sulfide stage II: formation of Mn-rich wolframite + scheelite (II) + sulfide (chalcopyrite), and Fe-chlorite and secondary muscovite at 250 – 350ºC; iii) sulfide stage III: formation of molybdenite (+bismuthinite) and Fe,Mg-chlorite at ≤ 250ºC.

3 Materials and analytic techniques

Secondary mica (muscovite and sericite) samples from different alteration episodes related to W- and Mo-mineralization were preliminary analyzed by electron microprobe analysis (backscatter), X-ray diffraction and infrared spectroscopy in order to select fresh samples devoid of mineral inclusions or alteration. Handpicked mica samples with grain sizes smaller than 0.15 mm were selected. The samples 6Ha, 6Hb, 11Ha and 11Hb were collected from SBH and the samples 5 and 6 from VB. Preparation of single- or multi-grain mica for 40Ar/39Ar dating by the stepwise heating or total fusion technique followed the guidelines of 40Ar/39Ar lab in Univ. of Potsdam. Samples were irradiated for 4 hours at the CLICIT facility in the OSTR Reactor, U.S.A. Sanidine age standard, FC3, prepared from the Fish Canyon Tuff by Geological Survey of Japan (GSJ) was used as the neutron fluence monitor with a reference age of 27.5 Ma obtained by GSJ (Uto et al. 1997; Ishizuka 1998). Measured isotopic ratios were corrected for mass discrimination, atmospheric Ar component blanks and irradiation-induced mass interferences. The decay constant was δ = 5.543 x 10-10 year-1 (Steiger and Jäger 1977).

4 Results

Mica samples were collected from the tungstate stage related to the SHB [wolframite, secondary muscovite and sericite (T = 250 – 350ºC)] and from the sulfide stage related to VB [molybdenite ± bismuthinite, secondary muscovite, sericite, and Fe,Mg-chlorite (Tº(C) ≤ 250)] The mica 40Ar/39Ar data incorporated apparent age spectra, atmospheric argon, and Ca/K ratios for each step. The ages (±1σ) are plotted against the cumulative released 39Ar fraction for the age spectra (Figs. 2 and 3, inset).

4.1 Tungstate stage

Sample 6Ha (muscovite) has a plateau age of 286.8 ± 1.2 Ma (±1σ) calculated from steps 4 to 7, which represent 62.5% of the total 39Ar released. The inverse isochron age of 288 ± 4 Ma (±1σ) from the plateau steps overlap the plateau age (Fig. 2a), so we prefer the plateau age with its smaller error.

Sample 6Hb (sericite) has a plateau age of 280.9 ± 1.2 Ma (±1σ) from steps 4 to 7, which represent 64.7 % of total 39Ar. The inverse isochron age of 280 ± 4 Ma (±1σ) from plateau steps overlap the plateau age (Fig. 2b), so we prefer the plateau age with its smaller error.

Sample 11Ha (muscovite) does not yield a plateau age, but the total gas age is 286.6 ± 1.4 Ma (±1σ). The inverse isochron age of 288 ± 3 Ma (±1σ) overlap the total gas age with its smaller error.

Sample 11Hb (sericite) does not yield a plateau age, but the total gas age is 279.0 ± 1.1 Ma (±1σ). The inverse isochron age of 279 ± 4 Ma (±1σ) overlap the total gas age with its smaller error.

4.2 Sulfide stage

Sample 5 (muscovite) does not yield a plateau age, but the total gas age is 277.3 ± 1.3 Ma (±1σ). The inverse isochron age of 284 ± 7 Ma (±1σ) with all plots overlap the total gas age within error, therefore we prefer the total gas age with its smaller error.

Sample 6 (muscovite) does not yield a plateau age, but the total gas age is 281.3 ± 1.2 Ma (±1σ). The inverse isochron age of 285 ± 4 Ma (±1σ) with all plots overlap the total gas age within error, then we prefer the total gas age with its smaller error (Fig. 2d).

5 Discussion

A key factor in controlling the W (± Sn), (Cu, Mo)
mineralizing system of Borralha could be the time of post-magmatic activity and cooling history, in addition to magma source and differentiation.

The muscovite $^{40}$Ar/$^{39}$Ar data yielded $286.8 \pm 1.2$ (±1σ) Ma to $286.6 \pm 1.4$ (±1σ) Ma (samples 6Ha and 11Ha) reflect the age of secondary muscovite formation probably from magmatic biotite or feldspar alteration. Sericite $^{40}$Ar/$^{39}$Ar data yielded $280.9 \pm 1.2$ (±1σ) Ma to $279.0 \pm 1.1$ (±1σ) Ma (samples 6Hb and 11Hb) reflecting the age of greisen alteration ($T = 300 \, ^\circ\text{C}$) where the W precipitated as disseminated mineralization during greisenisation. The muscovite $^{40}$Ar/$^{39}$Ar data of $277.3 \pm 1.3$ (±1σ) Ma and $281.3 \pm 1.2$ (±1σ) Ma (samples 5 and 6) reflect also the age of secondary muscovite (selvage) crystallized adjacent to molybdenite veins.

The same Mo-metallogenic event in the time window between $279 \pm 1.2$ Ma and $280.3 \pm 1.2$ Ma was found for the Mo ore-forming stage related with late to post-orogenic granite of Carris (Moura et al. 2014). Also, a younger K-Ar age of $273 \pm 1.1$ Ma was obtained on feldspar from epyplastic rocks of Carris facies from Gerês granite (Jaques et al. 2016).

Lifespans of tungstate and sulfide mineralizations using secondary mica $^{40}$Ar/$^{39}$Ar geochronometers confirm a multi-stage alteration and mineralization where the timing of hydrothermal circulation and the cooling history for the W-stage deposition was no longer than 7 Ma and 4 Ma for Mo-deposition. The $^{40}$Ar/$^{39}$Ar ages obtained provide evidence for an exceptionally prolonged and multi-stage alteration-mineralization widely assumed for a giant deposit.

Timing of magmatic and hydrothermal episodes measured on mica ($^{40}$Ar/$^{39}$Ar) and wolframite (U-Pb) from the French Central Massif, France (Puy-les-Vignes, Limousin) yielded ages around of $320 \pm 5.4$ Ma (mica) and $322 \pm 10$ Ma (wolframite) (Cuney et al. 2002; Harlaux et al. 2018). This could be interpreted as a weak expression of post-orogenic Variscan magmatism at French Central Massive contrarily to Central Iberian Zone, Portugal, where an important post-orogenic W-hydrothermal event followed after Sn-deposition event (estimated at about $331 \pm 5.6$ Ma to $301 \pm 4.2$ Ma, (Zhang et al. this volume) related to syn- and late-
orogenic magmatism.

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References


U-Pb geochronology of cassiterites from primary Sn mineralizations in Sn-W Variscan Metallogenic Province, Portugal

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Abstract. The Iberian Sn-W Metallogenic Province is one of the main sources of Sn and W in Europe. It is spatially related to syn-collisional and to post-collisional Variscan granites. With this study, different types of Sn mineralization can be distinguished and a sequence of different mineralization episodes can be considered based on the cassiterite U-Pb ages. The first episode, yielding 331 ± 5.6 Ma, corresponds to Sn-quartz veins hosted by a deformed muscovite-rich granite; the second episode, 318.8 ± 5.6 Ma, also consists of Sn-quartz veins in the exocontact of two-mica granites (mus>bi); a third episode, 310 ± 6 Ma, corresponds to Sn-pegmatite veins in the exocontact of biotite granites (bi>mus); and a fourth episode, in Panasqueira W-Sn deposit in the exocontact of a greisen cupola, which yielded 303 ± 3.3 Ma and 301 ± 4.2 Ma. A cycle of about 30 Ma can be considered as responsible for different episodes of Sn mineralization, with a first episode, contemporaneous of the orogenic metamorphism and a last one related to the beginning of the first mineralizing stage at Panasqueira. A later cycle is related to post-collisional magmatism and W (Cu, Mo, Sn) mineralizations.

1 Introduction

Portugal is currently a very minor Sn producer. However, Portugal has an important tungsten production. The only active mine producing cassiterite concentrates is Panasqueira with 105 t Sn and 1132 t WO₃ in 2017.

The Sn and W deposits are found in a zone stretching from Galicia (NW Spain) over Northern and Central Portugal (Fig. 1) and Castilla-Leon, Central-Western Spain, in the SW branch of the European Variscan Belt.

The Variscan belt, originated by the convergence, obduction, subduction and collision of Laurussia and the Gondwana continents, is characterized by several, geotectonic zones with specific and peculiar paleogeographic, tectonic, metamorphic and magmatic characteristics (Ribeiro et al. 1990). The Central Iberian Zone (CIZ) and the Galiza Trás-os-Montes Zone (GTMZ) correspond to the most internal zones of the Iberian Variscan Orogeny (Julivert et al. 1974). Most of the rocks outcropping in these zones are Variscan granites and metasediments with ages from the Upper Precambrian to Lower Cambrian to Devonian.

The number, the age and the relative importance of the folding events in the Iberian Belt have been for a long time, in debate between geologists studying the Geology of Iberia. Ribeiro et al. (1990) considered, not only based on field work, but also on geochronological data in granites from Northern Portugal and NW Spain, that the CIZ and the GTMZ owe their structural deformation to a sequence of three deformation phases corresponding to the third phase (D3) early-late Carboniferous (former Westphalian), D3 being the last Variscan ductile deformation phase. Simultaneously to D3 folding, vertical ductile shear zones can occur. In the late- and post-D3 periods, ductile-brittle and brittle deformation occurred along NNE-SSW and NNW-SSE fractures.

Since the 70’s, it is recognized that granite plutonism took place in various episodes during the Variscan orogeny from Upper Devonian, ca. 380 Ma, to Permian, ca. 280 Ma, subsequently confirmed by radiometric dating (Pinto et al. 1987, Dias et al. 1998). More recently, Pereira et al. (2018) and references therein, considering the U-Pb ages in zircons, distinguish two groups of granites: a group of S type granites related to the Gondwana-Laurussia collision with 336 to 306 Ma with three sub-groups 331-321 Ma, 317-315 Ma and 311-310 Ma, of mesocrustal origin related to orogenic metamorphism (335-315 Ma); and a second group of I type granites unrelated to the Gondwana-Laurussia collision with ages of 306 to 287 Ma.

The age of W-Sn mineralization is still a subject of debate. The data concerning the age of mineralization events are very scarce and, sometimes, of difficult interpretation considering the usual influence of late hydrothermal events and alteration. This work was carried out to confirm the possibility of a sequence of different Variscan Sn mineralization episodes with the determination of cassiterite U-Pb ages from hydrothermal Sn deposits, rare metal pegmatites and in W-Sn hydrothermal deposits.

2 Geological settings

Tin deposits in Portugal may be grouped into two types.
as follows: 1) cassiterite-rich aplite-pegmatites with little or no W; and 2) quartz-cassiterite veins (and/or with stockworks): 2a. cassiterite veins with little or no W; 2b. wolframite-cassiterite-quartz veins; and 2c. wolframite veins with little or no cassiterite.

Cassiterite-rich aplite-pegmatites have in the past been mined extensively for cassiterite and columbite-tantalite, but the grade is generally low. The pegmatite field of the Vieiros-Seixoso area in Northern Portugal is a good example and has been described by Lima et al. (2013). The mineralized pegmatite veins are hosted in schists with andalusite in the exocontact of biotite granites. In the Vieiros deposit aplite-pegmatite veins with cassiterite and columbo-tantalite were widely exploited. The veins have a preferred direction N25°E to 55°NW and are sub-horizontal. There are also intersecting veins that have preferred N-S direction. The average grade is of the order of 5 kg/t of cassiterite. In addition to Sn-Ta mineralization, the mineralogical study showed a sulphide mineralization. This sulphide mineralization presents a great variety of minerals characterized by the association Ni, Co, As, Ag, Bi and U, that is an evidence of a late hydrothermal episode controlled by fracturing. At the Seixoso pegmatite, the mineralization is predominantly of cassiterite, but with associated columbo-tantalite, which occurs disseminated in the veins, quite weathered to the surface, but hard at depth. The mineralized veins have variable direction and slope, but the main ones have N-S direction, dipping from 0° to 45° and vertical. The mineralogical study revealed a complex mineral association with well-expressed late sulphide stages with arsenopyrite, galena, sphalerite, pyrite, chalcopyrite and a carbonate stage.

The Gonçalo deposit corresponds to a lepidolite-rich pegmatite hosted in a porphyritic coarse-grained biotite granite. The vein field outcrops are determined by the sub-horizontal dipping and by late NNE-SSW to NE-SW and NW-SE sub-vertical faults that divide the vein field in several sectors. In a more detailed view, it is verifiable that there are sectors where only stanniferous sills outcrop, namely in lower topographic levels, and others with lithiniferous ones in the highest levels. The veins are composed of pegmatite and aplite and the main minerals are quartz, albite, K-feldspar, muscovite, Li-rich muscovite, topaz, apatite, beryl, tourmaline, Mn-oxides and zircon. The major ore mineral is Li-rich mica, but other Li minerals are present like petalite and amblygonite-montebrazite. Cassiterite and columbite-tantalite are also present. In the contact of pegmatite sills with the granite host rock the zinwalditization of biotite is observed (Ramos 2007). Quartz veins, only with cassiterite, or with predominant cassiterite are not very frequent. Cassiterite is often dispersed in quartz and usually shows a small particle size. In other cases, it concentrates near the host rock in muscovite selvages. Of the known occurrences, the examples of the Montesinho and Ervedosa deposits deserve a special mention. At Montesinho, most of the mineralized veins are hosted in Ordovician wall rocks, and a small part in the Montesinho deformed two-mica granite. The veins have a variable thickness from a few centimeters to more than 2 m, averaging 0.60 m. They are essentially quartz veins, with muscovite, cassiterite, beryl, arsenopyrite and iron oxides. Cassiterite is fairly coarse, brown to light-brown in colour, and preferably associated to muscovite selvages.

The Ervedosa deposit is located in the contact of a fine-grained muscovite granite (327 ± 9 Ma), intrusive in schists, lower Silurian in age, with a schistosity N70°W, (Gomes and Neiva 2001). The exploitation was made along a quartz vein with direction N40°W and dipping 70° to 80°NE to sub-vertical. This vein is poor, but it is associated with a network of veinlets with irregular shape, constituting a stockwork type deposit. The mineralization is located essentially in the veinlets cutting the two-mica granite that in the contact is intensely muscovitized. The veins contain quartz, muscovite, cassiterite, arsenopyrite, pyrrhotite, rutile, apatite, bismuth, pyrite, sphalerite, chalcopyrite, stannite, fluorite and inclusions of bismuthinite and matildite in arsenopyrite.

The wolframite-cassiterite quartz veins are the most important and are well represented by the Panasqueira deposit, which consists of a dense swarm of sub-horizontal wolframite-cassiterite-sulphide-bearing quartz veins. The mineralized area lies in Upper Precambrian schists, largely within a zone of spotted schists. This contact metamorphism is due to a buried granite whose roof was intersected by boreholes. A greisen cupula, recognized in underground works, rises above the irregular roof of a much larger granite massif. The greisen preceded the vein-type W-Sn mineralization. The mineral assemblage reveals a series of mineralizing stages separated in time by brecciation episodes (Kelly and Rye 1979, Pinto et al. 2015). Cassiterite is one of the first minerals and is, generally, contemporaneous with quartz, muscovite and topaz that represent the earliest mineral association; wolframite comes after cassiterite and is the main oxide of the "oxide silicate stage". Economically, this first stage is by far the most important. This is followed by a second main stage "the main sulphide stage" with arsenopyrite, pyrite, pyrrhotite, sphalerite, chalcopyrite, stannite and by the
“pyrrhotite alteration stage” with pyrite, marcassite chalcopyrite, galena, Pb-Bi-Ag sulphosalts and siderite. A late stage is characterized by a widespread carbonate, dolomite and calcite deposition.

3 Sampling and analytical methods

3.1 Selection of the samples

The Sn-W mines in Portugal were very abundant and several cassiterite crystals were selected for this study from: a) the Panasqueira W-Sn mine that currently produces Sn concentrates; b) the Gonçalo Li-rich pegmatite deposit that is exploited for the ceramic industry and where fresh rocks were sampled from the quarries; and c) the mineralogical collection of the LNEG Museum at S. Mamede Infesta, Portugal, and belonging to the deposits of Montesinho, Vieiros, Seixoso and Ervedosa.

3.2 Analytical methods

U-Pb isotopic and trace elemental analysis of cassiterite was carried out using a LA-ICPMS system at the CAS Key Laboratory of Mineralogy and Metallogeny, GIG-CAS, Guangzhou, China. The system consists of an Agilent 7900 ICP-MS coupled with a Resonetics RESOhution S-155 laser. This laser ablation system is large (155 × 105 mm). Cassiterite grains were analyzed using a laser energy density of 4 J/cm², a spot size of 74 μm, and a repetition rate of 6 Hz. NIST SRM 610 and an in-house cassiterite standard AY-4 (158.2 ± 0.4 Ma) were used as external elemental and isotopic calibration standards, respectively. Raw data reduction was performed off-line by ICPMSDataCal software. The uncertainty of single population, ratio uncertainty of the AY-4 reference material, and decay constant uncertainties were propagated to the ultimate results of the samples during the process of data reduction by ICPMSDataCal. Data uncertainties for isotopic ratios in the cassiterite samples are 1 σ. Isoplot 4.0 was used to calculate the U–Pb ages and draw concordia plots and weighted 206Pb/238U mean age diagrams.

4 Results

4.1 Cassiterite U-Pb ages

The U contents of the analyzed cassiterite grains are variable. The U-Pb ages have a wide span from 331 to 295 Ma. Some samples with low U contents exhibit large analytical errors (2σ): Gonçalo 295 ± 21 Ma; and Seixoso 316 ±13 Ma. However, there are samples with small analytical errors (2σ): Panasqueira 303 ± 3.3 Ma and 301 ± 4.2 Ma; Vieiros 310 ± 6 Ma; Ervedosa 318.8 ± 5.6 Ma; and Montesinho 331 ± 5.6 Ma. These ages indicate different periods for Sn mineralization suggesting three periods related to collisional granites.

A first cycle of about 30 m.y. can be considered as responsible for different episodes of Sn mineralization with a last period associated with the richest deposit. A second cycle of Sn mineralization corresponds to the cassiterite present in W (Cu, Mo, Bi, Sn) deposits associated with the mineralizations from the Gerês area related to post-collisional magmatism (Noronha 2017).

5 Discussion

5.1 Timing of tin mineralizations

Studies carried out in Central Portugal indicated a close spatial relationship with Middle Permian granites. However, studies in Northern Portugal indicated also a close spatial relationship in early-late Carboniferous (former Westphalian) (Schêmerhorn 1981; Ribeiro and Pereira 1982).

Panasqueira deposit is the only Portuguese W-Sn deposit with isotopic studies for mineralization dating. Clark (1970), dated white micas from the greisen and muscovite selvages from OSS and obtained K-Ar ages between 295 and 290 ± 10 Ma. Snee et al. (1988) dating fluid circulation using 40Ar/39Ar in muscovites from veins and of greisen, found ages ranging from 296.3 ± 0.8 to 291.6 ± 0.8 Ma. However, the two-mica granite (muscovite dominantly secondary), cut by drilling, gave a whole-rock, Rb-Sr ages of 289 ± 4 Ma (Priem and den Tex 1984).

Lima et al. (2013) determined U-Pb dates of minerals of the columbite-tantalite group in Seixoso-Vieiros pegmatite field and found an age 301 ± 4 Ma for Vieiros pegmatite and 316 ± 9 Ma in cores of two grains with low concentrations in U.

The W-Sn-Mo mineralizations from Carris (Gerês area) are later than I type granites emplacement and Re–Os dating of molybdenite from the ore quartz veins and surrounding granite yields ages from 279 ± 1.2 Ma to 280.3 ± 1.2 Ma, respectively (Moura et al. 2014), which are in very good agreement with the previous ID-TIMS U–Pb zircon age of 280 ± 5 Ma for the Carris granite (Dias et al. 1998).

The main types of Sn mineralizations are spatially related to syn-collisional and post-collisional Variscan granites. However, in spite of its importance, the geochronological data mainly concerns granite emplacement.

With the presented new results, it is possible to confirm the existence of different periods of Sn mineralization. Considering that the oldest Sn mineralization has an age of 331 Ma that is contemporaneous with the orogenic metamorphism responsible for crustal anataxis, it is possible to assume the existence of a specialized middle crust responsible by all specialized S type granites.

The youngest cassiterite is represented by Panasqueira hydrothermal quartz veins as result of a rapid crustal uplift that occurred at ca. 300 Ma. Surface heat flow anomalies were developed, enduring at least ca. 280 Ma. This heat flow regime supported a late extensive hydrothermal activity throughout the entire...
crust, involving distinct fluid sources in successively lower P-T conditions along a continuum that provided long-lived hydrothermal systems (e.g. Mateus and Noronha 2010, Noronha 2017).

Figure 2. U-Pb concordia plots (error envelopes are 2 sigma) and weighted mean age diagrams for cassiterite grains from Montesinho (A) Vieiros (B) and Panasqueira (C and D).

6 Conclusions

In this work we report the first U-Pb ages of cassiterites from Portuguese Sn-W deposits.

Considering the existing results concerning the age of peraluminous granite magmatism, it is possible to consider that: the age of the first episode of cassiterite mineralization corresponds to Sn-quartz veins hosted by deformed muscovite leucogranites yielding 331 ± 5.6 Ma, that is very close to the age estimated for the Variscan orogenic metamorphism that implied the melting of crustal metasediments and the genesis of the older (331-321 Ma) S-types granites; the Ervedosa cassiterite age (318.8 Ma) is compatible with the age of the D3 peraluminous granites; and Vieiros age (310 Ma) is compatible with the ages of syn- to late-D3 biotite granites. Cassiterites from Panasqueira with 303 ± 3.3 Ma and 301 ± 4.2 Ma are related to a younger event associated with late- to post-D3 biotite (bi>mus) granites.

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Early hydrothermal alteration stages at the giant San Rafael tin deposit, Peru

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Abstract. At the giant tin deposit of San Rafael, Peru, the early hydrothermal stages, preceding the economic tin mineralization, include successively: 1) potassic alteration represented by hydrothermal K-feldspar altering magmatic plagioclase; 2) sericite replacing magmatic plagioclase in the ground mass and hydrothermal K-feldspar, with greisen formation in the apical part of the intrusion; 3) widespread albitic alteration, both disseminated and as intense replacement along fractures, overprinting and obliterating the previous stages; 4) quartz-tourmaline veins rimmed by albitic alteration halos. In this contribution, the greisen-style alteration and sodic alteration, are studied in depth. Trace element analysis of hydrothermal albite reveals a marked enrichment in incompatible elements (B, Rb, Cs) compared to magmatic plagioclase, suggesting albitization was triggered by magmatic fluids exsolved from an evolved silicate melt.

1 Introduction

Early alteration taking place during magmatic-hydrothermal transition of granites hosting Sn-W mineralization, has been widely described. A typical feature of Sn-W deposits is the presence of early greisenization and albitization (Černý et al. 2005; Pirajno 2009). In the present contribution we focus on the hydrothermal alteration stages preceding Sn mineralization in the giant San Rafael Sn deposit (Central Andean Tin Belt, Peru; Kontak and Clark 2002; Mlynarczyk et al. 2003; Gialli et al., 2017). We report, in addition to the previously described potassic and sericitic alteration stages, development of greisen-style alteration in the apical part of the main intrusion. We have also found that albitization, already mentioned by Kontak and Clark (2002) is widespread and intense at San Rafael. This alteration feature, albeit commonly associated with many different deposit styles and settings, has received limited attention in the literature (Boulvais et al. 2007 and references therein). Combining optical microscopy, QEMSCAN, optical cathodoluminescence, EPMA and LA-ICP-MS analyses on samples representative of different pre-ore alteration styles, we present here a revised sequence of the early alteration stages at San Rafael and we discuss implications for fluid evolution at the magmatic-hydrothermal transition.

2 Geological setting

The San Rafael mining district is located in the Eastern Cordillera of southern Peru and is the largest and richest underground tin mine in the world, with resources of 11.2 million tons of ore at 1.99% Sn (Minsur corporate presentation 2018). The ore occurs as quartz-cassiterite-sulfide veins mainly hosted by a shallow peraluminous composite granitic intrusion (Kontak and Clark 2002; Mlynarczyk 2005) dated at 24.6±0.2 Ma (U-Pb zircon, Clark et al. 2000) and, subordinate, by surrounding Ordovician slates of the Sandia Formation. Main magmatic facies are biotite-cordierite megacrystic granite, volumetrically less important microgranite, in part as dismembered dikes, and late alkali granite. Lamprophyre dikes crosscut the granitic complex. The vein system formation is controlled by sinistral normal faults striking NNW-SSE and dipping at high angle towards the NE (Gialli et al. 2017; Fig. 1). We distinguish three main alteration and mineralization stages (Fig. 2): i) early pre-ore alteration stage with, from early to late, K-feldspar alteration, sericitic alteration, greisen formation, albitic alteration and tourmaline veining (Tur 2) with albitic halo (Fig. 3); ii) syn-ore stage in veins/breccias including Tur 3 and the main quartz-chlorite-cassiterite ± subsequent sulfide mineralization; and iii) post-ore stage consisting of late quartz ± carbonates ± fluorite ± adularia veins, which cut and overprint the earlier mineralization and alteration stages.
3 Results

The early pre-ore hydrothermal stage includes the following four major events (Fig. 2):

A) Potassic alteration. Pervasive potassic alteration is the earliest event of the pre-ore stage and consists of discrete patches of hydrothermal K-feldspar partially replacing magmatic plagioclase in the granitic rocks (Fig. 4A and D). This alteration is volumetrically restricted.

B) Sericitic alteration and greisen formation. Sericite commonly replaces magmatic plagioclase and hydrothermal K-feldspar (Fig. 4D). The intensity of the pervasive sericitic alteration increases progressively towards the upper part of the granitic intrusion where, in patchy areas, least altered granite grades toward intensely sericitized and albitized rocks (Fig. 4E). In the apical part of the pluton, cropping out in the south-eastern part of the studied area (Fig. 1B), an elongated area of intense greisenization extending for a few hundred meters in NNW-SSE direction has been recognized for the first time. The greisen mineral composition consists of quartz (~60%), muscovite (~35%), with minor amounts of tourmaline and dumortierite (<5%) (Fig. 4G).

C) Albitic alteration. Sodic alteration occurs as partial to almost complete replacement of magmatic plagioclase, hydrothermal K-feldspar as well as previous alteration minerals by albite (Fig. 4E). This pre-ore hydrothermal alteration episode is the most widespread and volumetrically important alteration event at San Rafael, affecting the intrusion as a whole, with variable degrees of intensity. Albitic alteration affects most of the samples that should be characterized as “fresh” by naked eye observation, from the bottom level of underground mining operations, till the surface outcrops of the granitic apophyses, with a vertical span of around 1500 meters. Hydrothermal albite occurs disseminated in the whole granitic intrusion, with alteration intensity varying from subtle to intense (Fig. 4E). Mass-balance calculations for albitized granite samples indicate a strong increase in Na and Si, relative increase in Al, and depletion in all other elements, in particular Ba, Y and LREE, leading to LREE-depleted patterns typical of strong albitic alteration (e.g. Boulvais et al. 2007). EPMA followed by LA-ICP-MS analyses were performed on hydrothermal albite and unaltered magmatic plagioclase, ranging in composition from andesine to oligoclase. In Figure 5, where highly incompatible

Figure 1. Geological map and cross-section of the San Rafael district, Southeast Peru. a) Location of the San Rafael deposit in the Central Andean Tin Belt (modified after Mlynarczyk et al. 2003); b) Geological map of the San Rafael district compiled from new mapping campaigns (Gialli et al. 2017, MINSUR S.A. unpublished data) and integrating older data (Arenas 1980, Palma 1981, Kontak and Clark 2002, Corthay 2014); c) Longitudinal cross-section of the San Rafael lode system from Gialli et al. 2017; modified after MINSUR S.A. unpublished data.

Figure 2. Simplified paragenetic sequence of the San Rafael tin deposit detailing the revised paragenesis of the early hydrothermal alteration stages.

dumortierite (<5%) (Fig. 4G).

Figure 3. Intense albitic alteration along a quartz-tourmaline (Tur 2) vein in biotite-cordierite megacrystic granite (sample KK-09).
elements (B, Cs, and Rb) are plotted vs. Ca/Na ratio, hydrothermal albite and magmatic plagioclase cluster in clearly different fields. The Ca/Na ratio varies from 0.25 to 0.75 for magmatic plagioclase and from 0.05 to 0.20 for hydrothermal albite. The concentrations of B, Cs and Rb are low in magmatic plagioclase (3.9 to 20.8 ppm, 0.1 to 1.2 ppm and 1.9 to 8.4 ppm respectively). In hydrothermal albite, concentrations range from 10 to 140 ppm B, 0.1 to 25 ppm Cs, and 4 to 207 ppm Rb.

D) Tourmaline veins and breccias. Pre-ore hydrothermal tourmaline (Tur 2) in veins and breccias ranges in composition from dravite to schorl (Harlaux et al. 2019). Tur 2 veins are systematically rimmed by albitic alteration halos (Fig. 3, 4A) and cut the megacrystic granite including the greisen body cropping out at surface.

4 Discussion

After a first alteration stage forming K-feldspar from a near neutral pH hydrothermal fluid exsolving from the crystallizing magma, pervasive sericitic alteration can be interpreted in terms of a fluid becoming more acidic during cooling or by increasing volatile proportion. Concentration of hot and acidic fluids in the apical part of the intrusion would explain the formation of greisen (Černý et al. 2005).

The widespread albitic alteration, followed by tourmalinitization (Tur 2), may be the result of a second hydrothermal pulse showing again an evolution path from neutral to acidic conditions.

The high concentrations of B, Cs and Rb in hydrothermal albite suggest a magmatic origin of the
fluid responsible for the widespread albitization. This interpretation is also supported by the results of Harlaux et al. (2019), indicating precipitation of Tur 2 at ~500°C, from fluids with magmatic isotopic signature. Our results underline the role of magmatic-dominated fluids at the magmatic-hydrothermal transition during the pre-ore alteration stage at San Rafael.

5 Conclusions

A detailed textural study combining microscopic observations, QEMSCAN, optical cathodoluminescence, and scanning electron microscopy, has been carried out at the San Rafael tin deposit. Focus has been placed on the greisen occurring in the apical part of the composite granitic intrusion and on the importance and volumetric extension of albitic alteration. This has allowed a new interpretation of the sequence of alteration events during the early pre-ore hydrothermal stage at the San Rafael tin deposit. The paragenetic sequence combined with LA-ICP-MS analysis of trace elements in hydrothermal albite strongly support a magmatic origin for the early hydrothermal fluids and suggest the existence of two distinct fluid pulses during the pre-ore hydrothermal stage.

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References

Mineralogical and geochemical aspects of vein-type ores from the Carnon River Mining District, Cornwall

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Abstract. The Carnon River Mining District, part of the Cornubian Ore Field in SW-England, hosts polymetallic and multi-phase tin and base metal vein mineralisation in the cupolae of Variscian granites. Geologically, the study area is composed of Devonian clastic metasedimentary rocks with intercalations of amphibolite, intruded by Late Variscian granites. Multi-phase cross-cutting polymetallic veins were emplaced by late granite-related magmatic-hydrothermal events.

Typical ore minerals are arsenopyrite, marcasite, chalcopyrite, sphalerite, galena, fahlore, cossiterite, and wolframite in different parageneses at Nangile and Poldice Mine. Stannite, cubanite, and pyrite occur as exsolution either from sphalerite or cossiterite, suggesting high temperature of formation and segregation at lower temperature. The ore minerals are accompanied by quartz, chlorite, and tourmaline, with minor epidote and rutile. Sphalerite is more common at Nangile, arsenopyrite and chalcopyrite is more widespread at Poldice.

Pulses of tin and tungsten mineralisation as well as mineralisation dominated by copper, lead, and zinc were recognised in thin sections and geochemical analysis. Free gold was not found in thin sections, but geochemical ratios between arsenic and gold suggest that the latter occurs within the lattice of arsenic bearing minerals.

1 Introduction

The Cornubian Ore Field in Cornwall has been exploited from the Bronze Age until the end of the last century. Mining activities were especially extensive during parts of the 18th and into the 19th century, a time span, during which it was one of the most important centres of mining in the world (Dines 1956). Thus, the counties of Cornwall and parts of Devon are characterised by their mining legacies. Although world-renowned for the production of tin, mining in Cornwall has also contributed a substantial portion of the historic copper, arsenic, and minor tungsten and lead (LeBoutillier 2002). Unrecorded quantities of gold were produced in the Carnubian Ore Field, and gold nuggets are kept in the Williams Collection at Caerhays Castle as well as at Royal Cornwall Museum.

2 Regional Geology

The Cornish peninsula is dominated by sub-greenschist facies Devonian and Carboniferous clastic metasedimentary rocks and minor metamorphosed limestone. These metasedimentary rocks have also been intruded by meta-gabbro and felsic dykes and sills. This lithologically mixed suite has subsequently been intruded by Late Variscian granites (Darbyshire and Shepherd 1985).

One of these granitic plutons is the relatively small Carn Marth Granite, a satellite stock of the larger Carnmenellis Granite, which intruded into metasedimentary units, locally known as 'kills'. Mineralised quartz-rich porphyritic dykes (Elvan Dykes), and polymetallic veins, called loads; make up the mineralised inventory of the Carnon River Mining District (Fig. 1). The Late Variscian mineralisation is spatially related to main ENE-WSW trending faults and fractures in an extensional tectonic setting and is mainly characterised by tin, tungsten, copper, arsenic as well as subordinately by other base metals.

3 Methods

The sampling campaign for this study was carried out in the Carnon River Mining District between St. Day, Chacewater, and Devoran. This district represents an impressive mining heritage site with a post-mining landscape, drainage system, tailing ponds, and mine dumps. Hard rock ore samples have been collected from old mine shaft collars of the Nangile and the Poldice Mine.

All samples have been geochemically analysed by a certificated laboratory (ALS, Ireland). Aqua regia
digestion with ICP-AES finish was used for analysing ore grades of base metals. Lithium metaborate fusion coupled with XRF finish was applied for analyses of the tin and tungsten concentration. Platinum and palladium, was determined by lead oxide collection fire assay and ICP-MS finish.

Imaging and investigation of the mineralogical composition of the ores was carried out with a scanning electron microscope (SEM JEOL JSM 6300), equipped with an EDX-detector XFlash 5010 (Bruker).

The sulphide mineral assemblages of the ore samples were additionally investigated by reflected light microscopy (Carl Zeiss Axiophot).

4 Mineral paragenesis of Poldice Mine

Microscopically, the ore samples show different assemblages of minerals as well as indications for brecciation, cavity fillings, and replacement textures in different stages. Furthermore, typical gangue minerals coupled to different mineralisation stages could be distinguished.

![Figure 2. Idiomorphic tourmaline (colourful prism) growing into quartz (white) within subhedral masses of tourmaline, finely intergrown with chlorite. These minerals occur associated with several of the mineralisation stages.](image)

Quartz is a highly abundant gangue mineral occurring in various quantities in all samples forming partly millimetre-sized idiomorphic phenocrysts without deformation features. Scaly to radiating green chlorite is also very common and fills cavities or overgrows epidote and biotite. Some thin sections show euhedral, colourful tourmaline up to a size of more than 300 microns, grown into quartz (Fig. 2) and ore minerals or forming fine-crystalline masses. Remnants of anhedral and mostly elongated mica in wall rock-dominated parts represent muscovite and biotite.

One of the main ore minerals is arsenopyrite, occurring as anhedral to subhedral masses, up to 2 millimetres in size and as arrays of euhedral crystals up to 500 microns in diameter. Almost all of these have characteristics of brittle fracturing and fracture fillings. (Fig. 3).

More rarely they have inclusions of galena or cassiterite. Chalcopyrite is also abundant commonly in veinlets crosscutting arsenopyrite or forming anhedral masses. Exsolution blebs of stannite and irregularly scattered, subhedral to euhedral cassiterite occur within chalcopyrite. Additionally, cassiterite can contain exsolutions of chalcopyrite (Fig. 4).

Marcasite shows locally twinning and is abundant within the ores. Fine-crystalline sphalerite and galena occur commonly enclosed in other ore minerals, but locally sphalerite forms also larger crystal aggregates. Pyrite is mostly intergrown with marcasite and pyrrhotite. Furthermore, wolframite occurs embedded in chalcopyrite and as separate crystals. Fahlore and sulfosalts were also observed.

![Figure 3. Quartz (black) is the main gangue mineral. Arsenopyrite (bright white) represent the most abundant sulphide in base metal associated ores from Poldice Mine. Both arsenopyrite and quartz are commonly brecciated and crosscut by chalcopyrite veinlets (bright yellow). Sphalerite (medium grey) and galena (white) is also included in the chalcopyrite. Pyrite (pale yellow) and marcasite (greenish white) are common within the samples.](image)

![Figure 4. Fractured arsenopyrite (white) filled with chalcopyrite (yellow) and sphalerite (medium grey). Exsolution blebs of chalcopyrite within cassiterite (dark grey) was recognised in several samples.](image)
5 Mineral Paragenesis of Nangile Mine

The main gangue mineral of Nangile Mine is euhedral to subhedral quartz, but also dynamically recrystallized areas of quartz were recognised. Some of them show patchy and undulose extinction suggesting their formation under a deformational regime. Anhedral masses of chlorite are also abundant. They fill cavities between quartz and ore minerals as well as fractures.

Idiomorphic tourmaline, up to 100 microns in size, occurs in some of the thin sections, forming partly clusters of fine-grained masses or growing into quartz and ore minerals. Subordinate amounts of epidote and remnants of biotite as well as muscovite, partly replaced by chlorite, are visible within the sections. Rarely, rutile was recognised as inclusions of quartz and cassiterite.

Figure 5. Exsolution textures in sphalerite (grey), produced by chalcopyrite (bright yellow), pyrite (pale yellow), and cubanite (reddish yellow). Cassiterite inclusions (higher relief) are also visible. This is a typical texture of sphalerite within the thin sections.

Sphalerite is one of the main ore minerals and appears in euhedral to subhedral masses up to 5 millimetre in size. Chalcopyrite, cubanite, fahlore, and minor stannite occur as exsolutions in sphalerite (Fig. 5). Deformational characteristics like fracturing or cavity filling were not observed.

Cassiterite occurs also as minute inclusions within sphalerite but also in other mineral phases like arsenopyrite and chalcopyrite or as separate minerals. Chalcopyrite and arsenopyrite occur as euhedral minerals up to 500 microns in size with small inclusions of galena and wolframite. Pyrite and marcasite are common minerals throughout the entire ore mineral assemblage, but they have not been recognised intergrown with sphalerite. More rarely, pyrrhotite and haematite was observed within the section.

Figure 6. Fractured arsenopyrite with crack fillings of chalcopyrite and pyrite. Arsenopyrite is generally brecciated and partly filled with ore minerals or chlorite and tourmaline, suggesting their chronologically relationship.

Some sections reveal mineralised fractures parallel to foliation getting cross-cut by later mineralised or chlorite veins. Brecciation was recognised mainly within arsenopyrite, followed by filling fissures with chalcopyrite or pyrite (Fig. 6).

6 Geochemistry of ores

Geochemical data for base metals and associated elements of Nangile and Poldice ores reveal differences. Generally, the copper, lead and arsenic as well as silver content of Poldice is higher than in samples from Nangile. In contrast to that, zinc and tungsten values from Nangile are higher. Cobalt, nickel and molybdenum are not enriched in both localities. Gold appears in similar concentrations in both.

Positive correlation between lead and silver were recognized, which most likely reflects the occurrence of silver in galena.

Two correlation paths between gold and arsenic can be distinguished for Nangile Mine and Poldice Mine (Fig. 7). The latter has higher arsenic to gold ratio than Nangile with similar gold content suggesting gold at Poldice preferentially occurs within the lattice of arsenopyrite. This ratio is lower in the ores from Nangile, suggesting gold is substituted in the crystal lattice of other minerals. A higher abundance of tennantite-tetrahedrite group minerals, which were microscopically described, can lead to a lower ratio of arsenic to gold.

Platinum and palladium are measurable in almost all samples from both mines, but show slightly higher concentrations at Poldice.

Some samples from both mines reveal a mineralisation associated with tin and tungsten, with partly elevated copper concentrations. In contrast, copper-lead-zinc mineralisation together with arsenic and high silver content occurs as well.
7 Conclusions

The vein development was influenced by several partly-coupled hypogene hydrothermal processes and supergene enrichment with the development of gossan. Mineralisation events, such as the formation of greisens, are associated with the enrichment of tin and tungsten as well as hydrothermal stages bearing base metal mineralisation. These were described in the literature concerning the study area. They can be partly confirmed by our investigations.

Generally, the mineral associations of Poldice Mine and Nangile Mine are similar, possibly due to their proximity to each other and a similar metallogenetic origin. However, several aspects are different. First of all, sphalerite is more abundant in samples from Nangile Mine than in samples from Poldice Mine, but exsolution fabrics were recognised in both, suggesting eutectic high temperatures of formation with subsequent segregation and exsolution at lower temperature. The same has been described for the formation of stannite in chalcopyrite (Ramdohr 1975). Chalcopyrite and arsenopyrite occur in both mines, but the distribution at Poldice Mine is more widespread than in Nangile. Cubanite is specific for Nangile Mine, although the limited number of samples needs to be taken into account.

Geochemically, the ores from Nangile have higher concentrations of zinc and tungsten and lower concentrations of copper and arsenic compared to Poldice, resulting in the observed respective mineral assemblages. Also, the concentration of lead is increased at Poldice compared to Nangile, leading presumably to more galena and therefore to higher silver concentrations. The occurrence and relationship of platinum and palladium within the system is not clear. Free gold as a phase was not observed in thin section, so far, but geochemical evidence suggests that gold occurs within the lattice of other minerals, for example arsenopyrite.

Results from our investigations of ore samples are similar to the mineral paragenesis described from the neighbouring Mt. Wellington Mine (Kettaneh and Badham 1978). At Mt. Wellington, tin and tungsten as well as base metal mineralisation, associated with quartz, tourmaline, and chlorite were recognized as well.

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References

Epithermal precious metal deposits of the Deseado Massif, Santa Cruz Province, Argentina

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Abstract. Epithermal ore deposits of the Deseado Massif, southern Patagonia Argentina, represent a widespread assemblage of gold-silver mineralization. They show a strong spatial relationship with an extensive Jurassic rhyolitic volcanism that covers approximately 30,000 square kilometers. The principal mineralization is the world class Cerro Vanguardia deposit. The main ore deposits and prospects have a marked regional tendency to group in several clusters identified as I, II, III and IV. Most of the epithermal deposits are composed of veins, veinlets, breccias and stockworks with predominant NW and minor NE and E-W strikes. Three main genetic model types of hydrothermal deposits occurred in the Deseado Massif: a) vein type, b) volcano-hosted type, and c) peribatholithic-epithermal type (Pb-Zn-In-Cu-Sn-W-Bi and Ag>Au).

1 Introduction

When Lindgren (1933) characterized the epithermal mineralisation type, he considered that one of the critical aspects for its understanding and classification is the detailed study of the metal association, gangue and alteration assemblages. During the last forty years, many geologists have worked on epithermal deposits in different parts of the world, however, their mineralogical features were not always thoroughly studied. The epithermal precious metal deposits of the Deseado Massif, Patagonia Argentina, are an example of this situation. In fact, their mineralogical and metallogenic knowledge is largely incomplete.

Since the late 1970s, the Deseado Massif has been the subject of numerous studies and investigations searching for gold and silver concentrations. As a result of these explorations many Au-Ag deposits have been discovered, some currently being mined.

This brief contribution aims to provide a broad review of the mineralogical characteristics of the main epithermal deposits of the Deseado Massif, in addition to proposing some general conclusions about their metallogenic models and regional distribution.

2 Regional setting

The Deseado Massif (DM) is a morphostructural region located in the Santa Cruz province, southern Argentina (Fig. 1). The most important geological characteristic of this area is an extensive plateau characterised by a Mid-Upper Jurassic volcanic event composed of intermediate to acid volcanic rocks of the Bahía Laura Complex (BLC). This voluminous volcanism originated during widespread extensional tectonism which extended across Patagonia and Antarctica related to the opening of the Atlantic Ocean (Pankhurst et al. 1998, Giacosa et al. 2010).

![Figure 1. Simplified geological map of the Deseado Massif showing the distribution of the main epithermal metal precious deposits.](image-url)
flows are much more extensive.

3 The epithermal metal precious deposits

3.1 Regional arrangement and general characteristics

Epithermal precious metal deposits of the DM (Fig. 1) comprise an important assemblage of gold-silver mineralization distributed across a large region of about 60,000 square kilometers (Schalamuk et al. 1997, 1999). Although there are many epithermal deposits and occurrences throughout the whole DM, the main ore deposits and prospects show a strong regional tendency to group in several clusters. Consequently, they have been subdivided into four assemblages: I) Northwestern region: it comprises San José (Huevos Verdes), Cerro Negro, Eureka and Lomada de Leiva ore deposits, II) Central region, with La Josefina and Cap-Oeste mines, and La Esperanza, Bajo Pobre-El Mirasol, Pingüino (El Piche), La Manchuria and Joaquín prospects, III) Southern region, comprising Cerro Vanguardia, Manantial Espejo and Martha mines, and El Dorado-Monserrat project (first sector where the gold mining exploration began), and IV) Eastern region, with Don Nicolás and Cerro Moro mines, and Bajo de la Leona, Falcon, Las Calandrias, Microondas-Martinetas, and Chispas prospects (Fig. 1 and Table 1). Only the Laguna Guadalosa prospect appears isolated because it is placed in the most southern sector separated from the other deposits by an extensive Quaternary sedimentary cover. This areal arrangement is the result of different geological evolutions. The great majority of the epithermal deposits are hosted by rocks of the Bahía Laura Complex. However, the eastern deposits are placed in much lower stratigraphical portions closely associated to basement rock outcrops which appear in several erosional windows. On the other hand, the NW cluster is placed in areas where the BLC has a large thickness but several drill holes have detected basement rocks at depths of between 50 and 150 m. Other factors consist of the different erosion levels according to the proximity to the great valleys of the Deseado and Chico rivers which limited the DM towards the north and the south, especially in the south and eastern boundaries. There are almost 600 m of difference of altitude between the NW region and the southern and eastern sectors (Fig. 2).

Most of the epithermal deposits (Fig. 2) are composed of veins, veinlets, breccias and stockworks with predominant NW and minor NE and E-W strikes. They show multi-episodic stages with the deposition of silica minerals (quartz, chalcedony and opal), calcite, rhodocrosite, adularia, barite, fluorite and zeolites, among others. Metaliferous minerals are scarce, approximately 1% in volume. They are mainly represented by native gold, electrum, native silver, acanthite, Ag-sulfosalts, pyrite, hematite, minor base metal sulfides (sphalerite, galena and chalcocpyrite) and some supergene minerals (oxides, hydroxides and Ag halogens).

The most frequent mineral textures are crustiform-banded, colloform, cockade, massive, breccia, climb and pseudomorph replacements.

Gold and silver occur together in varying proportions. In virtue of their abundance, the epithermal deposits of the DM are divided into three groups: a) gold deposits with variable amounts of silver (e.g. Cerro Vanguardia mine, among others.), b) silver deposits with minor amounts of gold (e.g. Martha and Manantial Espejo mines), and c) Zn-Pb (Cu-Ag) deposits with minor amounts of gold (e.g. Pingüino prospect).

The most important styles of hydrothermal alteration are silification, argillization (illite, smectite and kaolinite), sericitization and propylitization. They are poorly developed and are normally restricted to areas in the vicinity of veins. The width varies from a few centimetres up to several tens of metres, depending of the wall rock composition. Argillization may be quite incipient up to very strong (advanced argillization). Silification is pervasive or displayed in very thin veinlets, randomly arranged.

3.2 Main metalogenic models

At present, there are more than 50 important Au-Ag epithermal projects in diverse exploration stages; also, eight mines are currently active (Cerro Vanguardia, Manantial Espejo, San José, Cerro Negro, Cap-Oeste, La Josefina, Don Nicolás and Cerro Moro). The geochemical signature corresponds to typical epithermal deposits with anomalies in precious metals (Au-Ag), and other elements as As, Sb, Hg, Mo, Ba and Mn with a Au-Ag relation of about 20:1. Only one occurrence belongs to a singular type of polymetallic (Zn, In, Ag) veins related to Early Jurassic magmatism superimposed by a later epithermal system (Pingüino project). The mineralizing fluid composition of the main epithermal deposits is characterised by the presence of H2O-NaCl (KCl) components, neutral to slightly neutral pH, with salinities from 0.2 to 8.0 wt.% NaCl eq. and variable homogenization temperatures (100°C-320°C).

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<th>ORE DEPOSIT/PROSPECT</th>
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<td>CLUSTER I</td>
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<td>NORTHWESTERN REGION</td>
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<tr>
<td>San José-Huevos Verdes</td>
<td>46º 40' S</td>
<td>70º 18' W</td>
<td>Ag, Au sulf, Ele, Gal, Sp, Ac</td>
<td>veins, brx, NW-SE, NNE-SWW and ONO-ESW</td>
<td>crust, col, comb</td>
<td>andesitic lava flows, Bajo Pobre Fm.</td>
<td>intern arg, adv arg, sil, chlor</td>
</tr>
<tr>
<td>Cerro Negro District</td>
<td>46º 45' S</td>
<td>70º 14' W</td>
<td>Ag, Ele, Au, Ag sulf, and sulfos.</td>
<td>veins, WNW brx, disseminated</td>
<td>colo-crust, mass, brx</td>
<td>basalt-andesite, Bajo Pobre Fm. tuffs calc-alkalic lavas Chon Aike Fm</td>
<td>adv arg, ser</td>
</tr>
<tr>
<td>La Paloma (Lomada de Leiva and Sofia Breccia)</td>
<td>47º 03' S</td>
<td>70º 40' W</td>
<td>Au, Ag</td>
<td>veins, brx, qz, adl</td>
<td>brx, qz network</td>
<td>acid ignimbrites Chon Aike Fm</td>
<td>arg</td>
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<td>CLUSTER II</td>
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<td>Bajo Pobre-El Macanudo-Sol de Mayo</td>
<td>47º 15' S</td>
<td>69º 14' W</td>
<td>Au, Ag anomalies</td>
<td>qz, chal, cal</td>
<td>mass, crust, cock</td>
<td>bas. andes. Bajo Pobre Fm</td>
<td>prop, sil</td>
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<tr>
<td>Cap-Guiste (El Tranquilo)</td>
<td>47º 58' S</td>
<td>70º 25' W</td>
<td>Au, Ele</td>
<td>py, apy, pyrrhotite, trt</td>
<td>brx, NW-SE</td>
<td>brx</td>
<td>acid ignimbrites Chon Aike Fm</td>
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<td>La Esperanza</td>
<td>69º 44' S</td>
<td>47º 40' W</td>
<td>Au</td>
<td>qz, chal, oxi,</td>
<td>veins, replacement N-W</td>
<td>crust</td>
<td>acid ignimbrites Chon Aike Fm</td>
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<tr>
<td>La Josefina</td>
<td>47º 52' S</td>
<td>69º 23' W</td>
<td>Au, Ele</td>
<td>qz, chal, oxi,</td>
<td>veins, fractures</td>
<td>mass</td>
<td>aciid ignimbrites Chon Aike Fm</td>
</tr>
<tr>
<td>La Manchuria</td>
<td>48º 09' S</td>
<td>69º 54' W</td>
<td>Au, Ele, Ag</td>
<td>qz, chal, py, gal</td>
<td>veins, brx</td>
<td>mass, brx</td>
<td>acid ignimbrites Chon Aike Fm</td>
</tr>
<tr>
<td>Joaquin</td>
<td>48º 03' S</td>
<td>69º 34' W</td>
<td>Ag, pyrrhotite, Fe, stromeyerite, trt, pyr, steph</td>
<td>qz, adl, py, gal, hem</td>
<td>brx, veins, stvks</td>
<td>brx</td>
<td>Chon Aike Fm</td>
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<tr>
<td>El Piche-Pingüino</td>
<td>48º 01' S</td>
<td>69º 38' W</td>
<td>Sp, gal, coq, cu, Ag Sn sulfosilts</td>
<td>qz, sd, brs</td>
<td>sulfide veins &amp; quartz veins, brx NW-SE</td>
<td>crust</td>
<td>sandstone, tuffs, El Tranquilo and Roca Blanca Fm</td>
</tr>
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<td>SOUTHERN REGION</td>
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<td>Martha mine</td>
<td>48º 42' S</td>
<td>69º 43' W</td>
<td>pyr, ac, ag, sp, gal</td>
<td>qz, adl, cal, zoe</td>
<td>vein with silver ore shoots NW-SE, E-W</td>
<td>crust, mass, brx</td>
<td>acid ignimbrites Chon Aike Fm</td>
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<tr>
<td>Manantial Espejo</td>
<td>48º 48' S</td>
<td>69º 30' W</td>
<td>Au, Ele, Au, Ag sulf, py, sp, gal, cap, trt</td>
<td>qz, chal, oxi,</td>
<td>veins, stvks, NW-SE</td>
<td>crust, colo-crust, brx</td>
<td>acid ignimbrites Chon Aike Fm</td>
</tr>
<tr>
<td>Cerro Vanguardia</td>
<td>48º 23' S</td>
<td>69º 15' W</td>
<td>Au, Ag, Ele, Ag, Ag sulfosilts</td>
<td>qz, chal, oxi,</td>
<td>veins and veins WNW-ESW/70° NW-SE/70°</td>
<td>crust, brx, mass, comb</td>
<td>acid ignimbrites Chon Aike Fm</td>
</tr>
<tr>
<td>El Dorado-Monserrat</td>
<td>48º 26' S</td>
<td>69º 38' W</td>
<td>Au, Ele</td>
<td>qz, brt, adl</td>
<td>veins, brx, veins</td>
<td>crust, colo-crust, mass, andesite, and basalt, Bajo Pobre Fm</td>
<td>sil, ser, prop, pyrr</td>
</tr>
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<td>CLUSTER IV</td>
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<td>EASTERN REGION</td>
<td></td>
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<tr>
<td>Falcon</td>
<td>48º 36' S</td>
<td>67º 33' W</td>
<td>Au, Ag</td>
<td>qz, chal</td>
<td>veins with silica mineralized halo</td>
<td>brx</td>
<td>acid ignimbrites Chon Aike Fm</td>
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<tr>
<td>Las Calandrias</td>
<td>47º 36' S</td>
<td>67º 29' W</td>
<td>Au, Ele</td>
<td>pyr, mic, apy, Ag sulf</td>
<td>brx, veins</td>
<td>brx</td>
<td>rhyolite domes Chon Aike Fm.</td>
</tr>
<tr>
<td>Bajo de La Leona</td>
<td>48º 05' S</td>
<td>69º 19' W</td>
<td>Au, anomalies, cct</td>
<td>qz, hem, mic</td>
<td>veins WNW-ESW</td>
<td>mass, crust</td>
<td>Dv-Cb leucogranites La mima Fm</td>
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<tr>
<td>Micrones-Martinetas</td>
<td>47º 56' S</td>
<td>67º 31' W</td>
<td>Au, Ag</td>
<td>qz, chal</td>
<td>veins, replacement</td>
<td>mass</td>
<td>tuffs and dacitic dome Bahia Laura Complex</td>
</tr>
<tr>
<td>Don Nicolás</td>
<td>47º 56' S</td>
<td>67º 23' W</td>
<td>Au, Ele, Ag</td>
<td>qz, adl</td>
<td>sheeeted veins</td>
<td>mass, crust</td>
<td>acid tuffs and ignimbrites Bahia Laura Complex</td>
</tr>
<tr>
<td>Chispas</td>
<td>48º 23' S</td>
<td>68º 58' W</td>
<td>Au</td>
<td>qz, chal, qz, py</td>
<td>veins, stvks, NNE-SSW</td>
<td>mass, crust</td>
<td>acid ignimbrites Chon Aike Fm</td>
</tr>
<tr>
<td>Cerro Moro</td>
<td>48º 05' S</td>
<td>68º 39' W</td>
<td>Au, Ag, Ag sulf, and sulfos.</td>
<td>qz</td>
<td>veins, stvks</td>
<td>mass, crust</td>
<td>acid ignimbrites Chon Aike Fm</td>
</tr>
<tr>
<td>Laguna Guadalupe</td>
<td>49º 29' S</td>
<td>88º 23' W</td>
<td>Au anomalies</td>
<td>qz</td>
<td>veins NE-SW, E-W</td>
<td>crust</td>
<td>acid ignimbrites Chon Aike Fm</td>
</tr>
</tbody>
</table>
Fluid stable isotope data ($\delta^{18}O$) preserved in quartz crystals varies between -10 and +6 ‰ suggesting a main meteoric component, while the $\delta^{34}S$ data varies from -2.5 up to 5.0 ‰ revealing a magmatic provenance for sulfur.

Most of the epithermal deposits of the DM corresponds to the low sulfidation type and just a few mineralizations belong to the intermediate sulfidation type (e.g. Martha mine).

Three main genetic model types of hydrothermal deposits were identified in the DM (Fig. 3): a) vein type, b) volcano-hosted type (e.g. Las Calandrias Project, Cap-Oeste), and c) peribatholithic-epithermal type (Pb-Zn-In-Cu-Sn-W-Bi and Ag>Au, e.g. Pingüino Project and Bajo de la Leona prospect). On the other hand, the vein type comprises three subtypes: classic veins (Cerro Vanguardia, among others), veins accompanied with geothermal features (e.g. Cerro Negro, Manantial Espejo, and others), and blind vein deposits (e.g. La Mariana). The most frequent and relevant type deposits are largely the classic quartz veins which usually constitute extended vein fields.

4 Concluding remarks

The main epithermal deposits of the Deseado Massif are grouped in four regions or clusters with different structural and stratigraphical attributes and a diverse geological evolution.

The areal distribution is controlled by lithological, stratigraphical and structural elements. In most cases, there is a marked spatial relationship with the Jurassic acid ignimbritic volcanism of the Chon Aike Formation.

Structural features show a general WNW-ESE orientation in Cluster III, where the world class deposit Cerro Vanguardia presents some veins of more than 10 km in length (e.g. Vanguardia vein). However, the main veins with higher gold values show a NW-SE orientation.

Due to the lack of an integrated watershed and gold occurring as minute particles, rich placers are absent in the Deseado Massif.

References


Timing and P-T conditions of epithermal mineralization in the Bacis and La Cienega Mining districts, Durango, Mexico

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Abstract. The Bacis and La Cienega districts are Au-Ag hydrothermal deposits located in the Sierra Madre Occidental (SMO) in Mexico. The mineralization in both districts is related to NW-NNW trending structures and exhibits high Au-Ag ratio which become Ag-dominant at deeper levels.

New U-Pb ages from the volcanic host-rock, and K-Ar and 40Ar/39Ar ages in adularia and illite from the mineralization assemblages, allow a re-evaluation of the timing of the hydrothermal mineralizing events. In both districts the basement consists of the Lower Triassic and Upper Jurassic metasedimentary successions which are intruded by monzogranitic plutons and overlain by andesitic lavas belong to the Lower Volcanic Complex (LVC). These rocks are in turn covered by an Oligocene ignimbrite succession and rhyolitic domes of the Upper Volcanic Supergroup (UVS). Mineralizing veins affect all the stratigraphic column.

Fluid inclusion microthermometry and decrepitation studies yield comparable temperature ranges in both districts at 210 to 230ºC and 410-430ºC, suggesting the occurrence of a similar mineralizing event. The chemical composition and temperature of formation of chlorite associated with Ag-rich and Au-rich mineralization stages show a bimodal distribution with peaks at 330ºC and 270ºC, respectively.

1 Introduction

The SMO hosts many epithermal deposits of variable age related to a single geodynamic and magmatic event (Camprubí et al. 2003). Montoya et al. (2019) illustrate the importance of the polyphase formation of the hydrothermal mineralization in the large San Dimas district, suggesting that this process may have controlled the genesis of other unconventional deposits in the central part of the SMO.

We chose to study two examples of low sulfidation epithermal deposits to the NNW of San Dimas: the Bacis and La Cienega deposits (Figure 1). The Bacis deposit is described as a typical Au mineralizing epithermal event (Au/Ag =1/50), whereas La Cienega exhibits a more complex structural and paragenesis assemblage, suggesting a multi event formation (Au/Ag =1/50).

Previous works have proposed a metallogenic framework for these deposits (De la Garza et al., 2001; Camprubí and Albinson 2006). However, the magmatic events associated with mineralization have not been assessed in detail. Also, many of the geologic units are not dated and in the case of the few available K-Ar whole rock ages (Labarthe 1996), significant doubt remains about the extent of possible thermal resetting by later magmatic events.

To better understand these deposits, we re-evaluate the local geologic evolution and hydrothermal mineralization with new petrographic and geochronological studies.

2 Regional geology

The SMO is a major geologic province in western Mexico, which spans 1200 km in length and 400 km in width and extends from the U.S. border to the south up to the Trans-Mexican Volcanic Belt (Ferrari et al., 2007). In the central and southern SMO, volcano-sedimentary basement belonging to the Guerrero terrane is intruded and covered by the igneous rocks of the Laramide continental arc, also known as the Lower Volcanic Complex (McDowell and Keizer 1977). These rocks are covered by a 1 to 1.5 km thick succession of silicic ignimbrites, rhyolitic domes and basalts of late Eocene, Oligocene and early Miocene age, which constitute one of the main silicic large igneous province on Earth (Aranda et al. 2000; Bryan and Ferrari, 2013). These successions are affected by normal fault systems related to lithospheric extension that led to the formation of the Gulf of California rift (Ferrari et al. 2017). The
The basement exposed in the two study areas differs in lithology and age. In the Bacis, it consists of greenschist-facies quartz sandstones with lithics fragments. The youngest U-Pb detrital zircon population (LA-ICPMS) indicates a maximum age of deposition of 252 Ma. In La Ciénega the sedimentary basement consists of limestones interlayered with shales with some channels of conglomeratic sandstones. The youngest U-Pb detrital zircon population from the conglomeratic sandstones yielded a maximum deposition age of 150 Ma.

The Laramide continental arc outcrops in Bacis and La Ciénega are limited to batholith apophyses dated at ~95 and ~84 Ma respectively. The LVC volcanic units are restricted to andesite lava flows dated at ~86 to 84 Ma (U-Pb, LAICPMS; Figure 2).

In both districts, the UVS consists of ignimbrites with U-Pb LA-ICP-MS ages of ~36 Ma and ~30 Ma respectively. The ignimbrite succession is cut by rhyolitic dikes and domes. The rhyolitic domes range in age from 31 to 29.5 Ma (U-Pb and K-Ar ages respectively). The UVS volcanism is emplaced through fissures associated with a NNW-trending fault corridor.

### 3 Results

#### 3.1 Geochronology of the lithologies in the Bacis and La Ciénega mining districts

The basement exposed in the two study areas differs in lithology and age. In the Bacis, it consists of greenschist-facies quartz sandstones with lithics fragments. The youngest U-Pb detrital zircon population (LA-ICPMS) indicates a maximum age of deposition of 252 Ma. In La Ciénega the sedimentary basement consists of limestones interlayered with shales with some channels of conglomeratic sandstones. The youngest U-Pb detrital zircon population from the conglomeratic sandstones yielded a maximum deposition age of 150 Ma.

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#### 3.2 Mineralization paragenesis and dating

At Bacis, mineralization occurs along NW- to NNW-trending strike-slip faults, cemented by comb quartz followed by mosaic quartz texture that represents the vein-filling stage and hosts the Au-Ag mineralization. The mineralization stage begins with pyrite + sphalerite ± galena and finishes with acanthite traces and then electrum. Alteration consists of pervasive sericitization and propylitization.

La Ciénega deposit exhibits a more complex mineralization distribution and paragenesis. In the UVS the mineralization is characterized by high Au grades, pervasive sericitization and silicification, comb, mosaic, and colloform quartz textures, with the colloform quartz stage corresponding to the waning of the hydrothermal system. The metallic paragenesis is defined by Py+Sph+Gn±Cpy and acanthite traces.

In the LVS, mineralization is characterized by increasing Ag grade, adularia rhodochrosite and illite with comb mosaic quartz textures. The metallic paragenesis is composed of trace Sph+Gn±Py+Cpy and acanthite.

No phases suitable for geochronology were found in the mineralized assemblages at Bacis. The only constraint is the veins crosscut the ca. 30 Ma Oligocene rhyolitic dome.

At La Ciénega, adularia within a pervasive sericite halo in the shallow part of the LVC, and illite in the LVC deepest part of the deposit were selected for geochronology. The illite K-Ar data yield a minimum age of 34 Ma. The adularia 40Ar/39Ar dating experiment gave a step heating spectrum that was too disturbed to calculate a plateau age. Single steps range from 34 to 26 Ma, with a cluster of steps at 30 Ma.

#### 3.3 Microthermometric data

Samples of mosaic quartz cement from mineralized structures were collected at different depths in both districts. Only primary fluid inclusions were identified and analyzed (Roedder, 1984; Van den Kerkhof and Ulrich, 2001). Salinities were estimated using the fluid
inclusion melting temperature in the numeric model of Lecumberri–Sanchez et al (2012). At Bacis, the homogenization temperatures range from 165 to 234 ºC displaying a unimodal distribution with peak at 210ºC. Salinity estimates range from 0.53 to 9.21 wt% NaCl. At La Cienega, the homogenization temperatures range from 140-240°C, with a bimodal distribution with peaks at 180 and 210ºC. Salinities variation is more restricted than Bacis, from 0.18 to 5.26 wt% NaCl.

Figure 2. Stratigraphic columns of the Bacis and La Cienega mining districts

3.4 Decreptometry data

The maximum temperatures of the mosaic quartz cement hydrothermal event were estimated by decreptometry using the methodology of Burlinson et al (1983). At the Bacis fluid inclusion decrepitation occurs in a temperature range from 300 to 500°C, with a modal distribution peak at ca. 430°C. At La Cienega, the decrepitation temperature pattern present a wider variation range from 300 to 650ºC with a bimodal distribution. The two maximum peaks are identified at 430 and 550ºC.

3.5 Chlorite geothermometry

Chlorite minerals were sampled in different sites of the districts for representative parts of the mineral paragenesis. The crystallization temperatures were calculated using the Kranidiotis and MacLean (1987) equation. At Bacis the chlorite crystallization temperatures are a very restricted, clustering at ~270±6°C. For the La Cienega deposit, the data obtained exhibit a larger variation ranging from 240 to 372°C with a well-defined bimodal distribution with peaks at 250 and 330 ±10°C

4 Discussion

Dating of Au-Ag mineralization (using both direct and indirect approaches) indicates that the Bacis and La Cienega districts share a common mineralization event at ca. 30 Ma. This age overlaps with Oligocene silicic volcanism in the UVS and in particular within the rhyolitic domes which host some of the veins. In both districts, the mineralization is dominated by gold, pervasive sericitization, silicification, and propylitization. The thermal ranges of this Au mineralization event are also comparable with minimum temperatures from FI homogenization of 230ºC and a maximum temperature from FI decrepitation of 430ºC. Chlorite geothermometers from both deposits indicate comparable crystallization temperatures of 250 and 270±6ºC for La Cienega and Bacis respectively. Taking into account the fluid inclusion salinity (~5%eq NaCl), and the fluid inclusion homogenization and chlorite crystallization temperatures, the maximum depth of ore precipitation is estimated at ca 1000m in Bacis and 1500m in La Cienega.

The deeper part of the La Cienega deposit show particularities compare to the rhyolitic domes mineralizing areas. The deepest parts are characterized by adularia/rhodochrosite cements, the increase of acanthite and molybdenite. The chlorite chemistry, and the homogenization and decreptometry temperatures ranges show bimodal distribution suggesting the occurrence of a second mineralization events. The adularia experiment yielded a spectrum too perturbed to establish a plateau age. The higher temperature step heating ages (~34Ma) are comparable to the K-Ar age of illite and to the emplacement of the LVC andesite (~36Ma). However, both adularia and illite isotopic ages are minimum ages, that were likely reset by Oligocene and Miocene thermal events as illustrated by the adularia step-heating spectra. Illite and adularia have an isotopic closure temperature of ca. 250ºC, which are comparable with the observed chlorite crystallization temperatures and below the decrepitation temperatures.

We conclude that the ages of both illite and adularia were partially reset, and that the illite K-Ar age has no geological meaning. The close presence of two districts with Eocene silver mineralization, Topia and San Dimas (Louck et al. 1988; Montoya et al., 2019), suggest that La Cienega deposit could have been affected by an Eocene intrusion associated with a discrete silver and adularia/rhodochrosite Eocene mineralization event. Taking into account the fluid inclusion salinity (~5% eq NaCl), and the fluid inclusion homogenization and chlorite crystallization temperatures, the depth of mineralization precipitation is estimated below 1500m in good agreement with the local stratigraphic column evolution.
5 Conclusion

Our new geological, petrological, geochemical and geothermometric reevaluation of the Bacis and La Ciénega mining districts provides new constraints on formation models for both deposits:

Both mining districts have a common mineralization event related to the emplacement of Oligocene rhyolite domes. This Oligocene mineralization event is characterized by high Au/Ag high ratios, the presence of quartz in comb, mosaic, and colloform textures, pervasive sericitic, silica, and propylitic alteration, metallic paragenesis of Py+Sph+Gn with acanthite and then electrum, and a minimum temperature (from FI homogenization) of 180 - 230 °C and a maximum temperature (from FI decrepitation) of 430°C, with salinities of 5wt% NaCl, and chlorite crystallization temperatures of 250-270°C.

At La Ciénega mining district a more complex mineralization model can be envisaged. The K-Ar and 40Ar/39Ar data coupled with petrographic evidence imply an Eocene mineralizing event characterized by higher Ag grade, the presence of quartz in comb and mosaic textures, pervasive sericitic and propylitic alteration, metallic paragenesis of Sph+Gn+Py+Cpy traces with acanthite, and a minimum temperature (from FI homogenization) of 240°C to a maximum temperature (from FI decrepitation) of 550°C, with salinities of 5% NaCl, and a chlorite crystallization temperatures of 330°C.

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Subdivision of wall rock alteration zoning in the Hishikari epithermal gold deposit, southern Kyushu, Japan

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Kyushu University

Abstract. Detailed analysis of wall rock alteration seeks to establish discrete hydrothermal alteration zoning around the Hishikari low-sulfidation gold deposit. Samples from four underground cross cuts and five drill holes were collected. As a result of analysis, samples derived from underground cross cuts exhibit a dominant chlorite-smectite interstratified mineral (C/S). Core samples exhibit C/S, but chlorite is also present, which is an index mineral for the exploration of the veins. In the deeper part of the core sample around the Sanjin area, epidote is present which can be used as an index mineral for alteration zoning.

1 Introduction

The Hishikari deposit is an epithermal vein-type gold deposit with high-grade Au (30-40g/t of gold), and is located in Kagoshima prefecture, southern Kyushu, Japan.

Izawa et al. (1990) divided the alteration zoning around the Hishikari deposit into the following four zones: cristobalite-smectite (zone I), quartz-smectite (zone II), interstratified clay minerals (zone III), and chlorite-sericite (zone IV). In the exploration of the veins, zone IV has been used as an index of the proximal host to the mineralized veins. However, even in zone IV there are areas that do not host veins. In addition, some veins occur within zone III. Given these inconsistances, a new alteration zoning proxy that is sensitive to the mineralized veins is under review.

Yasuhara (2004) identified the alteration mineralogy of the host rocks mainly in the Yamada zone, western part of the Hishikari deposit. Yasuhara (2004) conducted XRD analysis on altered host rocks of 230 core samples in 21 bore holes and 50 underground samples. Based on the proportion of chlorite in C/S interstratified clay minerals, zone III was subdivided into 3 subzones as follows: Zone IIIa - chlorite is 0-30%; Zone IIIb - chlorite is 50-60% (corrensite); Zone IIIc - chlorite is 80-100%. By means of the subdivision, two small anomalous zones in the Yamada district were identified. Yasuhara (2004) showed that discrimination of zone III can be useful for exploration.

Therefore, mainly the eastern part of the Hishikari deposit, the Honko-Sanjin zone is studied in this work, with the goal to establish a new alteration index by subdividing the previously established alteration zones.

2 Outline of Hishikari deposit

The basement rock to the Hishikari deposit is the Cretaceous Shimanto-Supergroup, which consists mainly of sandstone and shale. In the mining area, the Shimanto-Supergroup has a Turonian age (88.5 to 90.4 Ma), based on a fossil bivalve identified as Inoceramus (Mytiloides) cf. Labiatus (Schlotheim) (Hayasaka 1999). The group is covered by Late Pliocene to Pleistocene volcanic rocks, including the Hishikari Lower Andesites with the age of 0.98 to 1.62 Ma based on K-Ar ages (Izawa et al. 1993).

The mine consists of the following three deposits: the Honko deposit, the Sanjin deposit, and the Yamada deposit. The veins of the Honko and Sanjin deposits are hosted mostly by the Shimanto-Supergroup. In contrast, the veins of the Yamada deposit are hosted by the Hishikari Lower Andesites. The strike of the veins are N30°E-50°E, with dips of 70°NW-90° (Ibaraki and Suzuki 1993).

By means of the K-Ar age-dating, the most economically important mineralization, Hosen, Zuisen and Keisen veins, is considered to have occurred around 0.90 Ma (Sekine et al. 2002). Also, hydrothermal activity is considered to have been active for a longer period for mineralization in the Yamada deposit (from 1.21 to 0.64 Ma) in contrast to the Honko-Sanjin deposits (from 1.01 to 0.88 Ma) (Sanematsu et al. 2005). Fluid inclusion microthermometry has revealed the temperature of mineralization in the Hishikari deposit was 180–250°C (e.g. Izawa et al. 1990; Hayashi et al. 2000; Etoh et al. 2002; Sanematsu et al. 2005, Takahashi et al. 2017; Shimizu et al. 2018).

3 Sampling and methodology

The samples were collected from four underground crosscuts (50W147, 50W163, 70E17, and D70KE) and five drill holes (XV-1, XV-14, SV-4, SV-5, KV-26) from the Hishikari mine (Fig. 1). The core samples were collected at intervals of 15 to 20 m in each crosscut and drill core. The Shimanto-Supergroup is considered to have suffered not only hydrothermal alteration but diagenesis and metamorphism, therefore the present study focuses on alteration of volcanic rocks.

Microscopic observation and X-ray diffraction (XRD) were utilized to identified mineral assemblages. Bulk, oriented and ethylene-glycol (EG)-treated samples were analyzed to distinguish smectite or interstratified mineral from other clay minerals such as chlorite or illite.
4 Results and discussion

4.1 Mineral assemblage

The identified alteration minerals are: chlorite, illite, chlorite-smectite interstratified mineral (C/S), illite-smectite interstratified mineral (I/S), carbonates, quartz, pyrite, epidote; C/S includes corrensite.

Underground, most of samples include the chlorite-smectite interstratified mineral (C/S). The proportion of chlorite in C/S is variable, with the abundance of chlorite very scarce in samples from the four underground cross cuts. Therefore, the alteration zone along the four crosscuts is considered to belong to zone III.

From drill hole SV-4, which is located in the Sanjin area, chlorite occurs around 500m depth. This part belongs to the zone IV. In contrast, in drill hole SV-5 in Sanjin, the proportion of chlorite in C/S tends to decrease, suggesting that the hole is distal from the heat source.

4.2 Presence of epidote

In DDH SV-4, epidote is found in the interval between 480-520m. Epidote is generated at higher temperatures than chlorite and illite in general (Inoue 1995). The presence of epidote in the hydrothermally altered volcanic wall rock in the Hishikari deposit has not been reported in previous studies. Therefore, this mineral may have potential as a new index mineral for the division of alteration zoning.

For the Yamada deposit, previous research has not shown the presence of epidote. This suggests the existence of a higher temperature fluid in the Honko-Sanjin deposits than the Yamada deposit.

5 Future work

In order to subdivide the altered zone, the application of geothermometry on chlorite and/or illite will be conducted. In addition, hydrogen and/or oxygen isotope analysis will be applied to the hydrothermal minerals such as chlorite and illite, in order to understand the isotope halo due to the hydrothermal activity.

Acknowledgements

We are grateful to Sumitomo Metal Mining for providing access to underground workings and drill cores of the Hishikari gold deposit. We thank Mr. Takayuki Seto, the manager of Geology & Exploration Section, Hishikari mine, for his kindness of the permission and suggestion to the publication of the present study. We also thank the staff of Sumitomo Metal Mining, especially Mr. Atsuhiro Kuroda for his various kinds of help and assistance during fieldwork and core sampling.

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Pb-Bi(-Cu) and Pb-Sb sulfosalts from Stan Terg area, Kosovo

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Abstract. Chemical analysis of lead-bismuth, lead-bismuth-copper and lead-antimony sulfosalts from Mazhiq and Vllahi in Trepça Mineral Belt (northern Kosovo) were performed using electron micro probe analyzer. Bismuthinite, krupkaite, aikinite, cosalite and native bismuth were identified as main Bi-bearing minerals. Presence of Pb-Sb sulfosalts as boulangerite, semseyite and chovanite was confirmed in listwaenite type of mineralization from Vllahi. Cosalite tends to have constant chemical composition, whereas minerals of bismuthinite-aikinite series are characterized by broad degree of aikinite-type of substitution in individual members. Bismuthinite has nₐ=0.56 up to nₐ=9.69, krupkaite nₐ=47.50 up to nₐ=58.35 and aikinite nₐ=83.92 up to nₐ=93.91. Study indicate possible presence of other phases of bismuthinite-aikinite series.

1 Introduction

Stan Terg is the largest Pb-Zn deposit in Trepça Mineral Belt, historically important European district for ore mining (Kołodziejczyk et al. 2015). Several other small deposits and mineral occurrences had been found in this region.

Many previous researches had been describing ore mineralization in Stan Terg region. Some of them reported presence of Pb-Bi(-Cu) and Pb-Sb sulfosalts (Terzić et al. 1974; Kołodziejczyk et al. 2015; 2017). However some specific minerals and mineral groups need further investigation, as authors believe.

The aim of this study is to obtain new data of presence, chemical composition and replacement events of Pb-Bi(-Cu) and Pb-Sb sulfosalts with putting special emphasis on bismuthinite-aikinite series. These could give clues to conditions of ore-forming processes evolution in investigated area (Topa et al. 2002).

2 Geological setting

Stan Terg Pb-Zn deposit is placed in the center of 80-km-long Trepça Mineral Belt in northern Kosovo, within Vardar tectonic zone (Hyseni et al. 2010). Vardar tectonic zone is elongated trending NNW-SSE regional suture between the Serbo-Kosovaro-Macedonian Massif to the east and the Dinarides to the west (Hyseni et al. 2010).

The Stan Terg area contains Triassic sediments, phyllites, volcanoclastic rocks and Upper Triassic carbonates, Jurassic ultrabasic rocks and serpentinites (ophiolite), Cretaceous clastics, serpentinites, volcanics and volcanoclastic rocks of basaltic composition and carbonates and Oligocene-Miocene volcanics (Hyseni et al. 2010). Ore mineralization is linked to Oligocene-Miocene magmatism activity (Kołodziejczyk et al. 2017) of andesite, trachyte and latite composition.

Several types of ore mineralization, such as skarn, hydrothermal replacement, listwaenite-type and faults-controlled vein mineralization had been described (Kołodziejczyk et al. 2017).

Figure 1. Geological map of Trepça Mineral Belt (from Hyseni et al. 2010).

3 Samples and methods

3.1 Investigated material

Samples containing sulfosalts mineralization were collected from outcrops of altered and weathered ore in three places in Stan Terg region: Vllahi and Mazhiq (two places) villages.

Material from Vllahi is represented by greenish listwaenites, partially brecciated and sillificated. Macroscopically visible galena is disseminated in gangue minerals (mostly quartz). Ore from Mazhiq I contains zones with massive arsenopyrite, pyrite and chalcopyrite in quartz and carbonates. Needles of bismuth sulfosalts up to 2 cm are usually disseminated in quartz or chalcopyrite. Ore from Mazhiq II contain samples with listwaenites and quartz breccia with massive gersdorffite, pyrite and arsenopyrite impregnations. Needle-like crystals of sulfosalts up to few cm are disseminated in carbonates or galena.
3.2 Analytical methods

Chemical analyses were carried out by electron micro probe analyzer (EPMA) using EOL Super Probe JXA-8230 at the Critical Elements Laboratory AGH-KGHM in Kraków, Poland. Operating conditions were an accelerating voltage of 20 kV, a beam current 20 nA, peak time of 20 sec, and a background time of 10 sec, with following standards natural: (pyrite, stibnite, chalcopyrite, galena, arsenopyrite) or synthetic (native silver, native bismuth) and spectral lines: Ag(Lα), Pb(Mα), Sb(Lα), Cu(Kα), Fe(Kα), Bi(Mα), As(Lα) for sulfosalts.

4 Results

4.1 Ore mineralogy

Ore minerals being present in investigated samples from Mazhiq I and Mazhiq II are: chalcopyrite, galena, arsenopyrite, pyrite, sphalerite, cosalite, tennantite-tetrahedrite, bismuthinite-aikinite series minerals, marcasite and native gold. These minerals occur in numerous different associations. Bi-sulfosalts are associated with native Bi and Au, in some cases are prior to the last stage of galena and chalcopyrite crystallization.

Mineralogy of Vllahi mineral occurrence is different. Galena and sphalerite are only base metals’ sulfides here. Ni mineralization represented by niccolite and gersdorffite (and probably other Ni/Ni -Co sulfides) constitute first association in samples from there. It is prior to boulangerite, semseyite and chovanite. Pb-Sb sulfosalts are associated with galena. Tennantite-tetrahedrite, sphalerite, and bouronite are later.

4.2 Boulangerite, semseyite and chovanite

Pb-Sb sulfosalts occur only in samples from Vllahi. All three phases form zonal crystals from tens up to 500 μm in size (Fig. 3). They are usually euhedral and partially digested. Usually they form intergrowths with galena, where they are overgrowing galena aggregates. Three phases – boulangerite, semseyite and chovanite were identified (Fig. 2).

Calculated average formulas of investigated minerals: boulangerite Pb4.81(Sb4.15As0.03)Σ8.10S21.11, semseyite Pb8.89Fe0.01(Sb8.03As0.06Bi0.01)Σ14.36S36.21, chovanite Pb14.62Fe0.01Cu0.01Ag0.01(Sb3.95As0.30Bi0.02)Σ16.17S31.68.

Table 1. Average chemical composition of investigated sulfosalts based on EMPA. Number of analyses in brackets. 1 – boulangerite, 2 – semseyite, 3 – chovanite, 4 – cosalite from Mazhiq II, 5 – cosalite from Mazhiq I, 6 – bismuthinite from Mazhiq II, 7 – bismuthinite from Mazhiq I, 8 – krupkaite, 9 – aikinite, na – not analyzed.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Pb wt%</th>
<th>Fe wt%</th>
<th>Cu wt%</th>
<th>Ag wt%</th>
<th>Bi wt%</th>
<th>Sb wt%</th>
<th>As wt%</th>
<th>S wt%</th>
<th>Total wt%</th>
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<td>0.01</td>
<td>0.00</td>
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<td>27.25</td>
<td>0.13</td>
<td>19.20</td>
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<tr>
<td>2(22)</td>
<td>52.40</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
<td>0.06</td>
<td>27.82</td>
<td>0.14</td>
<td>19.26</td>
<td>99.69</td>
</tr>
<tr>
<td>3(13)</td>
<td>50.94</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
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<td>28.56</td>
<td>0.49</td>
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<td>99.62</td>
</tr>
<tr>
<td>4(24)</td>
<td>38.46</td>
<td>0.02</td>
<td>0.85</td>
<td>1.25</td>
<td>44.57</td>
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<td>5(31)</td>
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<td>1.28</td>
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<td>0.43</td>
<td>0.00</td>
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<td>0.59</td>
<td>0.03</td>
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<td>9.80</td>
<td>0.01</td>
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<td>0.15</td>
<td>na</td>
<td>16.69</td>
<td>101.74</td>
</tr>
</tbody>
</table>

Figure 2. Chemical variation of Pb-Sb sulfosalts as a function of a ternary plot in terms of Sb+As, Cu+Fe+Ag, and Pb+Bi. Black circles – this study, crosses – ideal chemical composition of minerals.
Figure 3. Back-scattered electron image showing compound zonal crystal of Pb-Sb sulfosalts. Bou – boulangerite, Cho – chovanite, Sem – semseyite.

crystals. It appears often also as tens up to 200 μm in size euhedral inclusions within quartz and sulfides.

Chemical analyses of cosalite from Mazhiq I gave average formula as \((\text{Cu}_{0.80}\text{Ag}_{0.32})_{\Sigma 1.12}\text{(Fe}_{0.03}\text{Pb}_{7.40})_{\Sigma 7.43}\text{Bi}_{8.43}\text{Sb}_{0.10})_{\Sigma 8.53}\text{S}_{20}\) calculated on basis of Topa & Makovicky (2010). Cosalite from Mazhiq II has average formula as \((\text{Cu}_{0.53}\text{Ag}_{0.46})_{\Sigma 0.99}\text{(Fe}_{0.01}\text{Pb}_{7.36})_{\Sigma 7.37}\text{Bi}_{8.45}\text{Sb}_{0.07})_{\Sigma 8.52}\text{S}_{20}\). Both of them have significant Ag and Cu substitution. Ag max. content attains 1.02 wt.% in cosalite from Mazhiq I and 1.40 wt.% in samples from Mazhiq II. Max. Cu content is 1.76 wt.% and 1.13 wt.% respectively: Compared with standard chemical composition, investigated cosalite have broader 2(Cu+Ag)↔Pb and Ag+Bi↔2Pb substitutions. Chemical composition of cosalite from this study is substantially stable. Mean chemical composition in Table 1.

4.4 Bismuthinite – aikinite series

Bismuthinite is present in samples from Mazhiq I and Mazhiq II, other minerals of bismuthinite – aikinite series (krupkaite and aikinite) occur only in Mazhiq I. Bismuthinite is the most common phase from the series. Krupkaite and aikinite tend to occur on the boundaries between dominant phases – bismuthinite and cosalite (Fig. 4), usually replacing these previous minerals.

Bismuthinite often forms elongated needle-like crystals up to few centimeters long, crosscutting carbonates or prior chalcopyrite. It occurs also as aggregates of anhedral crystals in interstices between quartz crystals. This mineral could occur as practically dominant or monomineral Bi-sulfosalts in a sample as well as in association with cosalite, krupkaite and aikinite. It is often associated with native bismuth and rarely with native gold. Its chemical composition is variable. Degree of aikinite-type substitution (on basis of Topa et al. 2002) has values from \(n_a=0.56\) to \(n_a=9.69\) in samples from Mazhiq I and \(n_a=0.53\) to \(n_a=6.15\) in samples from Mazhiq II. Average formula calculated on basis of Topa et al. (2002) is \((\text{Bi}_{7.76}\text{Sb}_{0.12}\text{Cu}_{0.18}\text{Pb}_{0.16}\text{Fe}_{0.01})_{\Sigma 8.00}\text{S}_{11.22}\) for bismuthinite from Mazhiq I and \((\text{Bi}_{7.61}\text{Sb}_{0.15}\text{Pb}_{0.12}\text{Fe}_{0.01})_{\Sigma 8.00}\text{S}_{11.35}\) for that from Mazhiq II. Bismuthinites from both localities have variable Sb content. In Mazhiq II it varies from 0.24 to 3.38 wt.%, in Mazhiq I from 0.06 to 4.04 wt.% Fe and Ag content is negligible.

Krupkaite forms thin (usually to 10 μm) fringes on a boundaries of bismuthinite crystals (Fig. 4) or irregular elongated exolutions within bismuthinite. Usually it is product of bismuthinite or cosalite replacement. Its average formula represents as \((\text{Bi}_{4.75}\text{Sb}_{0.02}\text{Cu}_{1.60}\text{Pb}_{1.61}\text{Fe}_{0.01})_{\Sigma 8.00}\text{S}_{9.21}\). Degree of aikinite-type substitution varies from \(n_a=47.50\) to \(n_a=58.35\). Analyses cover practically whole known krupkaite range according to Topa et al. (2002). Average chemical composition of investigated krupkaite is very close to theoretical one.

Aikinite occurs similarly as krupkaite. It forms tens up to 100 μm in size irregular crystals on a boundaries of, or within other Bi-sulfosalts. Also it is a product of bismuthinite, cosalite and krupkaite replacement. Its average formula is \((\text{Bi}_{3.21}\text{Sb}_{0.02}\text{Cu}_{2.39}\text{Pb}_{2.37}\text{Fe}_{0.01})_{\Sigma 8.00}\text{S}_{8.06}\). Degree of aikinite-type substitution varies from \(n_a=83.92\) to \(n_a=93.91\).

5 Discussion

5.1 Cosalite

Cosalite from Stan Terg area was previously reported in Stan Terg deposit (Terzić et al. 1974; Kołodziejczyk et al. 2017) and in Mazhiq I (Mederski et al. 2018). Chemical composition of mineral from this study differs significantly from researches carried out on material from Stan Terg deposit and is similar to data obtained by Mederski et al. (2018).

Kołodziejczyk et al. (2017) described cosalite with strongly variable Sb content up to 13.6 wt. % caused by advanced Sb-Bi substitution. Cosalite from Mazhiq I and Mazhiq II have much lower and very stable Sb content.

Content of Ag and Cu is higher in Mazhiq I and Mazhiq II than in Stan Terg deposit (0.27 – 0.72 apfu of Cu+Ag in Stan Terg. Kołodziejczyk et al. 2017). This is probably a result of more advanced Ag+Bi↔2Pb and 2(Cu+Ag)↔Pb substitutions (Topa & Makovicky 2010), however obtained data does not show such statistical
5.2 Bismuthinite – aikinite series

Bismuthinite was previously described as widespread mineral in different ore types from Stan Terg deposit, associated with lilli anite, ikunolite and native bismuth, often within galena (Kołodziejczyk et al. 2015). It was also reported in Mazhiq I (Mederski et al. 2018). This study delivers more data of bismuthinite chemical composition, suggesting higher degree of aikinite-type substitution. Analyses cover nearly entire bismuthinite field, determined by Topa et al. (2002) and based on aikinite mol.%. Some analyses give results above this field (Fig. 5), but they were excluded from calculations and need further investigation. They show possible broader range for aikinite substitution in bismuthinite. Similar bismuthinite is widespread in the nature and need only crystallographic investigation to prove broad range of aikinite substitution in bismuthinite (Pršek et al. 2008). Analyses which fall between krupkaite and aikinite fields needs more study to prove presence of other phases of bismuthinite-aikinite series in Mazhiq I occurrence. Sb content is highly variable and has values up to 3.78 wt.% in Mazhiq I, which is much more than in previous analyses (up to 1 wt.% in Mederski et al. 2018), but is still low compared to Kutná Hora area in Czech Republic (up to 6.6 wt.%). Pažout et al. (2017) or Brezno-Hviezda occurrence in Slovakia (up to 26 wt.%). Pršek et al. 2008).

Mederski et al. (2018) first reported presence of krupkaite and pekoite as other mineral member of bismuthinite-aikinite series in Stan Terg area. This study confirms occurrence of krupkaite of wider range of krupkaite field (Fig. 4), based on aikinite mol.%. According to obtained data, krupkaite does not have significant admixtures (av. 0.17 wt.% Sb and 0.03 wt.% Fe).

Presence of aikinite in Stan Terg area has not been reported so far. Analyses give results in wide range of aikinite field (Fig. 5). Mineral does not have significant admixtures (av. 0.15 wt.% Sb and 0.05 wt.% Fe).

Occurrence of only these three minerals of bismuthinite – aikinite series indicates low fluid temperature (up to 250°C) and rather constant crystallization conditions (Topa et al. 2002).

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References


Nickel mineralization in hydrothermally altered serpentinites (listwaenites) in the broad area of Stan Terg mine, Vardar Zone, Kosovo

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Abstract. The presence of various Ni bearing minerals in hydrothermally altered serpentinites from the broad Stan Terg area is documented. Ni minerals occur in the hydrothermally altered serpentinites (Vllahi, Melenica), hydrothermal base metal mineralization in contact with serpentinites (Mazhiq) or in carbonate veins in listwaenites (Selac). Niccolite, millerite, gersdorffite, and maucherite were identified as the main Ni-bearing minerals. They occur in the paragenesis with minerals of the thiospinel (violarite, Co bearing violarite, siegenite, Fe bearing siegenite and polydymite) group and rammelsbergite, gersdorffite-krutovite solid solution, Nimarcasite and main Zn-Fe-Cu-Pb-Sb sulphides and sulphosalts. This is the first described occurrence of nickel mineralization in the area of Stan Terg mineralizing system.

1 Introduction

Kosovo is characterized by rich occurrences of polymetallic mineralization of economic importance. The most important are hydrothermal Zn-Pb deposits with associated Au-Ag (Cu, Bi, Te, Sb). The presence of Ni mineralization is known only from the listwaenite occurrences close to Crnac deposit in the Rogozna Mountains, Northern Kosovo (Radosavljevic et al. 2015) or from the weathered and hydrothermally altered serpentinites in schists of Veles series in Donje Ljupce (Szczygieł 2017). Minerals such as millerite, bravoite, niccolite, various members of the gersdorffite-ullmannite series in paragenesis with various Cu-Ag-Pb-Sb-Zn-Sn minerals and native elements were indentified in Crnac. Additionally millerite, siegenite, polydymite and pentlandite were identified in Donje Ljupce. In the Stan Terg area, only base-metal mineralization with precious metal epithermal mineralization occurs without any known nickel phases (Kołodziejczyk 2016). The aim of my research is to characterize nickel mineralization in the broad Stan Terg mine area in the Kopaonik Mountains, Vardar Zone, Kosovo.

2 Geological setting

The Vardar Zone is an elongated belt extending from Bosnia through Kosovo, Macedonia and Greece to Turkey in a NNW-SSE trend. It is interpreted to be a transitional zone between the Serbian-Macedonian massif from the east and Dinaric Alps to the west. It was formed during the late Cretaceous closure of Neo-Tethys ocean basin, as a result of the Adria and Eurasia craton collision. The Vardar Zone mainly consists of marine and continental sedimentary rocks which are characterized by different grades of metamorphic and tectonic deformation. Additionally, as a result of continental collision, younger felsic rocks intruded into the sequence. The age of these volcanic rocks is between late Cretaceous and Miocene (Zelic et al. 2010). This structure consists of fragments of Paleozoic crystalline rocks discordantly lying on the Triassic clastic rocks and upper Triassic carbonates. Jurassic rocks mainly consist of an ophiolite sequence. Cretaceous strata is represented by a clastic series. During the Oligocene and Miocene period, voluminous volcanic activity occurred. These rocks were intruded and often exhibit a different chemical composition. In areas where igneous andesite/lavite rocks intruded into serpentinites, listwaenite formed (Hyseni et al. 2010). In Kosovo, part of Vardar Zone - the Trepça Mineral Belt is the main metallogenic unit which was recognized. This belt is one of the more important areas for Zn-Pb ores in Europe. His length is above 80 km and start in the northern part of Kosovo (Kolodziejczyk et al. 2016).

3 Samples and methods

3.1 Investigated material

Samples with nickel mineralization were collected from
outcrops of altered listwaenites with visible disseminated mineralization (Vllahi, Melenica), from carbonate veins with ore mineralization (Selac) as well as from weathered ore (Mazhiq, Vllahi).

Material from Vllahi is represented either by greenish listwaenites, partially brecciated and sillificated or by massive sulphide ore. Galena is only visible as a disseminated sulphide in listwaenite. Ore from Selac contains massive Fe-Mg-Ca carbonate veins with nests of niccolite and maucherite up to few cm in size. Carbonate veins occur in the tectonic zone with listwaenite occurrences. The Mazhiq samples were collected from the Fe-Mn carbonate blocks in the listwaenite zone. Samples are usually brecciated with quartz, carbonates and sulphides as massive gersdorffite, pyrite impregnations, needle-like crystals of Bi sulfosalts with galena, sphalerite, tetrahedrite and chalcocyprite. Samples from Melenica are represented by greenish listwaenites, partially silicified with galena, sphalerite veinlets and pyrite, millerite and arsenopyrite crystals.

3.2 Analytical methods

Chemical analyses were carried out by electron microprobe analyzer (EPMA) JEOL Super Probe JXA-8230 at the Critical Elements Laboratory AGH-KGHM at AGH-UST University in Kraków, Poland. Operating conditions featured an accelerating voltage of 20 kV, a beam current 20 nA, peak time of 20 sec, and a background time of 10 sec and using the following natural standards (pyrite, stibnite, chalcopyrite, arsenopyrite) and synthetic standards (Bi:Se, pure Co and Ni) and spectral line used Sb (La), S (Ka), Fe (Kα), Co (Kα), Ni (Kα), Cu (Kα), Bi (Mα), As (Lα).

4 Results

4.1 Ore mineralogy

Ore minerals which were identified in the Ni mineralization and Ni-bearing samples include: pyrite, galena, chalcocyprite, marcasite, arsenopyrite, sphalerite, Pb-Sb and Bi sulfosalts, hematite, Cr-bearing spinels and quartz, carbonates and Cr-bearing micas. Ni minerals identified in the paragenesis were: niccolite, maucherite, rammelsbergite, krutovite, violarite, siegenite, usually disseminated, but sometimes found as thin sulphide veinlets of polyanthite, gersdorffite and millerite. Mineralization is sulphide nests occur. Ore mineralization in listwaenites was formed at least in two stages. The older stage (Ni-bearing stage) is represented by sulphides, sulphoarsenides and arsenides of Fe-Ni-Co: mainly millerite, gersdorffite, niccolite, maucherite, gersdorffite and pyrite/marcasite. The younger phase is typical by presence of base-metal mineralization with galena, sphalerite, chalcopyrite, tetrahedrite, pyrite as well as various sulphosalts. Ore minerals usually occur as small individual grains or intergrowths of different size – from 50 up to 500 µm. They rarely could reach few cm in size. The average chemical composition of all identified nickel phases is presented in the Table 1. Chemical variation of Ni mineralization is presented on figure 2.

Table 1. Average chemical composition of investigated Ni minerals based on EMPA. Number of analyses in brackets. 1–Millerite (n=17), 2–Niccolite (n=30), 3–Gersdorffite (n=53), 4–Rammelsbergite (n=20), 5–Maucherite (n=57), 6–Siegenite (n=8), 7–Violarite (n=7), 8–Gersdorffite-Ullmannite (n=47), 9–Gersdorffite-Krutovite (n=10), 10–Fe bearing Gersdorffite (n=13), 11–Polydymite (n=1).

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Figure 2. Chemical variation of Ni mineralization in Stan Terg area as a function of a ternary plot in terms of S, As+Sb, Fe+Co+Ni. (R – rammelsbergite (n=20), Mi – millerite (n=17), G – gersdorffite (n=53), N – niccolite (n=30), G-K – gersdorffite-krutovite (n=10), G-U – gersdorffite-ullmannite (n=47), Fe G – Fe bearing gersdorffite (n=13), P – polydymite (n=1), S – siegenite (n=8), V – violarite (n=7), Ma – maucherite (n=7)).
4.2 Millerite

Millerite was identified in samples from Melenica, Selac and Vllahi. In Melenica it occurs as small elongated crystals in association with siegenite, Sb-bearing gersdorffite-ullmannite, chalcopryite, galena and bouronite. Often it is overgrown or replaced by gersdorffite (Fig. 4d). It is a common mineral in the samples. In Vllahi, it is rare, forming elongated crystals up to 100 µm enclosed in galena together with siegenite and gersdorffite, or disseminated needles in carbonates with marcasite and violarite (Fig. 4f). In Selac, it is also rare occurring as needle like crystals with polidyrite/siegenite veinlets cutting aggregates of Ni-arsenides. The size of the millerite needles is up to 100 µm. The chemical composition of millerite is close to theoretical with small content of Fe up to 0.94 wt.% and As up to 0.45 wt.%.

4.3 Niccolite, Rammelsbergite and Maucherite

Ni arsenides were found only in samples from Selac; in the Vllahi samples Ni arsenides are rare. They form massive aggregates up to 2 cm in size. Niccolite is intergrown with maucherite, whereas rammelsbergite forms zones in maucherite-niccolite aggregates (Fig. 4b). Niccolite was also identified as small inclusions in galena from Vllahi together with gersdorffite and possible breithauptite. Rammelsbergite from Vllahi was found only in few crystals where it forms small inclusions in galena. Niccolite is slightly enriched in Sb with contents up to 1 wt.%. Similarly, associated maucherite is also enriched in Sb up to 1.28 wt.%. Rammelsbergite has a different chemical composition and it is enriched in S up to 3.28 wt.%, Sb up to 2.16 wt.%, Fe up to 2.70 wt.% (samples from Vllahi) and Co up to 1.81 wt.%. (samples from Selac).

4.4 Gersdorffite

Gersdorffite is the main Ni-bearing phase in the listwaenite type of mineralization. It is present in samples from Mazhiq, Melenica and Vllahi but was not identified in Selac. Usually it forms euclidean crystals, sometimes zone (Fig. 4e), in association with other Ni phases as well as pyrite, galena, tetrahedrite, arsenopyrite and chalcopryite. The size of the crystals is usually up to 100 µm but sometimes aggregates of gersdorffite crystals can reach 1 cm (Mazhiq). On the basis of chemical analysis we can distinguish several different types of gersdorffite: gersdorffite, Fe bearing gersdorffite (only at Mazhiq), Sb-bearing gersdorffite and gersdorffite-ullmannite solid solution (Vllahi) and gersdorffite-krutovite solid solution (only at Vllahi). Pure, low Fe gersdorffite is the most common phase.

4.5 Thiospinels

Members of thiospinels mineral group are a common mineral in the Ni paragenesis. They were identified in typical listwaenite disseminated mineralization or in the vein type form (Fig. 4c). Usually they form euclidean crystals in association with other Ni minerals like gersdorffite, millerite or Ni arsenides. The size of the crystals is small, usually up to 50 µm. A few different phases were identified: violarite, siegenite, Fe bearing siegenite and polydymite. Siegenite is the most common of the phases, and occurs mainly in association with gersdorffite-ullmannite solid solution. Polydymite was found only in Selac as a thin vein with millerite crystals cutting a niccolite-maucherite aggregate. Violarite is typical for Vllahi polymetallic mineralization, where it forms needle like crystals disseminated in carbonates or as intergrowths with marcasite. Siegenite and intermediate members between siegenite and violarite usually form euclidean crystals in association with millerite and gersdorffite as well as inclusions in galena. Chemical composition of that phases is different. Violarite is enriched in Co up to 4.15 wt.% and Siegenite is usually close to ideal composition whereas siegenite from Melenica is enriched in Fe up to 9.78 wt.%. Polydymite is enriched in Co up to 6.38 wt.%. Chemical variation of thiospinels is presented on figure 3.

![Figure 3](image-url)

Figure 3. Chemical variation of thiospinels as a function of a ternary plot in terms of Ni/3, Fe, Co. S – Siegenite (n=8), P–Polydymite (n=1), V – Violarite (n=7).

5 Discussion

Ni mineralization in this area is described for the first time. Our research gives information about the composition, structures, textures, relationship between nickel bearing phases and other ore minerals. Nickel mineralization identified in the area has a broad diversity in mineral phases as well as chemical compositions. A similar paragenesis and association were identified in the other part of Kosovo in the same listwaenite type of mineralization (Radosavljević et al. 2015). They described millerite, niccolite, gersdorffite-ullmannite series and bravoite from Crnac, Rogozna Mountains, Northern Kosovo.
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Figure 4. Reflected light (a; b; c) and BSE (d; e; f) photomicrographs demonstrating ore paragenesis. a. Aggregate consisting of niccolite (nicc) with veins of rammelsbergitte (ram). b. Aggregate of maucherite (mau), niccolite (nicc) with rammelsbergitte vein (ram). c. Vein of Ni sulphides cut Ni arsenides: siegenite (sieg), millerite (mill), polydymite (pd). d. Milliterite (mill) needle replaced by gersdorffite (grf) with small inclusion of violarite (vio). e. Zonal gersdorffite with zones of Sb bearing gersdorffite (grf) and Fe bearing gersdorffite (Fe grf). f. Idiomorphic crystal of millerite (mill) with violarite (vio) chalcopyrite (ccp) and sphalerite (sph) in polimineral aggregate.

Similar Ni mineralization was described for the Kamariza Mining District, Lavrion, Greece. Authors described zoned gersdorffite in association with galena, pyrite and arsenopyrite. The gersdorffite displays oscillatory zoning in terms of Fe, Ni, and As contents, varying from ~1.5 to 9.0 wt.%, ~24 to 32 wt.% and 47 to 60 wt.%, respectively. There is an almost perfect linear correlation between Fe–Ni and As–S in the gersdorffite structure. Additionally gersdorffite from the Clemence deposit contains up to 0.2 wt.% Se, which likely substitutes for sulfur in the structure. At the “km3” locality, gersdorffite contains ~0.5–2 wt.% Fe, 46–48 wt.% As, and ~31–34 wt.% Ni. Millerite (NiS) was found in association with gersdorffite as small inclusions or as euhedral needle-shaped crystals enveloped by galena. As-bearing ullmannite, Ni(Sb,As)S, occurs as inclusions in gersdorffite, whereas vaesite (NiS₃) rims gersdorffite. Cobalt (of up to 0.35 wt.%) substitutes for Ni in vaesite and millerite (Voudouris et al. 2018). Samples from Stan Terg have a similar trend in Fe-Ni-As contents. The main differences between these areas is a lack of vaesite at Stan Terg. From all published data, it is clearly seen that nickel mineralization in the listwaenite rocks is nearly identical with similar trend in chemical composition of main phases.

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Iron-oxide ores in the Takab region, North Western Iran

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Abstract. The siliceous iron ore deposits in the NW part of Iran (Takab region) are hosted within paragranietic rocks, and are attributed to a Late Proterozoic age. They comprise massive, banded, nodular and disseminated ore types, which are mainly composed of magnetite. Magnetite contains traces of Al. It is variously hematized. Hematite shows higher Al, Si and Ca contents than the magnetite. The iron oxides contain inclusions of zircon, apatite, uraninite, Mn-carbonate and euhedral monazite. Later hydrothermal solutions precipitated goethite surrounding the magnetite-hematite-maghemite grains and replacing hematite. Barite occurs in fractures of iron oxides, Mn-Ba-Pb oxy-hydroxides and scheelite occur interstitial to iron oxides. The $\delta^{56}$Fe values observed for magnetite decrease from disseminated to nodular iron ore, averaging +1.3, +0.4 and -0.4 % (± 0.2 %), respectively. Iron isotopes of hematite in disseminated and layered ore show higher $\delta^{56}$Fe values than those of magnetite, in the range of +2 to +4 % (± 0.2 %). Volcano sedimentary primary processes are thus superposed by a secondary (magmatic?) hydrothermal process.

1 Introduction

Iran’s annual iron ore export reaches about 23.5 million tonnes. Over 90% is exported to China. Projections to 2025, indicates that iron ore production will triple, up to 66.2 MT (Hastorun et al. 2016). Most of the iron deposits are located in the northeastern and central part of Iran, while iron ore deposits of the northwestern part are still unstudied. Here we present results from the Takab Iron ore NW of Zanjan. Our study comprises mineralogy, geochemistry and Fe-isotopic composition.

2 Geological setting

In the Takab region, two types of iron ore deposits occur: (1) related to the Sanandaj-Sirjan Zone: their formation possibly related to the back-arc extension during the Prototethys subduction beneath the Cadomian magmatic arc (Ghorbani 2013; Nabatian et al. 2015). (2) South of Takab: Meso-to Cenozoic: iron oxide–apatite deposits of Kiruna-type are associated with plutonic rocks (Nabatian 2012; Nabatian et al. 2013). The latter present multiple vein deposits <1000 t of iron ore. At present, the Morvarid and Sorkhe-Dizaj deposits (400 000 t) are mined.

Figure 1. Tectonic and structural map of Iran (modified after Alavi 1991; Aghanabati 1998; 2005). The location of the study area is shown the red square, red star: volcanosedimentary iron ore, red dot: Kiruna type iron ores.

The mineralization forms thin layers and lenses interlayered with quartzite and amphibolites (Nabatian et al. 2015). In the study, the iron oxide mineralogy is essentially described as hematite and goethite, with barite as an accessory mineral. The age of the iron may be Late Proterozoic (Ghorbani et al. 2013).

3 Analytical methods

Optical microscopy in transmitted and reflected light
modes, SEM and electron microprobe analyses were performed on polished thin sections at the Centre Camparis, Sorbonne Université, UPMC Univ Paris 06, Paris, France. X-Ray diffraction was carried out at GEOPS, Université Paris Saclay, Orsay, France. Iron isotope measurements were performed by SIMS at CRPG (Nancy), and elemental geochemistry at SARM, CRPG, Nancy (XRF, ICP-MS).

4 Results

4.1 Petrology and mineralogy

The studied samples are massive, banded and nodular iron ores; disseminated ore is also present (Fig. 2). Massive, banded and nodular ore occurs as decimetric layers within folded mica schist.

The host rocks of the massive magnetite are epidotized, amphibolitized, chloritized fine grained plagioclase-rich rocks, crosscut by veins of magnetite and carbonate. These rocks may represent metavolcanic rocks (basalts). X-ray diffraction on banded and nodular ore samples indicates that all samples contain similar major mineralogy quartz, magnetite, hematite, maghemite, goethite in different proportions. Small peaks are attributed to barite (BaSO₄). The magnetite and hematite host 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. %).

The banded ore shows coarse and discontinuous banding with interstitial quartz (Fig. 2A). Magnetite forms individual grains (~50 µm to several hundreds of µm), hosting detrital zircons (sometimes corroded) and droplet-like inclusions of PbS and ZnS. It is partly altered to hematite. Iron oxide veins occur perpendicular to the iron oxide bands. Goethite is abundant around hematized magnetite and in veins, sometimes hosting pyrite relics and P-bearing minerals. In the matrix, apart from quartz, Mn-Ba-oxides and barite (partly replacing Ba-feldspar - hyalophane) and, rare uraninite occur. The matrix quartz grains show undulose extinction, indicating deformation.

The nodular ore is composed of mm-sized iron oxide agglomerates, partly elongated and disrupted in the quartz matrix (Fig. 2B). Other matrix minerals correspond to those in the layered ore. Magnetite is not hematized. It hosts inclusions of phosphates, Mn-and Fe-carbonates and uraninite.

In the disseminated ore, magnetite forms euhedral grains (~400 µm-1.5 mm), which are slightly hematized. The matrix minerals are quartz, minor K-feldspar and phengite. The feldspars host P (U, Th)-bearing phases, zircon and barite. Rutile, phosphates, scheelite, barite also occur interstitial to the matrix grains.

![Figure 2. Polished thin section scans. a. Banded iron ore: alternating quartz and iron oxide bands and subhedral magnetite grains partly hematized; b. Nodular iron ore in quartz matrix; magnetite shows minor hematitization; c. Disseminated iron ore with euhedral magnetite grains](image)

4.2 Geochemistry

The massive magnetite contains 77 wt.% total iron (Fe₂O₃) of which 22.5 wt.% of FeO. It is silica rich (14 wt.% SiO₂), and contains 1.7 wt.% Al₂O₃, 2.7 wt.% CaO and 0.35 wt.% CO₂. MnO and TiO₂ are low (0.08 wt.% and 0.05 wt.%, respectively). Trace elements comprise
50 ppm Cu, 80 ppm Co, 88 ppm W, 14 ppm V, 25 ppm Sn, 40 ppm Zn and 30 ppm Zr. Arsenic and U are low (7 and 1 ppm respectively). The host rocks of the massive magnetite, the epidotized metabasalts contain about 54 wt.% SiO₂, 10 wt.% Al₂O₃, 9.8 wt.% total iron (Fe₂O₃), with two third FeO (6.6 wt.%), 7.7 wt.% MgO, 8.8 wt.% CaO and 3.2 wt. % Na₂O. TiO₂ reaches 0.5 wt.%. Arsenic and U are as low as in the massive magnetite however, the host rock is richer in Cr (270 ppm), Ni (70 ppm), V (132 ppm), Sc (25 ppm) Sr (170 ppm) and Ba (440 ppm).

The banded ore hosts variable iron contents (13-53 wt.% total Fe₂O₃, 0.56-12 wt.% FeO). Silica (SiO₂) ranges from 44 to 57 wt.%, Al₂O₃ from 0.08 to 0.33 wt.%. CO₂ contents are low, however S reaches up to 4.6 wt.% (barite). Barium is highest in this ore type (3300 ppm to about 15 wt.%). Traces such as As, Mo, V, Zn are also higher than in other ore types (<80 ppm, ≤12 ppm, ≤84 ppm, ≤110 ppm, respectively).

The nodular ore is high in Fe₂O₃ (60 wt.% and FeO (11 wt.% and low in Al₂O₃ (0.1 wt.%). Pb, Zn (1000 ppm) and Cd (60 ppm) are higher than in other ore types. Ba is low (<2000 ppm), As and V similar than the other ore types.

The disseminated ore is rich in SiO₂ (70-79 wt.% SiO₂), Total iron (Fe₂O₃) varies from 6 to 20 wt.% (0.9-4.6 wt.% FeO). Al₂O₃ reaches 14 wt.% in iron poor rocks, and is <0.2 wt.% in iron rich rocks. Arsenic reaches 31 ppm, while U is < 2 ppm. Barium contents range from 900 to 2450 ppm, Rb from 20 to 370 ppm, Zr from 50 to 250 ppm, V from 6 to 39 ppm and W from 38 to 122 ppm.

Rare-Earth-Element + Yttrium composition: PAAS normalized REE+Y patterns of the studied samples are shown in figure 3. All samples show a strong positive Y anomaly, and, except for the massive magnetite and calcschist, a positive Eu anomaly. The massive magnetite shows a positive Ce anomaly and a strong enrichment in HREE. The banded ores show variable REE+Y (PAAS normalized) patterns. Most ore samples are characterized by an HREE enrichment and LREE depletion except for one banded ore (23). Banded and nodular ores show both negative and an absence of Ce anomalies. The calcschist has a negative Ce anomaly. The Ba rich layered ore exhibits the lowest LREE. The Y/Ho varies between 23.2 and 40. Highest values are observed in nodular ores (24: 40,4) and calcschist (35), most oscillate around values typical for shales (25-27).

4.3 Iron- and oxygen isotope geochemistry

All ore types were analyzed for δ⁵⁶Fe (Fig. 4). In the banded ore, the magnetite is characterized by δ⁵⁶Fe (-0.3 to +1 ‰ ± 0.2 ‰) and variable δ¹⁸O (-2 to +2 ‰).

The δ⁵⁶Fe values observed for magnetite decrease from disseminated to nodular iron ore averages: +1.3, +0.4 and -0.4 ‰ (± 0.2 ‰), respectively. Iron isotopes of hematite in disseminated and layered ore show higher δ⁵⁶Fe values than those of magnetite, in the range of +2 to +4 ‰ (± 0.2 ‰).

In the nodular ore, the magnetite is characterized by δ⁵⁶Fe (-1 to +0.5 ‰ ± 0.2 ‰) and δ¹⁸O between +4 to +6 ‰.

In the disseminated ore, the magnetite is characterized by δ⁵⁶Fe (+0.7 to +2 ‰ ± 0.2 ‰) and δ¹⁸O between 0.5 ‰ and +4 ‰.

4.3 Iron- and oxygen isotope geochemistry

5 Discussion and conclusions

Petrological and mineralogical studies (Orberger et al. 2017) showed that primary magnetite 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. Based on REE + Y compositions it can be concluded that reducing seawater with a contribution from hot hydrothermal solutions is the source of magnetite ores.

Regional deformation is indicated by grain boundary migration during the recrystallization of quartz grains. The nodular ore most likely represents a highly deformed banded iron ore, where magnetite bands were disrupted and recrystallized. Sulphides 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 oxy-
hydroxides and associated scheelite and barite. This
episode is most likely contemporaneous to the W
mineralisation in this region (Ghorbani 2013).

This scenario is supported by increasing δ⁵⁶Fe and
δ¹⁸O with progressive oxidation from banded, nodular to
disseminated magnetite reaching highest values in
hematite (Orberger et al. 2018). A shift in δ⁵⁶Fe towards
positive values in oxidizing environments was also
observed for example by Rouxel et al. (2008).

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Geochemistry of hematite veins in IOA-IOCG deposits of SE Missouri, USA: relation to felsic magmatism and caldera lakes

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Abstract. The paragenesis, textures, and chemical compositions of secondary hematite in regional potassic altered rhyolites, four IOA deposits, the sedimentary iron deposit at Pilot Knob and the Boss IOCG deposit in SE Missouri were determined and compared to primary magnetite from the IOA and IOCG deposits. Magnetite is composed of elements characteristics of mafic to intermediate intrusions whereas hematite is enriched in elements characteristic of felsic igneous rocks. These results suggest that magnetite formed from fluids discharged from mafic to intermediate composition intrusions. Hematite precipitated from fluids discharged from felsic intrusions or fluids that evolved in caldera lakes. Hematite in the sedimentary iron deposit at Pilot Knob formed in an evaporative caldera lake with fluid inputs from felsic intrusions.

1 Introduction

The Mesoproterozoic St. Francois Mountains terrane in SE Missouri, USA, contains several iron-oxide-apatite (IOA) ± rare earth element (REE) deposits and one iron-oxide-copper-gold±cobalt (IOCG±Co) deposit. Many of these deposits seem to correspond to the magmatic magnetite-dominated endmember of the IOA-IOCG class, however hematite domains are present locally. In addition, a hematite-dominated sedimentary iron deposit is juxtaposed with a typical magnetite IOA deposit at Pilot Knob and Pea Ridge is altered to hematite near crosscutting REE-enriched breccia pipes. Only minor, hematite infill and/or replacements are observed at Bourbon and the Lower Pilot Knob deposit.

2 Geology

In the St. Francois Mountains terrane, 1.4 Ga igneous rocks are principally subalkaline/ferroan rhyolite ignimbrites and flows, underlain by coeval granite plutons, but also include volumetrically minor tholeiitic basaltic andesite and dacite. Geologic and geochemical relations suggest that these rocks are rift related (Day et al. 2017, and E. du Bray, U.S. Geological Survey, written communication 2018).

3 Samples and methods

Regional potassic altered rhyolite tuffs and flows were sampled in the Ironton (i.e., Grassy Mountain, Lake Kilarney, and Royal Gorge) and Eminence areas (Upper and Lower Coot Mountains and Stegall Mountain). Some of the regional samples are more proximal to known iron deposits than others. Hematite and magnetite samples were collected at the Pea Ridge, Bourbon, Iron Mountain, Boss, and
Upper and Lower Pilot Knob iron deposits. Hematite and magnetite were identified by reflected light microscopy and analyzed via scanning electron microscopy-backscatter electron (SEM-BSE) imaging, electron microprobe (EMP), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS; Longerich et al. 1996). Iron contents from EMP were used as internal standards for LA-ICP-MS analysis. LA-ICP-MS data were reduced to remove the effects of mineral inclusions however some anomalous element enrichments in hematite may reflect mineral inclusions. Both magnetite and hematite were analyzed using the same suite of elements.

Results generated by EMP and LA-ICP-MS analysis were plotted on the Al+Mn vs. Ti+V discrimination diagrams of Nadoll et al. (2014) and multi-element variation diagrams of Dare and Barnes (2014).

4 Petrography of hematite assemblages

In regional rhyolites, either distal or proximal to iron mineralization, magnetite and ilmenite phenocrysts are commonly pseudomorphically replaced by submicron-sized hematite and rutile. In potassically altered rhyolites, the pseudomorphs are recrystallized and grain size and porosity increase. Euhedral 25-500 µm hematite laths and or spongy 2-20 µm hematite aggregates fill some cavities. This generation of hematite is associated with K-feldspar ± hematite-muscovite-quartz and is referred to as assemblage 1 (A1).

In IOA-IOCG deposits, hematite is restricted to assemblage 4 (A4), which consists of hematite-chlorite ± sulfides-muscovite-quartz-fluorite-carbonate-epidote-garnet-amphibole and assemblage 5 (A5), which consists of hematite ± barite-carbonate-K-feldspar-muscovite-chlorite-quartz-REE phosphates. A4 is most likely a combination of propylitic and phyllic alteration, whereas A5 most likely represents hydrolytic alteration. A key distinction is that A4 hematite is associated with sulfides (pyrite ± chalcopyrite) and A5 hematite is associated with barite. A4 typically crosscuts all of primary magnetite-bearing assemblages in the IOA deposits, whereas A5 overprints all of the other stages.

A4 hematite forms 50-750 µm needle-like laths intergrown with sulfides (Fig. 1a, b), locally is zoned, subhedral to anhedral, and forms 25-100 µm crystals intergrown with rutile. These grains are typically recrystallized and or overgrown by coarser grained hematite that is rutile-poor. A5 hematite typically consists of platy laths that fill open spaces; some individual grains are ≥500 µm (Fig. 1d, e). Both A4 and A5 hematite completely or partially replaces preexisting fine- to coarse-grained, euhedral to anhedral, 15-1500 µm magnetite, especially along grain boundaries and/or in inclusion-rich magnetite cores (Fig. 1a, c). Nano- to micrometer mineral inclusions are also present in open space filling A1, A4, and A5 hematite. In laminated and agglomerate iron ore at Upper Pilot Knob, A5 hematite consists of fine-grained, ≤100 µm, aggregates and coarser laths that are often intergrown with barite and muscovite (Fig. 1f).

5 Hematite trace element chemistry

Open space filling (OS) hematite was analyzed to avoid chemical contamination from preexisting magnetite.

On the Al+Mn vs. Ti+V discrimination diagram of Nadoll et al. (2014), compositions of OS hematite from A4 and A5 form two broad arrays. Each array extends...
from the magmatic Fe-Ti and V deposit field into the hydrothermal Porphyry, Kiruna, IOCG, Skarn, and BIF fields (Fig. 2). But, A5 hematite generally plots above A4 hematite, which may suggest that hematite formed by multiple fluid inputs and that most hematite formed at low temperature. A5 hematite from Upper Pilot Knob forms another array between A5 and A4, which may imply mixing between fluids that produced the upper and lower arrays. Compositions of A1 and A5 hematite overlap, indicating similar fluid.

Figure 2. Open space hematite from IOA-IOCG deposits and Upper Pilot Knob in SE Missouri. See text for details. Hm=Hematite, OS=Open Space.

The trace element chemistry of OS hematite is compared to that of primary magnetite on the multi-element variation diagrams of Dare and Barnes (2014) that are normalized to bulk continental crust values from Rudnick and Gao (2003). On these diagrams, A1, A4, and A5 hematite are also compared to one another. Trace element-normalized patterns of inclusion-poor magnetite from amphibole- and magnetite-dominated alteration zones in IOA-IOCG deposits consist of a similar group of elements, typically V, Mn, Zn, Co, Ga, Ni, Ti, Mg, P, and Al with lesser amounts of Cr, Th, and U (Fig. 3a). Hematite is enriched in a distinctly different group of elements including; Sn, Sb, Mo, Nb, Ta, U, W, Pb, Th, Zr, and Hf, with lesser amounts of La, Ce, Y, Cu, Ba, Sr, K, Cs, Rb, and Si (Fig. 3b, c, d). Many of the elements present in hematite are often below detection limits in magnetite.

A1 hematite, characterized by Mo, Sb, Pb, Th, and Cs with lesser Rb, Ba, and K enrichments and lacking significant Cu, Co, and Ni, is most similar to A5 hematite. In addition to the aforementioned elements in A1, A5 hematite locally contains Ni, lacks Zn and Cs, and contains no significant enrichments in Pb or Th. A4 hematite contains minor Zn, Co, and Cu enrichments, but lacks significant enrichments in Zr, Hf, Mo, Sb, K, Cs, Rb, and Ba. A1 is more enriched in A5 than in A4. The element enrichment pattern of laminated and agglomerate A5 hematite from Upper Pilot Knob is similar to A5 hematite from IOA-IOCG deposits, but it is more enriched in U, Mo, and Sb within the laminated ore. Minor differences in trace element enrichments of A1 and A5 hematite compared to A4, including contrasting abundances in Al, may indicate differences in fluid source and/or temperature.

These geochemical signatures suggest that the magnetite in IOA-IOCG deposits precipitated from fluids discharged from mafic to intermediate intrusions. In contrast, A5 hematite precipitated from fluids discharged from felsic intrusions, whereas A4 hematite may have formed from evaporated caldera lake water. Laminated and agglomerate A5 hematite in Upper Pilot Knob formed in an evaporative caldera lake that received inputs of fluid from felsic intrusions.

6 Conclusions

Our results show that hematite has multiple origins distinct from those responsible for magnetite crystallization. Late OS A1 hematite in regional rhyolites is compositionally similar to late A5 hematite in altered rock near REE-enriched breccia pipes at Pea Ridge, hematite-cemented breccias at Boss, and some hematite veins at Bourbon. These hematites all have element enrichments that are consistent with fluids derived from felsic intrusions, including a perhaps more fractionated alkalic intrusion at Pea Ridge (Hofstra et al. 2017). In contrast, A4 hematite alterations at Iron Mountain and locally at Pea Ridge near REE-enriched breccia pipes, along with hematite veins and cavity infill within magnetite ores at Pea Ridge, Boss, Bourbon, and Lower Pilot Knob may be consistent with fluids derived from an evaporative caldera lake. At Upper Pilot Knob, evaporative lake water may have received inputs of fluids associated with felsic intrusions. Most of the iron in hematite was likely remobilized from preexisting IOA-IOCG deposits and or nearby mafic to intermediate intrusions. In summary, the hematite alteration zones in IOA-IOCG deposits and the sedimentary iron deposit at Upper Pilot Knob are related to felsic magmatism and perhaps evaporated caldera lake water, whereas magnetite is associated with mafic to intermediate composition intrusions.
Figure 3. A. Magnetite data from IOA-IOCG deposits. B1 hematite data from regional potassic altered rhyolites C-D. A4 and A5 hematite data from IOA-IOCG deposits and Upper Pilot Knob. See text for details. Hm=Hematite, Ilm=Ilmenite, Mt=Magnetite, OS=Open Space.

References


Day WC, Slack JF, Ayuso RA, Seeger CM (2016) Regional geologic and petrologic framework for iron oxide ± apatite ± rare earth element and iron oxide copper-gold deposits of the Mesoproterozoic St. Francois Mountains terrane, SE Missouri, USA. Econ Geol 111: 1825-1858


Advances in Understanding Hydrothermal Processes
Absence of magnetite microlites, geochemistry of magnetite veins and replacements in IOA deposits, SE Missouri, USA: relations to intermediate intrusions

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Abstract. The paragenesis, textures, and chemical compositions of magnetite in two mafic to intermediate intrusions and four IOA deposits in SE Missouri were studied to discriminate between igneous and hydrothermal sources. In this study, we found that replacement magnetite with mineral inclusion-rich cores yields erroneously high Ti, Al, Si, Mg, and Mn contents as determined by EMP and LA-ICP-MS due to rutile and silicate inclusions. Thus, identification of high-Ti microlites on the basis of inclusion-rich cores with high Ti contents is an analytical artefact. Since the high-Ti magnetite microlite flotation model is critically dependent on this type of analysis, it may be invalid.

The presence of coarse-grained high-Ti vein magnetite with ilmenite lamellae enveloped by replacement magnetite with inclusion-rich cores in ore zones suggests that the veins were high-temperature conduits for low-temperature replacement ores. The trace element compositions of vein and replacement magnetite suggest that iron was sourced from mafic to intermediate intrusions. These results support a magmatic-hydrothermal origin for IOA systems in SE Missouri.

1 Introduction

The Mesoproterozoic St. Francois Mountains terrane in SE Missouri, USA, contains several iron-oxide-apatite (IOA) ± rare earth element (REE) deposits for which a variety of genetic models have been proposed. Recently, Simon et al. (2018 and references therein) proposed that IOA deposits form from buoyant aqueous emulsions containing high-Ti magnetite microlites derived from underlying intrusions that are overgrown by low-Ti hydrothermal magnetite at the sites of ore formation. This model pertains to microlites identified at Los Colorados in Chile (Knipping et al. 2015a, b) and Pea Ridge and Lower Pilot Knob in SE Missouri (Childress et al. 2016). Although Hofstra et al. (2016) found no evidence of high-Ti microlites at Pea Ridge and Meighan et al. (2017) show that the high-Ti microlites identified by Childress et al. (2016) are actually hematite-rutile intergrowths inherited from the host rocks, Simon et al. (2018) maintain that the model does apply to deposits that lack microlites because, as Simon et al. (2018) suggest, microlites may be destroyed by subsequent dissolution-reprecipitation processes.

To resolve these inconsistencies and further evaluate the applicability of the microlite flotation model to IOA deposits, we documented the paragenesis, textures, and chemical composition of magnetite in igneous rocks and IOA deposits from SE Missouri and compare the results to those for Los Colorados.

2 Geology

The 1.4 Ga igneous rocks in the St. Francois Mountains of SE Missouri consist of subalkaline/ferroan rhyolite ignimbrites and flows underlain by coeval granite plutons. Although tholeiitic basaltic andesite and dacite are volumetrically minor at the surface, geophysical surveys show they are abundant in the subsurface (McCafferty et al. 2018). Geologic and petrologic relations suggest that these rocks are rift related (Day et al. 2017, and E. du Bray, U.S. Geological Survey, written communication 2018).

The Pea Ridge, Bourbon, and Lower Pilot Knob IOA deposits are hosted in a series of high-silica rhyolite tuffs and flows (Panno & Hood 1983; Seeger et al. 2001). In contrast, the Iron Mountain IOA deposit is hosted in mafic to intermediate intrusions that are either interlayered with or intrude a series of high-silica rhyolite tuffs (Murphy & Ohle 1968). Pea Ridge is enclosed and underlain by inferred granitic intrusions that are surrounded by an annular mafic to intermediate composition intrusion (Day et al. 2016). Bourbon is located near, and is partially surrounded and underlain by, the same ring intrusion. Iron Mountain and Pilot Knob are located along the margin of a caldera ~50 km SE of Pea Ridge and Bourbon.

These IOA deposits are composed mainly of magnetite, apatite, and amphibole with lesser amounts of phlogopite and chlorite. In many places, these deposits are characterized by magnetite-cemented amphibole alteration veins adjacent to or enveloped by massive magnetite ore bodies. Iron Mountain is largely overprinted by later hematite alteration and Pea Ridge is altered to hematite near REE-enriched breccia pipes.
Figure 1. Secondary electron microscopy-backscattered electron (SEM-BSE) images showing magnetite textures from each assemblage. See text for details. Amph=Amphibole, Ap=Apatite, Chl=Chlorite, Ilm=Ilmenite, Mt=Magnetite, Phl=Phlogopite, Qtz=Quartz, Rt=Rutile.

3 Samples, methods, and Monte Carlo simulations

Mafic to intermediate intrusions were sampled at Bourbon and Iron Mountain. Magnetite was collected from Pea Ridge, Bourbon, Iron Mountain, and Lower Pilot Knob. Magnetite was identified using reflected light microscopy and analyzed via scanning electron microscopy-backscattered electron (SEM-BSE) imaging, electron microprobe (EMP), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS).

EMP analyses were obtained at 15Kv and 100nA using a spot size of <1 µm. Monte Carlo simulations were used to model the effects of secondary fluorescence as a function of distance from rutile and chlorite inclusions in magnetite (Salvat et al. 2006; Llovet et al. 2012). Iron contents determined by EMP served as the internal standard for LA-ICP-MS analyses; data reduction follows Longerich et al. (1996). Inclusion-rich cores and inclusion-free rims of magnetite were analyzed by LA-ICP-MS using 24 and 32 µm spot sizes. The data from inclusion-rich cores were reduced in two ways: (1) filtered to remove the effects of mineral inclusions and (2) unfiltered to show the effects of mineral inclusions on the results.

Results generated by EMP and LA-ICP-MS analysis were plotted on the Al+Mn vs. Ti+V discrimination diagrams of Nadoll et al. (2014).

4 Petrography of magnetite assemblages

In many places, the mafic to intermediate intrusions surrounding Bourbon and Iron Mountain contain 50-250 µm phenocrysts of tabular ilmenite and equant magnetite ± ilmenite (Fig. 1a). In IOA deposits, magnetite occurs in two assemblages. Assemblage 1 (A1) consists of amphibole ± apatite-magnetite-ilmenite-phlogopite-quartz that fill open spaces. Assemblage 2 (A2) consists of magnetite ± apatite-phlogopite-quartz-rutile-sulfide replacements with lesser pore infillings that often surround A1. Mg-chlorite may also fill remaining pore space in A2.

A1 magnetite consists of coarse subhedral to euhedral 250-1500 µm grains that are frequently intergrown with coarse ilmenite and or contain ilmenite lamellae (Fig. 1b). A2 magnetite consists of finer-grained anhedral to subhedral 15-500 µm grains without ilmenite lamellae. A2 magnetite generally contains mineral inclusions, such as rutile and silicates, and some grains have inclusion-rich cores and inclusion-poor rims (Fig. 1c). Coarser A2 magnetite grains are often observed as overgrowths on A1 magnetite, or in breccias. A1 magnetite is present in deep drill holes at Bourbon, Iron Mountain, and Pea Ridge, but was not identified at Lower Pilot Knob. A2 magnetite is also present at Bourbon, Pea Ridge, and Lower Pilot Knob but was minimal at Iron Mountain.

5 Magnetite compositions and Monte Carlo results

Consistent with an igneous origin, magnetite phenocrysts from mafic to intermediate intrusions plot in two clusters within the magmatic Fe-Ti and V deposit field (Fig. 2). Inclusion-poor A1 magnetite plots in two arrays that extend from igneous magnetite phenocryst endmembers into the hydrothermal Porphyry, Kiruna, IOCG, Skarn, and BIF fields, which suggests high
temperature formation. Most inclusion-poor A2 magnetite plots in the BIF field, though limited data plot in the IOCG and Skarn fields, which suggest low temperature formation.

Figure 2. Inclusion-poor magnetite from IOA deposits in SE Missouri. See text for details. Hm=Hematite, Ilm=Ilmenite, Mt=Magnetite, Rt=Rutile.

Magnetite phenocrysts from mafic to intermediate composition intrusions surrounding Bourbon and Iron Mountain contain significant Ti, Mn, V, Cr, Zn, Co, Mg, Al, P, Zr, and Nb, with lesser amounts of Ga, Pb, U, Mo, Y, La, Ce, and Ta. Inclusion-poor A1 and A2 magnetite contain a similar suite of elements, though at lower concentrations, including V, Mn, Zn, Co, Ga, Ni, Ti, Mg, P, and Al with lesser amounts of Cr, Th, and U. These results suggest that A1 and A2 magnetite precipitated from fluids discharged from mafic to intermediate intrusions. Inclusion-rich cores of A2 magnetite contain a similar trace element suite and include higher abundances of incompatible elements such as Si, Ti, Al, Mg, and to a lesser extent Mn that are associated with mineral inclusions.

Monte Carlo simulations exhibit exponential profiles of apparent Ti and Al concentrations in magnetite versus distance from inclusions, such as rutile or chlorite, that are consistent with secondary fluorescence (Fig. 3). Correspondingly, only EMP analysis spots >30 µm from mineral inclusions yield reliable results. The close spacing of mineral inclusions in A2 magnetite cores (Fig. 1c, 1d) suggests that obtaining reliable EMP data from these sorts of materials is essentially impossible. Consequently, concentrations measured in A2 magnetite cores will be erroneously high. To illustrate this phenomenon, EMP analyses of "clean" inclusion-poor rims and "contaminated" inclusion-rich cores are plotted on Al+Mn vs. Ti+V discrimination diagram (Fig. 4a). For comparison, LA-ICP-MS spot analyses are plotted. A shift to higher Ti and/or Al concentrations parallels the compositional shift corresponding to analyses for inclusion-poor versus inclusion-rich magnetite and therefore defines an apparent contamination trend consistent with magnetite contamination by mineral inclusions.

Figure 3. Monte Carlo simulations showing apparent Ti and Al concentrations in magnetite due to secondary fluorescence versus distance from rutile and chlorite inclusions.

Last, the results for Pea Ridge and Pilot Knob were compared to those from Los Colorados (Fig. 4b). Los Colorados magnetite plots in the Porphyry field, which is consistent with its subduction-related magmatic arc setting. The positive shift in Ti and Al concentrations of mineral inclusion-rich magnetite cores is similar to that observed for magnetite cores from Pea Ridge and Pilot Knob. These high core concentrations, which extend into the magmatic field, likely reflect secondary fluorescence associated with inclusions. The interpretation that the inclusion-rich cores are high-Ti magnetite microlites is therefore highly suspect.

6 Conclusions

Mineral inclusions are common in replacement ores of many deposit types. Consequently, the presence of inclusion-rich magnetite among IOA deposits suggests that these deposits formed by replacement processes. Our data show that the inclusion-rich cores of A2 replacement magnetite from Pea Ridge and Lower Pilot Knob can be misidentified as high-Ti microlites due to rutile and aluminosilicate inclusions. Similarly, high-Ti microlites at Los Colorados may reflect an analytical artefact associated with analysis of inclusion-rich magnetite cores. We infer that no high-Ti magnetite microlites were involved in ore formation.
in SE Missouri IOA deposits. Similarly, high-Ti magnetite microlites may not actually be present at Los Colorados. If so, the magnetite microlite flotation model of Knipping et al. (2015a, b) may be invalid and may instead reflect an analytical artefact.

Since the textures and composition of high-Ti magnetite veins and low-Ti magnetite replacements are preserved, we suggest that the high-temperature veins were conduits for the fluids that generated the low-temperature replacement ores. The suite of trace elements in magnetite suggests that iron was derived from mafic to intermediate intrusions. In summary, our results support a magmatic-hydrothermal origin for IOA deposits in SE Missouri, and perhaps those at Los Colorados.

References


The Waschleithe W-skarn – a distal relative of skarns in the Schwarzenberg district, western Erzgebirge, Germany?

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Abstract. The Waschleithe skarn located near Schwarzenberg in eastern Germany hosts sub-economic polymetallic W-Zn-Pb-Cu-Fe mineralisation. Its mineralogy is dominated by prograde clinopyroxene and subordinate garnet. The garnet and pyroxene colours of this skarn as well as low garnet/pyroxene ratios are typical for distal skarn settings. Ore minerals (magnetite, sphalerite, galena, chalcopyrite, pyrite, scheelite) in the prograde skarn do not show a clear association with the weakly developed retrograde overprint consisting mainly of late chlorite and calcite.

1 Introduction

The Erzgebirge/Krušné hory metallogenic province, straddling the border between Germany and the Czech Republic, is host to a broad variety of syn- and post-Variscan hydrothermal ore deposits including greisen, skarn, and vein-type mineralisation. Skarn deposits are known to occur across the entire Erzgebirge and in different stratigraphic positions. Their host lithologies comprise dominantly low-grade metasedimentary units (rarely meta-volcanics). Some skarns contain polymetallic mineralisation (Sn, W, Zn, Pb, Fe, Cu, In) (e.g., Baumann et al. 2000; Hösel 2003; Schuppan and Hiller 2012) and have been mined historically for Fe, Sn, W, Zn and Pb. Despite hosting the majority of Europe’s Sn resources (Bock 2009; ITRI 2016) the understanding of the genesis and resource potential of these deposits is surprisingly poor.

The Schwarzenberg district in the western Erzgebirge comprises numerous skarn bodies that are concentrically distributed around the Schwarzenberg Gneiss Dome (SGD). Although garnet and pyroxene skarns are most common, there is considerable compositional variation related to the degree of retrograde overprint and metal tenor. Their origin and genetic history remain controversial. Some researchers favour a metamorphic provenance for the skarns (e.g., Lefebvre et al. 2018) whereas others present evidence for a magmatic-hydrothermal origin (e.g., Burisch et al. 2019; Kern et al. 2018) affiliated with late-/post-Variscan magmatism. Moreover, the genetic relationships between individual skarn bodies of the Schwarzenberg district are still unknown. The question remains whether this is one skarn system that evolved in time and space or if the different skarn bodies are related to several localized hydrothermal events.

In this study, we focus on the Waschleithe skarn which represents one of the northernmost skarns of the SGD (Fig. 1). This skarn is only poorly documented and modern geochemical data is entirely missing. Due to its distal position relative to the large and well mineralized skarn systems of Hämmerlein-Tellerhäuser and Breitenbrunn, the Waschleithe skarn may provide new insights into ore-forming processes on the district-scale. We use structural and petrographic observations as well as qualitative data on mineral chemistry to better understand the origin of the Waschleithe skarn.

2 Sampling and methodology

Skarn and host rock samples from the upper (USH) and lower (LSH) skarn horizon were collected from seven sampling locations within the historical Herkules-Frisch-Glück underground mine. Of these, a total of 13 polished thin sections as well as 6 double-polished sections for fluid inclusion analyses were produced. Additionally, nine covered thin sections of three drill cores, provided by the Geological Survey of Saxony (LfULG), were also studied. Qualitative SEM-EDX measurements were performed on a JEOL CarryScope JCM-5700 equipped with a Bruker Quantax X-Flash 6/30 EDS detector at an accelerating voltage of 20 kV.

3 Regional geology

The Erzgebirge crystalline complex is a ~145 x 35 km SW-dipping antclinal structure situated along the N-border of the Bohemian Massif in the Saxothuringian Zone of the European Variscides. Peak regional metamorphism occurred at around 340 Ma (Rötzler and Plessen 2010). The resulting metamorphic units comprise a complex succession of medium- to high-grade rocks including (ultra-) high pressure gneisses
Figure 1. Simplified geological map of the Schwarzenberg district modified after (Baumann et al. 2000; Hösel and Haake 1965). Position of the historical Herkules-Frisch-Glück mine and other skarn occurrences is indicated. Low- to medium-grade meta-sedimentary units are grouped concentrically around the Schwarzenberg Gneiss Dome (SGD). The inset shows position of the SGD (red star) in Germany.

eclogites as well as low- to medium-grade phyllites, meta-carbonates, meta-volcanics, and mica schists. The latter are the host rocks for the skarn mineralisation. The crustal pile was intruded by voluminous post-kinematic plutons as well as subvolcanic dikes, microgranites and lamprophyres between 330-295 Ma (Förster and Romer 2010; Seifert 2008).

4 The Waschleithe skarn
4.1 Local geology

The Waschleithe skarn is situated at the northern margin of the SGD. It is hosted by greenschist facies meta-psammites, mainly mica schists and paragneisses, locally known as the Obermittweidaer formation (Baumann et al. 2000; Hösel 1972; Hösel and Haake 1965). In the study area the metasedimentary rocks reach a thickness of more than 900 m and comprise two discrete meta-carbonate horizons. These horizons predominantly consist of relatively pure calcite marble rarely exceeding thicknesses of ~10 m. They host several skarn bodies and have been intersected by core drillings at depths of up to 150 m. Skarn forms stratabound lenses concordant with the metasedimentary sequence dipping at 25 to 35° towards N. Laterally, the thickness of both skarn horizons is highly variable, reaching average thicknesses of 4 m and 6 m for the USH and LSH, respectively (Hösel 1972; Meyer and Röthig 1967). The marbles are typically only partially altered to skarn. A complete alteration of the marbles to skarn is only recognized in zones of intense deformation (Hösel and Haake 1965), clearly overprinting older metamorphic structures. The distance of the Waschleithe skarn to the underlying granites of the Eibenstock and Aue-Schwarzenberg suites is not well constrained but exceeds 1000 m (Hösel 1972). The skarn bodies are accessible at the Herkules-Frisch-Glück underground mine, where both skarn horizons are exposed over a length of ~250 m. Furthermore, four boreholes from the 1960’s and 70’s intersect the skarn bodies.

4.2 Skarn mineralogy

The USH and LSH show similar mineralogy and mineral paragenesis. Consequently, we summarize their petrographic description and highlight only differences.

The marble is dense and appears whitish-grey in colour with very few dark grey, cm-thick schlieren. Microscopically, it consists of anhedral calcite with grain sizes of 40 to 600 µm. Calcite exhibits abundant pressure twinning. The marble shows a characteristic granoblastic texture. Locally, fine-grained (100 to 200 µm) subhedral epidote-group minerals and elongated or platy muscovite grains with grain sizes of up to ~500 µm are finely dispersed within the calcite matrix. Veinlets of quartz and fluorite crosscut the marble.

In sharp contrast, the skarn is composed of dense to coarse-grained brownish-green pyroxenes as the major constituent as well as minor amounts of dark green chlorite. Clinopyroxene (most likely diopside-hedenbergite series) shows fan-like intergrowth of cm-sized prismatic crystals as well as fine-grained aggregates. Grain sizes vary between <40 µm to >5 mm. Pale yellowish-green garnet is less abundant than pyroxene and occurs as euhedral zoned crystals (Fig. 2A) with grain sizes between 50 to 600 µm but also as fine-grained anhedral aggregates. Preliminary observations suggest two generations of garnet, one pre-dating and one post-dating pyroxene (Fig. 3). Anhedral ilvaite pervasively replaces pyroxene and is only observed in the LSH. Epidote-group minerals form fine-grained (50 to 100 µm) anhedral crystals that replace clinopyroxene and are associated with quartz and rarely scheelite. Anhedral quartz fills voids within clinopyroxene but also occurs together with fluorite in veinlets post-dating the calc-silicates. Fluorite is mostly associated with sphalerite, galena and quartz and is restricted to the USH where its abundance is highest close to the marble-skarn contact. Elongate, subhedral vesuvianite replaces clinopyroxene. It is restricted to the USH. Milky
Calcite is often rimmed by greenish-brown chlorite. Chlorite mostly forms fine grained platy aggregates and preferentially replaces clinopyroxene along grain boundaries and fractures. Occasionally, chlorite shows pseudomorphs after clinopyroxene.

The skarn-marble contact is very sharp. Microscopically, a ~5 mm transition zone can be observed. From marble to skarn, a ~1.5 mm thin silicified zone is present, which evolves into a ~3.5 mm thin quartz+fluorite+muscovite+chlorite zone. The latter appears to have overprinted only the primary skarn minerals.

4.3 Ore minerals

Sulphide and oxide minerals are restricted to the skarn and do not occur within the unaltered marble. They are unevenly distributed within the samples and occur in veins, as disseminations, or massive patches. Three distinct assemblages have been observed:

1.) Oxide assemblage: Anhedral magnetite is the dominant oxide in this assemblage. It is closely associated with ilvaite, corroding its grain boundaries and pervasively replacing it from outside to inside (Fig. 2C). Magnetite is only observed in the LSH.

2.) Sulphide assemblage: This comprises mostly of sphalerite, galena, pyrite and chalcopyrite. Sphalerite is the most common sulphide. It occurs as anhedral crystals and aggregates replacing pyroxene and ilvaite. Sphalerite often shows chalcopyrite disease. Anhedral galena mostly occurs with sphalerite but is slightly younger (Fig. 2B). It also occurs disseminated in the skarn where it replaces pyroxene. Sphalerite and galena are often associated with fluorite and quartz. Minor euhedral to anhedral pyrite is strongly associated with sulphides and has never been observed directly replacing skarn minerals. It occurs as fine-grained cubic crystals or massive patches with sphalerite. Anhedral chalcopyrite replaces pyroxene but is mostly associated with older sulphides (Fig. 2C).

3.) Scheelite assemblage: Anhedral scheelite with grain sizes up to 2.2 mm occurs disseminated within the pyroxenes. It is mostly accompanied by sphalerite, galena and quartz (Fig. 2D). It seems to replace pyroxene along fractures indicated by irregular-shaped corroded grain boundaries of pyroxene in contact to...
scheelite. Preliminary observations suggest only a weak relationship between sulphides and chlorite.

With respect to their ore mineralogy both the USH and LSH are dominated by disseminated sulphides. However, the USH is more mineralized than the LSH and its ore mineralogy is dominated by Sp+Gn±Ccp, whereas the LSH is dominated by Sp+Ccp±Py(±Mag). Disseminated scheelite mineralisation can be observed in both horizons.

5 Discussion and conclusions

For a given protolith and oxidation state the garnet and pyroxene colour as well as their modal ratio have been recognized to be indicative of the relative distance of skarn mineralisation to its fluid source (Meinert et al. 2005). Pale yellowish-green garnet, dark pyroxenes, the marble front and low garnet/pyroxene ratios of the Waschleithe skarn are typical for distal skarns (Meinert et al. 2005). In contrast, the Hämmerlein-Tellerhäuser skarns (<10 km to the S) contain additional pale brownish-red garnet and have significantly higher garnet/pyroxene ratios, indicating a more proximal position to the fluid source relative to the Waschleithe skarn (Burisch et al. 2019). Taking the enormous lateral extent of the Hämmerlein-Tellerhäuser (~5 km) and Breitenbrunn (~4.4 km) skarns into account, it is likely that the Waschleithe skarn (~7 km to the N) is a distal skarn mineralisation related to the same hydrothermal event/system which also formed the other skarn bodies of the Schwarzenberg district. This hypothesis will be tested with U-Pb geochronology of garnet and carbonates. Furthermore, we are planning to conduct detailed mineralogical and fluid inclusion studies on the local as well as the district scale to better understand the processes that cause the observed mineral zoning within the Schwarzenberg district.

Acknowledgments

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References


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Fertile window of skarn formation in orogenic belts: LA-ICP-MS U-Pb geochronology of skarn-related garnet from the Variscan Erzgebirge, Germany

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Abstract. Uranium-lead LA-ICP-MS geochronology of garnet from skarns in the Erzgebirge, a classic metallogenic district in the European Variscan belt, constrains the timing and origin of metasomatism and associated Sn, W, Fe, Zn, Cu and In mineralization. Geochronological data of 20 samples from ten skarns distributed across the entire Erzgebirge region, include garnet from three different lithological contexts that yield distinctly different ages. The first group includes sub-calcic garnets with ages between 343 and 331 Ma, the age of peak regional metamorphism in the Erzgebirge. The second group is represented by grandite garnets associated with skarnoid rocks; these yield ages ranging between 325 and 313 Ma and are temporally associated with late-orogenic magmatism. Coarse-grained metasomatic grandite garnets with ages between 308 and 295 Ma define the third group. The latter garnets are related to extensive post-collisional magmatic-hydrothermal processes yielding world-class Sn-Zn-In skarn deposits. Results illustrate that U-Pb geochronology of skarn-related garnet can serve as a sensitive exploration vector to identify fertile skarn environments in complex orogenies.

1 Introduction

Although the majority of skarns are associated with subduction-related magmatism, they also can occur in collisional terrains (e.g. Erzgebirge/Germany, Tien Shan/China or Anatolia/Turkey). In such orogenic zones they typically are polymetallic containing, amongst others, Fe, Zn, Pb, W, Sn and/or Au and contribute significantly to Europe's Sn resources and China's Sn and Au reserves (Chen et al., 2007; Elsner, 2014). While detailed genetic models for subduction-related skarn systems exist (hundreds documented in Meinert et al., 2005) the precise source of hydrothermal fluids and the timing of fertile skarn formation (skarns with significant metal endowment) in orogenic settings remains poorly constrained. Some of this lack of understanding is related to the scarcity of robust geochronological constraints for most of these mineral systems. Recent applications of LA-ICP-MS U-Pb geochronology to garnet (Deng et al., 2017; Seman et al., 2017; Gevedon et al., 2018; Wafforn et al., 2018) now allows direct age dating of prograde metasomatism in orogenic skarn systems. Results can be used to identify temporal windows of skarn formation within the context of regional geotectonic evolution.

2 Geology of the Erzgebirge

As part of the European Variscides, the Erzgebirge is a ~145 x 35 km SW-NE trending erosional window comprising predominantly metamorphic and igneous basement rocks (Fig. 1). These rock units include high-grade gneisses (E, SE) and low- to medium grade phyllites, marbles, meta-volcanics and mica-schists (W, NW), which experienced peak metamorphic conditions at around 340 Ma (Kröner and Willner, 1998). After rapid uplift, these metamorphic lithologies were subsequently intruded by igneous rocks - predominantly peraluminous leucogranites associated with the late-orogenic phase (325 to 318 Ma (Förster et al., 1999) ) of the Variscan collision. Abundant younger (sub-)volcanic rocks record intense post-orogenic magmatic activity from 310 to 290 Ma (Kempe et al., 2004; Seifert, 2008; Hoffmann et al., 2013)

3 Skarns in the Erzgebirge

The Erzgebirge is a classical metallogenic province with a multitude of economically important greisens, skarn and vein-type ore deposits (Baumann et al., 2000). Much of this hydrothermal mineralization is genetically associated with late- to post-orogenic magmatism (Zhang et al., 2017; Burisch et al., 2018; Ostendorf et al., 2018). Skarns are particularly widespread across the Erzgebirge; they vary significantly in size, metal tenor and mineralogy (Hösel, 2003; Schuppan and Hiller, 2013; Hiller and Schuppan, 2016). The majority are hosted by Palaeozoic metamorphic rocks, which comprise alternating sequences of meta-pelites and meta-limestones. A few skarns are associated with
small marble lenses within high-grade gneiss units.

The metal tenor associated with the skarns is variable and may include Sn, W, Fe, Zn, Cu, In and/or Ag. Skarn mineralization is known to include several prograde and retrograde stages but robust age constraints are lacking for all of these in the Erzgebirge skarns. A recent attempt to age date the Hämmerlein skarn was based on Rb-Sr dates of muscovite (~340 Ma; Lefebvre et al., 2018) of a gneiss spatially – but not necessarily genetically - associated with the skarn.

The degree of retrograde overprint of the primary skarn minerals ranges from subordinate to very intense. For the latter, many of the ore minerals are associated with the retrograde alteration (Schuppan and Hiller, 2013). Direct geochronology of the skarn-related minerals has not been successful to date. As a consequence, the origin and the timing of skarn mineralization in the Erzgebirge remains unclear.

4 Sampling and methods

Twenty samples of skarn-related granitoid and sub-calcic garnet were selected from the scientific collection of the TU Bergakademie Freiberg and from accessible historic underground mines. Only fresh garnets, which have not been affected by retrograde alteration were selected for analyses.

Samples were screened and analysed in situ from polished sections using a RESOLuton S-155 (Resonetics) 193 nm ArF Excimer laser (CompexPro 102, Coherent) equipped with a two-volume ablation cell (Laurin Technic, Australia) coupled to a sector field ICP-MS (Element 2, Thermo) at Goethe University, Frankfurt. Ablation was performed in a He atmosphere (0.3 l/min) and mixed in the ablation funnel with 1.0 l/min Ar and 0.06 l/min N. Signal strength at the ICP-MS was tuned for maximum sensitivity while keeping oxide formation below 0.2 % (UO/U) and element fraction low (e.g. Th/U = 1). Static ablation used a spot size of 257 μm and a fluence of c. 1.5 J/cm² at 15 Hz. This yielded for SRM-NIST 614 a depth penetration of c. 0.8 μm/s and an average sensitivity of 460000 cps/ppm for 238U. The detection limits (4 x standard deviation of background signal) for 206Pb and 238U were c. 0.07 and 0.05 ppb, respectively. Each analysis consists of 20 s background acquisition followed by 20 s of sample ablation and 25 s washout. During 40 s data acquisition, the signal of 206Pb, 207Pb, 208Pb, 232Th and 238U were detected by peak jumping in pulse counting mode with a total integration time of c. 0.1 s, resulting in 400 mass scans. Depth penetration was measured with SEM images and 3D photogrammetric reconstruction of an ablation pit and was estimated at c. 0.6 μm/s with a total depth of less than 15 μm including a 5 s pre-ablation.

Soda-lime glasses SRM-NIST 614 were used as reference materials together with two garnet standards. Raw data were corrected offline using an in-house Microsoft Excel spreadsheet program (Gerdes and Zeh, 2006; Gerdes and Zeh, 2009). The 207Pb/206Pb ratio was corrected for mass bias (0.08 %) and the 208Pb/238U ratio for inter-element fraction (c. 25 %), including drift over the 12 hours of sequence time, using SRM-NIST 614 (n = 26). Additional matrix correction of -14.5 % has been applied on the 206Pb/238U for garnet samples, which was determined using Mali 1 garnet reference material dated by TIMS (202.0±1.2 Ma; Seman et al., 2017), and confirmed by another in-house Mali reference material (called here MaliGUF). Although, Mali 1 and MaliGUF come from the same area, they are distinctly different in composition. Mali 1 is an almost colourless grossular with Ca/Fe of ~7, while MaliGUF is a yellowish-greenish andradite-grossular with Ca/Fe of ~2. Based on the soda-lime glass and the non-common Pb-corrected Mali data the 206Pb/238U fractionation during 20 s depth profiling was non-detectable, thus, no additional correction has been applied. After correcting for drift, mass bias, inter-element fractionation and 14.5 % matrix-offset, the MaliGUF (n = 26) 206Pb/238U ratio of sequence 1 reproduce to 203.0±1.1 Ma (MSWD = 0.6) and that of sequence 2 to 201.3±0.9 Ma (MSWD = 1.3). Common Pb corrections were not applied, due to its high variability, although common Pb content was determined, using the 238Pb signal after subtracting the radiogenic 206Pb (Millonig et al., 2012). According to the analysed standard materials accuracy and repeatability of the method can be assumed to be better than 2 %.

Points of each sample data set derived from a small area (< 1 cm²) and defining linear arrays in the 207Pb/206Pb vs 238U/235U space (TW diagram, Tera and Wasserburg, 1972) interpreted to be a mixture of initial common-Pb and Pb that formed due to in situ decay of U since mineralization. The age of formation is defined by the lower intercept with the Concordia curve. Plots and ages were calculated using Isoplot 3.71 (Ludwig, 2007). All uncertainties are reported at the 2σ level.

5 Results

In the following, we summarize the geochronological data (671 analyses) including the lithological context of the analysed samples. According to their lithological context, mineral chemistry and age, garnets associated with skarns in the Erzgebirge can be subdivided into three different types:

Figure 1. Representative examples of different garnet types.

5.1 Garnet type A (Grt-A)

Grt-A is of sub-calcic composition and forms irregularly shaped dark-red lenses, which may reach up to several cm in size. Individual garnet grains are anhedral and fine-medium grained. Besides pyroxene and magne
abundant quartz accompanies this type of garnet. Lower intercept ages range from 342.9±5.1 to 330.7±10 Ma. Grt-A is locally associated with reaction skarns that occur at interfaces of chemically contrasting lithologies within high grade gneiss units - without any affiliation to intrusions. These skarns do not host significant metal endowment and are therefore not considered to be fertile. Niederschmiedeberg and Boden are examples where this garnet-type occurs.

5.2 Garnet type B (Grt-B)

Grt-B is a pale to dark red garnet, which typically occurs as alternating layers along with pyroxene, vesuvianite and calcite, which results in a skarnoid texture (intermediate between metamorphic hornfels and metasomatic skarn) parallel to the surrounding lithologies. Individual granulate crystals are fine-grained and subhedral. Primary skarn minerals are often associated with fine-grained scheelite and/or cassiterite. Zinc-Fe-Cu-sulfides occur abundantly, but are often associated with retrograde overprint of the primary skarn mineralogy. These skarns typically host significant quantities of Sn, W, Zn, Cu and Fe - consequently, these are considered as fertile. Dates of Grt-B (Fig. 2A) range from 325.5±2.3 to 312.8±3.4 Ma. Type B garnet is present in skarns that occur in close vicinity (0 to 200 m) to granitoid intrusions (e.g. Zobes). Meta-pelitic hornfelses are often associated with these skarns, which typically contain cordierite and andalusite (Hiller and Schuppan, 2016). Additionally, Grt-B may occur early in the paragenetic sequence of skarns, which also contain abundant type C garnet (e.g. Hämmerlein and Breitenbrunn).

5.3 Garnet type C (Grt-C)

Grt-C is pale brown-green to pale green and forms masses of medium-coarse grained euhedral crystals. This garnet is associated with coeval pyroxene. Primary skarn minerals form an isometric, metasomatic fabric and are accompanied by coeval magnetite, sphalerite and minor amounts of cassiterite (Hösel, 2003). Lower intercept ages range from 308.1±3.6 to 295.5±4.4 Ma (Fig 2B), except one outlier, which has an age of 313.1±4.4 Ma. Skarn bodies with Grt-C (e.g. Hämmerlein, Breitenbrunn and Berggießhübel; Fig. 1) may reach up to several km in lateral extent (Schuppan and Hiller, 2013) and are typically well-mineralized. Investigated garnet grains are from distal skarn environments, hundreds to thousands of m away from known intrusions. Although the majority of cassiterite and sulfides in such skarns are related to the retrograde stage of skarn formation, the occurrence of Grt-C is still regarded as an indicator of skarn fertility.

6 Discussion and conclusion

Economically most important skarns (e.g. Hämmerlein and Breitenbrunn) are not genetically associated with known late-orogenic intrusions. Instead, they are affiliated with a younger, post-orogenic magmatic phase (Fig. 2C) - the actual source intrusion to the largest skarn system (Schwarzenberg District) remains as yet undiscovered. Consequently, distal skarns (hosting Grt-C) may occur anywhere, where hydrothermal fluids encountered receptive lithologies. Undiscovered proximal skarns (with Grt-B) could occur in deeper crustal levels where reactive lithologies are present. Two skarn bodies with exceptionally rich metal endowment - the Hämmerlein and the Breitenbrunn skarns - host two distinctively different garnet generations which are related to different magmatic-hydrothermal events. As a consequence, skarns affected by multiple hydrothermal overprinting seem
generally to be most fertile.

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Chemistry of magnetite in a Mg-skarn iron deposit from the Serranía de Ronda, SW Spain

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Abstract. This communication provides the first-ever scientific study of the mineralogy and chemistry of magnetite of the Mg-skarn iron deposit of San Manuel, Serranía de Ronda in SW Spain. This iron deposit is hosted in marbles overlying migmatites found forming a tectonic slice along the southern contact of the Ronda ultramafic massif. Prograde and retrograde skarn stages have resulted in zoning of magnetite, characterized by variations in the chemistry and typology of mineral inclusions. Using laser-ablation ICPMS we have measured the contents of trace elements in magnetite, fingerprinting the origin of the mineralizing fluid as related to the migmatites that originated during host emplacement of the upper mantle peridotites in the continental crust.

1 Introduction

Magnetite has been mined intermittently in the Serranía de Ronda, southern Spain since the middle of the IX century till late XIX century. These orebodies share most of the features of magnesial skarns but have the singularity that they are located near the contact between upper mantle ultramafic and metasedimentary rocks, a very rare setting for this type of ore. Despite systematic mining and the abundance of studies dealing with the Ronda Massif, few scientific efforts have focused to understand the genesis of these deposits. In particular, the potential role that the ultramafic rocks played in the formation of the skarns is still unknown.

Within the last few years, the analysis of trace elements in magnetite has been proposed as a tool for understanding the tectonic geodynamic setting and for classification of iron deposits (Dupuis & Beaudoin, 2014; Dare et al., 2014; Nadoll et al., 2014; Hu et al., 2015, 2017; Wang et al., 2018) despite the fact that there is more and more evidence that this approach is not definitive and is unable to distinguish between magmatic and hydrothermal magnetite nor the type of mineralization (Velasco et al., 2016; Broughm et al., 2017). However, trace element geochemistry of magnetite can be useful for distinguishing between different generations of magnetite. This approach relies on the fact that magnetite is an oxide-type mineral that may host variable concentrations of a wide suite of minor (e.g., Mn, Co, Ni, V, Ti, Zn) and trace (e.g., Ga, Ge, Y, Zr, Nb, W, Pb, Sb) elements in enough amounts to be measurable using a wide range of techniques for in-situ microanalysis such as electron microprobe and LA-ICPMS.

An ever increasing body of work has shown that magnetite in different suites of magmatic-hydrothermal deposits may exhibit complex patterns of zoning (Hu et al., 2014, 2015; Knipping et al., 2015). Zoning is related to single pulses of variation in the composition/nature of the parental magma or hydrothermal fluid, which left its characteristic chemical fingerprint in the magnetite itself. Additionally, a given chemical composition of the magnetite can be related to a specific type of assemblage of nano-to-micron sized mineral inclusions in the given sectors of the magnetite grain (Deditius et al., 2018).

A combination of electron microprobe and laser-ablation microprobe (LAM) coupled to an ICPMS was used for the in-situ measurement of minor and trace elements in zoned magnetite from the Mg-skarn iron deposit of San Manuel, Serranía de Ronda, southern Spain. Our preliminary results suggest that during the emplacement of the mantle peridotites in the continental crust, fluids separated during the anatexis of the host rocks could have contributed to the remobilization of iron from metasediments, leading to the precipitation of magnetite ore in the overlying dolomitic marbles.

2 Geological setting of the San Manuel iron deposit

2.1 The Ronda ultramafic massif and its crustal envelope

Three large (> 60 km²) massifs of ultramafic rocks known as Ronda, Ojen and Carratraca occur widespread in the internal zones of the Betic Cordillera, SW Spain (Fig. 1). These ultramafic massifs correspond to portions of an ancient (1.2-1.8 Ga) subcontinental
lithospheric mantle (SCLM) (Reisberg and Lorand, 1995; Marchesi et al., 2010; González-Jiménez et al., 2013). Among these massifs, Ronda is the largest one. It is thought to be the largest exposure (~300 km²) of SCLM on Earth. This massif consists of lherzolite and harzburgite with minor amount of dunite as well as different types of pyroxenite. Crustal emplacement of these upper mantle rocks took place during the Late Oligocene/Early Miocene, related to a period of extension that promoted the opening of the Alboran marine basin in the western realm of the Mediterranean Sea. The peridotite was emplaced into the continental crust by means of a thrust-fold structure. Thus, they are overlain by a thick unit of up to 7 km of metapelitic rocks (varying from acid granulite, gneiss and migmatite, to schist, phyllite and locally marble) and underlain by Triassic dolomitic marbles. The emplacement of the peridotite into the crust was still relatively hot, promoting dehydration and subsequent anatexis of the metasediments, and leading to the formation of dikes and migmatite that intruded the peridotite between 22 and 18 Ma.

**Figure 1.** Geographical location and simplified geological map of the ultramafic massifs of the Serranía de Ronda in southern Spain showing the location of the San Manuel Mg-skarn iron deposit.

2.2 Characterization of the Mg-skarn and structure of the iron deposit

The San Manuel iron mineralization is hosted in dolomitic marble overlying migmatite, both forming a tectonic slice imbricated into peridotite along the lower thrust of the southern contact of the Ronda ultramafic massif. An exposed section of ~ 25m of this tectonic slice contains, from the bottom to the top, (1) ~12 m of dolomitic marble completely replaced by a retrograde magnesial skarn (chlorite, serpentine, brucite); (2) a body (1-2.5 m) of massive iron ore; (3) ~ 9 m of prograde magnesial skarn characterized by the presence of olivine, calcite and diopside. Magnetite may be found forming the massive body as well as disseminations along the whole profile. Other metallic minerals include pyrite and chalcopyrite, which are found disseminated in the groundmass of the semi-massive magnetite or in the metasomatized carbonatic rock.

3 Petrography and texture of magnetite

Magnetite at San Manuel includes massive (>85% magnetite) to semi-massive (60-85% magnetite) and disseminated (< 30 % magnetite) textures. In addition, it shows three texturally different types according to the zoning (Fig. 2): (1) Type-A zoning found in semi-massive samples, which shows cores of Mg-ferrite (Mt-1) hosting inclusions of dolomite. It is surrounded by four distinct rims of magnetite (Mt2, Mt3, Mt4 and Mt5). Type-B zoning consisting of cores of Mg-ferrite (Mt1) rimmed by porous magnetite (Mt2) in turn enclosed by homogenous magnetite free of inclusions (Mt5). Type-C zoning consists of cores of magnetite with abundant small inclusions of spinel (Mt3) and hosted by magnetite with inclusions of spinel and chlorite (Mt4) and an external rim of magnetite lacking of inclusions (Mt5).

4 Chemical composition of magnetite

4.1 Major elements

Magnesian ferrite (Mt1) forming cores of Type-1 and Type-2 zoning (Fig. 2) shows Fe³⁺/Fe²⁺+Al³⁺ = 0.99-1, Fe²⁺/Fe²⁺+Mg²⁺=0.43-0.64 and Mg+Mn =6.8-10.9. Porous magnetite (Mt2) hosting inclusions of dolomite ± serpentine surrounds these cores, showing similar Fe³⁺/Fe²⁺+Al³⁺ = 0.98-1 and Fe²⁺/Fe²⁺+Mg²⁺=0.78-0.1 but lower Mg+Mn <4.11. The third rim of magnetite (Mt3) characterized by the presence of abundant tiny inclusions of spinel show wider Fe³⁺/Fe²⁺+Al³⁺ = 0.89-1 and Mg²⁺/Fe²⁺+Mg²⁺=0.09-1 and Mg=Mn=0.02-6.08 than Mt1 and Mt2. Magnetite hosting inclusions of spinel and chlorite (Mt4) shows Fe³⁺/Fe²⁺+Al³⁺ = 0.96-1 and Fe²⁺/Fe²⁺+Mg²⁺=0.63-0.84 and Mg+Mn=2.38-7. Finally, the outermost rim of magnetite free of inclusions (Mt5) exhibits Fe³⁺/Fe²⁺+Al³⁺ = 0.99-1 and Fe²⁺/Fe²⁺+Mg²⁺=0.96-1 and <0.72. Other elements including Cr₂O₃, CaO, ZnO, NiO, MnO and MgO are below or marginally higher than the detection limit of electron probe at the conditions used for these analyses.
Figure 2. Different patterns of zoning of magnetite in the studied ore. A: Type-A zoning, B: Type-B zoning, C: Type-C zoning.

4.2 Minor and trace elements

The analysis of minor and trace elements of the different magnetite rims using LA-ICPMS show the following ranges of Ti (in ppm): 0.1-325 (Mt1), 0.44-100 (Mt2), 1.33-18200 (Mt3), 38.6-37.5 (Mt4), 5.2-475 (Mt5). The cores of Mg-ferrite have relatively similar contents of Ga (0.66-9.10 ppm) than the rims of Mt2 (0.28-7.5 ppm) and Mt4 (2.8-7 ppm) and Mt5 (0.2-11 ppm) but lower than the rims of Mt3 (0.54-57.55 ppm). Overall, there are core-to-rims trends characterized by a progressive increasing of the Ti/V and Ga/Al contents. In plots Zn+Co+Mn vs Ga each magnetite type defines a very distinct group with a progressive increasing of Ga content from Mt1 to Mt2 and Mt3 and Mt4, respectively (Fig. 3).

Figure 3. Plot of trace elements Ga vs. Zn+Co+Mn for the different types of magnetites identified in the San Manuel magnetite skarn deposit.

Characteristically, Mg-ferrite cores show relatively higher contents of W (2.8-370 ppm) than the rims of Mt2 (0.42-210 ppm) and Mt4 (0.11-2.46 ppm) but lower than Mt3 (<914 ppm) and Mt5 (845 ppm). Similarly, there is a progressive core-to-rim increase of Hg (Mt1 <2500 ppm, Mt2<2300 ppm, Mt3<2710 ppm, Mt4< 3460 ppm, Mt5<3100 ppm) but decreasing of Pb (Mt1 <4.2 ppm, Mt2<2.11 ppm, Mt3<2.87 ppm, Mt4 and Mt5 < 0.74).

5 Discussion

Textural and chemical variation of the studied magnetite from the San Manuel Mg-skarn iron deposit can be related to two distinctly different mineralizing events, which are probably related with the prograde and retrograde evolution of the skarn. Being part of a skarn, this magnetite is thought to have been precipitated from hydrothermal fluids by fluid-rock interaction. It is worth noting that the relic cores of Mg-ferrite hosting dolomite inclusions are found in grains exhibiting Type-A and Type-B zoning, which are distributed along the entire section of the Mg-skarn including the prograde and retrograde portions. This suggests that the crystallization of Mg-ferrite during the first stage of prograde skarn was very likely from a hydrothermal fluid that supplied Fe and leached Mg during the replacement process. This is consistent with the fact that Type-A zoning predominates the proximities of the major
orebody located between the prograde and the retrograde skarns. In contrast, the formation of a second generation of porous magnetite (Mt2) in these zoned grains is characterized by the presence of inclusions of dolomite ± chlorite ± serpentine and similar Fe3+/Fe2++Al3+, Fe2+/Fe2++Mg2+ and lower Mg and Mn, pointing out that the Mt2 is due to the replacement of the Mg-ferrite during the prograde skarn stage. Moreover, the formation of rims of Mt3 and Mt4 hosting inclusions of spinel and spinel + chlorite indicate further alteration of the pre-existing magnetite by fluids progressively enriched in Al. This later event of alteration may be linked to a stage when the retrograde skarn was more developed, consistently with the fact that the grains of magnetite lacking of Mt1 and Mt2 but consisting of cores of Mt3 surrounded by Mt4 and Mt5 (i.e., Type-C zoning) predominate in the retrograde Mg-skarn.

On the other hand, the analysed magnetite exhibits relatively high contents of W, Hg and Pb. These elements are not typically supplied from hydrothermal fluids derived from upper mantle rocks. Rather, this enrichment is consistent with the hydrothermal fluids being derived from crustal rocks. Indeed, this trace element fingerprint tracks the source of the hydrothermal fluids as related with the dehydration/anatexis of metasediments during the hot emplacement of the peridotites. Variations of these trace elements along the cores and rims of the differently zoned magnetite grains may highlight individual changes in the composition of the parental hydrothermal fluid, each one left behind a characteristic chemical fingerprint in the magnetite itself, similarly to reported zoned magnetite from magmatic-hydrothermal deposits elsewhere (Deditius et al., 2018).

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References


Magnetite skarns: precursor and process controls on iron mineralization (Bohemian Massif, central Europe)

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Abstract. Regional metamorphic complexes in the Bohemian Massif (central Europe) host numerous occurrences of magnetite-mineralized calcic skarns. A well exposed and petrographically variable body near Malešov contains pyroxene, garnet, epidote and magnetite skarn varieties. The pyroxene and magnetite skarns represent products of successive metasomatism of carbonate-rich precursors, whereas the garnet and epidote skarns were produced by replacement of carbonate-siliciclastic precursor. The extent of magnetite mineralization has been controlled by high carbonate reactivity in the appropriate precursor types, coupled with positive feedback of porosity formation during decarbonation reactions. Trace-element distribution in the skarns and in magnetite favors the carbonate replacement hypothesis over the formation by isochemical metamorphism of iron-rich exhalative or sedimentary horizons.

1 Introduction

The Malešov magnetite skarn deposit is located 7 km SW of the town of Kutná Hora, in the central part of the Bohemian Massif, Czech Republic. It is one of the most prominent magnetite skarn deposits in the Bohemian Massif, historically exploited for iron. The origin of magnetite mineralization of skarn type in high-grade metamorphic complexes of the Bohemian Massif has been intensely debated. Accordingly, the magnetite skarns represent (1) metamorphosed ironstones (Zoubek 1946; Vrána 1987; Drahota et al. 2005), (2) metamorphosed iron-rich exhalative-sedimentary horizons (Pertold et al. 2000; Pertoldová et al. 2009), or (3) products of metasomatism of carbonate or marly precursors (Němec 1991; Žáček 1997; 2007). In order to test these competing hypotheses, we have performed detailed mineralogical and geochemical study of the Malešov skarn body, owing to its internal variability, extent of exposure, and accessibility.

Twenty-two hand specimens of skarns and adjacent host rocks were collected in the ground level adit of the mine (Fig. 1) and investigated using optical microscopy, SEM (Tescan Vega, X-max 50; Faculty of Science, Charles University, Prague), EPMA (CAMECA SX100, Faculty of Science, Masaryk University, Brno), and whole-rock geochemistry (Actlabs, Lancaster). Detailed description of the studied samples and analytical conditions can be found in Bubal (2013).

Figure 1. (a) Geological map of the Malešov skarn deposit area, after Štedrá et al. (2011); (b) mine-scale detailed geological map depicting variation in the skarn types at the Malešov skarn deposit.
2 Geological setting

The Malešov magnetite skarn forms an approx. 300 m thick lenticular body, hosted by paragneisses and migmatites of the Kutná Hora Crystalline Complex (Fig. 1a). The dominant calc-silicate minerals are garnet and pyroxene, locally transformed to retrograde hydrous assemblages containing amphibole and/or epidote. Recrystallization of primary skarn assemblages and the formation of hydrous mineral assemblages is associated with Variscan regional metamorphism (Kachlík 1999; Štědrá and Nahodilová 2009) and subsequent emplacement of up to 1 m-thick granite-pegmatite dykes along brittle fractures. Magnetite can be disseminated in pyroxene-dominated skarns or concentrated into massive NE-SW-oriented lenticular bodies (Fig. 1b), typically in anticlinal structures of the folded metamorphic complex. Occasionally, massive magnetite bodies contain traces of younger Fe-sulfides (e.g. pyrrhotite, pyrite).

3 Skarn mineralogy

Eight petrographic and textural varieties of skarns are recognized in the Malešov body (Figs. 2 and 3): (1) fine-grained pyroxene skarn with 80–90 vol% hedenbergite-rich clinopyroxene (Hd60-90Di19-36) and minor garnet, amphibole, chlorite, albite and magnetite (e.g. sample ML4); (2) fine-grained garnet skarn with up to 90 vol% optically isotropic andradite-rich garnet (Adr78-88Grs9-19Alm2-4) and minor epidote, amphibole and calcite (sample ML18); (3) massive coarse-grained garnet skarn with older grossular-rich garnet cores (Adr13-28Grs31-50Alm29-36) and younger andradite-rich rims (Adr28-66Grs21-37Alm12-33), with up to 85 vol% garnet in the whole rock (sample ML14); (4) garnet-pyroxene skarn with approx. 60 vol% garnet and 30 vol% clinopyroxene, and minor amphibole, calcite, accessory magnetite, albite, epidote, muscovite, chlorite, titanite and zircon (samples ML3, ML5); (5) fine-grained epidote skarn (more than 70 vol% epidote; sample ML15); (6) garnet-epidote skarn with approx. 70 vol% garnet and 15 vol% epidote, with minor calcite and amphibole and accessory titanite (sample ML11); (7) magnetite skarn containing 50–60 vol% magnetite that replaces pyroxene and minor amounts of secondary amphibole, hematite and leucoxene (samples ML1 and ML17); and (8) partially silicified and amphibole-bearing skarn formed by retrograde overprint associated with emplacement of granite-pegmatite dykes (sample ML2). Amphibole, which formed at the expense of primary pyroxene, is close to hastingsite in composition, while amphibole in cross-cutting albite-calcite-amphibole veinlets evolves from ferrohornblende to actinolite.

Magnetite-rich skarns contain fine-grained, equant to sub-equant magnetite grains that enclose relics of clinopyroxene, and are locally replaced by amphibole. Magnetite has essentially pure endmember composition, and contains very low amounts of minor and trace elements: 0.43–0.76 wt% Al2O3, 0.04–0.12 wt% TiO2, 0.04–0.11 wt% MnO, 0.001–0.006 wt% V2O3, 0.003–0.012 wt% Cr2O3, and 0.002–0.008 wt% NiO. Low abundances of trace elements, in particular Ni, Cr and V, are characteristic of hydrothermal-metasomatic replacement of carbonate precursor (Dupuis and Beaudoin 2011; Nadoll et al. 2012).
Pressure-temperature conditions of the metamorphic overprint were assessed using univariant equilibria involving solid solutions and thermodynamic modeling. The association garnet-clino.pyroxene-magnetite is stable at temperature above 500 °C and pressure of 0.5–1.5 GPa. Univariant exchange equilibria between garnet and clino.pyroxene correspond to 670 °C at 1.0 GPa, indicating local Mg-Fe exchange during peak metamorphic conditions. Retrograde amphibole (hastingsite) formed at 550 °C and 0.6 GPa, followed by hornblende and actinolite below 440 °C and 0.4 GPa.

4 Whole-rock geochemistry

Individual skarn varieties are grouped into three categories based on major and trace element composition: (1) magnetite and pyroxene skarns are characterized by very low concentrations of the HFSE, Y, alkalis, and P. They have very low abundances of Al₂O₃ (<1.5 wt%), MnO (<0.2 wt%) and REE (4.4–13.1 ppm). (2) Garnet skarns have higher concentrations of HFSE, Al₂O₃ (5.8–10.4 wt%), and REE (44.1–71.6 ppm), but comparable amounts of alkalis and P₂O₅ (<0.1 wt%). (3) Retrograde epidote skarns generally contain the highest concentrations of Al₂O₃, HFSE and REE.

The chondrite-normalized distribution of REE shows two distinct sample groups (Fig. 4): (1) pyroxene and magnetite skarns with low total REE concentrations, enrichment of LREE as opposed to HREE, and weak positive Ce anomaly; (2) garnet, garnet-epidote and epidote skarns with high REE concentrations and strong positive Eu anomaly. The adjacent paragneiss host rock (sample ML13) shows the same REE enrichment but a prominent negative Eu anomaly. Skarns with coarse-grained, recrystallized andradite-rich garnets are enriched in LREE compared to those with early grossular-rich garnets. This decoupling is due to partitioning of REE between garnet and hydrothermal fluids that facilitated its recrystallization.

5 Mass changes

We used isocon diagrams and quantitative evaluation of mass changes in order to assess the plausible range of precursor composition and the magnitude of mass transport during hydrothermal skarn formation. Chemical composition of the precursor has been estimated by mixing of pure carbonate (calcite) with variable amounts of siliciclastic material, approximated by adjacent paragneisses (sample ML13), and assuming negligible mobility of Al₂O₃, TiO₂ and Zr. The low-Al skarn varieties (pyroxene or magnetite skarns) are best reproduced by metasomatism of precursor with 79 % carbonate and 21 % siliciclastic material, whereas the high-Al skarn types (garnet or epidote skarns) require precursor with 46 % carbonate and 54 % siliciclastic component (Fig. 5). Mass balance calculations suggest significant addition of Fe, Mg, Mn, and P in all skarn types, and removal of Ca, LILE and REE during ore-forming metasomatism.

6 Implications and conclusions

Geochronological variation in Al, Ti, Fe, and immobile trace elements (e.g. Zr, Hf, Nb) in skarns, together with low trace element concentrations (e.g., Ti, V, Mn, Cr) in magnetite suggest that the skarn body and its magnetite mineralization formed by hydrothermal-metasomatic replacement of a carbonate-siliciclastic (marly) precursor. The clinopyroxene skarns were formed by metasomatism of relatively pure carbonate precursors (~20 % siliciclastic detrital component), with low concentrations of trace elements including immobile ones, while the garnet and epidote skarns formed by replacement of carbonate rocks with higher amount of siliciclastic detrital component (~45 %). This difference in precursor composition is also supported by the presence of distinct and essentially monomineralic skarn horizons.

Magnetite skarns were formed by advanced metasomatic replacement of the pyroxene skarn horizons. This process has probably been controlled by greater reactivity and more efficient porosity formation in carbonate-rich precursors. By contrast, the garnet skarns have not been mineralized further and only underwent recrystallization from early fine-grained and grossular-dominated to massive, coarse-grained and andradite-dominated types, and partially replaced by epidote.

Skarns together with their host rocks were subjected to Variscan regional metamorphism, leading to formation of compositional layering due to selective partitioning and accommodation of deformation in the mineral assemblages of the skarn bodies. Post-Variscan exhumation of the metamorphic complex led to brittle deformation, dismembering of the skarn bodies and intrusion of pegmatite dykes that caused local silicification and formation of amphibole in anhydrous skarn assemblages.
Figure 5. Isocon diagrams for (a) magnetite skarn, (b) pyroxene skarn, and (c) garnet skarn. See text for details.

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Two types of skarn garnets from West Rhodopes, South Bulgaria: LA-ICP-MS U-Pb dating and tracing evidence

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Abstract. The mineralogical and geochemical characteristics of two types of skarn Ca-garnets from the Velingrad area in the West Rhodopes were studied in order to apply U-Pb geochronometry using LA-ICP-MS. The garnets differ by their mineral assemblage, chemical composition, occurrence, trace element signatures, formation processes and timing. Type 1, presented as syntectonic porphyroblasts with grossular composition in close association with diopside, plagioclase, quartz, titanite and pyrite are formed by metasomatic diffusion catalyzed by metamorphic deformation in the host marbles. Type 2 garnets are Fe-rich grossulars, formed by fluid infiltration in marbles on the contact with cross-cutting pegmatite veins. Their mineral assemblage includes epidote, Fe-rich diopside, plagioclase and apatite. Trace element contents in both types show isomorphic substitution into the garnet structure, evidenced by the smooth ablation profiles. The incorporation of V, Cr, Ga, Ge, Y, Zr, Nb, Sn etc. in the contact garnets is one order of magnitude higher compared to porphyroblasts composition. The low U content (1.2-1.7 ppm) in type 1 combined with possible overprinting processes hampers the precise age record, yielding 88±26 Ma. Contact garnets (U content within 1.7-3 ppm) are dated at 42.97±0.66 Ma suggesting genetic link to the 42-37 Ma Cenozoic granites of the Rila-West Rhodope batholith.

2 Geological setting

The studied garnets, outcropping 2-3 km SW of the Velingrad town in West Rhodopes Mts, are formed by skarnification processes in the marble levels of the metamorphic sequence of the Chepinska Unit, composed mainly of amphibolites, calcisilicate rocks, various gneisses and migmatites (Sarsov et al. 2009). These rocks act as the metamorphic frame to parts of the RWRB comprising plutonic bodies with different age and tectonic position (Kamenov et al. 1999 and references therein). The Unit 1 granodiorites are interpreted as constituents of an older (~80 Ma) symmetamorphic pluton with calcalkaline affinity and crust-contaminated mantle-derived composition. This pluton outcrops as two bigger bodies that are dated at 67-70 Ma by U-Pb zircon method (Von Quadt and Peytcheva 2005; Peytcheva et al. 2007). The Units 2 and 3 granites (35-40 Ma) are genetically related in between phases of a post-metamorphic pluton with high-K calcalkaline signature (Kamenov et al. 1999; Peytcheva et al. 2007). Crosscutting pegmatite veins and processes of migmatization are assigned to the second and third phases of RWRB and to the Late Alpine metamorphism (43-37 Ma, Cherneva et al. 2006).

3 Analytical procedures

The mineral relationships were studied by optical microscopy and BSE on SEM-EDS. Major elements were determined by EPMA. U-Pb isotope and trace element composition of the garnets were defined at the Institute of Geochemistry and Petrology of ETH Zurich, Switzerland. A Resonetics Resolution 155 laser ablation system coupled to a Thermo Element XR Sector-field ICP-MS was used, equipped with some improvements compared to similar systems previously described. Energy density on sample was ca. 3 J/cm², repetition rate was 5, and ablation craters of 40 μm were applied as standard conditions. Mali garnet (Seaman et al. 2017) was used as primary external standard for dating and NIST 612 for trace element analysis. Analytical protocols include the two SRM at the beginning, every
10-15 analyses and at the end. The results were calculated using Iolite combined with Vizual Age to obtain ages and ratios corrected for instrumental drift and down-hole fractionation. The plots were processed using ISOPLOT 3.0 or ISOPLOT 4.15. Iolite or SILLS programs and the SiO₂ content in garnet (as internal standard from EPMA and mineral stoichiometry) were used for calculation of the chemical composition (48 major and trace elements). Additional trace element analysis of the garnets and associating minerals was performed using the New Wave UP193FX laser ablation system attached to Perkin-Elmer Sciex ELAN DRC-e ICP-MS at the Geological Institute, BAS, Sofia, with 75 μm laser craters, 8 Hz repetition rate and ca. 6 J/cm² energy density on sample.

Figure 1. Macro- (A, C), microphotographs (B, D, E), and BSE images (F-H) of the garnets mineral association: A-B) type 1 porphyroblasts, showing garnet-dominated central parts and diopside periphery; C-D) type 2 – massive aggregates of contact garnets formed in the marble along a crosscutting pegmatite vein; D) close view of the skarn-pegmatite sharp contact, showing formation of diopside in the pegmatite part and grossulars in the marble; E) cross section along a porphyroblast, starting from the central garnet parts to the calcisilicate host rock; F) BSE image on the diopside-garnet zones in porphyroblasts, showing formation of titanite and pyrite as accessory minerals; G) inhomogeneous in composition garnet grains with irregular shape; H) well-shaped zonal diopside crystals with Fe-rich cores overgrown by garnet. Abbreviations refer to: Gar-garnet, Di-diopside, Ep-epidote, Pl-plagioclase, Ab-albite, Qtz-quartz. Tit-titanite, Py-pyrite.

4 Results

The studied grandite garnets were formed as a result of marble skarnification by regional or contact metamorphic processes. They are divided in two types according to the mineral assemblage, chemical composition and trace element signatures, temporal and genetic characteristics (Table 1).

4.1 Mineralogy

Type 1 garnets are observed as 1-2 to 5-6 cm porphyroblasts in the marbles (Fig. 1A), wrapped in diopside shells and displaying quartz-plagioclase pressure shadows. Diopside and garnet are intimately intergrown in the central parts of the aggregates (Fig. 1B), while garnet is not observed in the diopside peripheral zone.

Type 2 garnets occur as massive nests in association with epidote and quartz (Fig. 1C) at the marble side separated with sharp contacts from the cross-cutting pegmatite veins. Single diopside crystals formed in the
pegmatite environment in assemblage with albite and quartz (Fig. 1D) and could be interpreted as endoskarns.

Pyrite is very typical for the peripheral parts of the porphyroblasts, forming bands of irregular single grains at the diopside/host rock boundary (Fig. 1E). Scarse pyrite grains are observed in between the diopside and garnet zones, associated with abundant titanite crystals (Fig. 1F). The contact skarns show no evidence of sulphide mineralization. The only accessory mineral here is found to be apatite.

From a compositional standpoint the type 1 garnets are determined as grossular (Al₂O₃ is ~17-22 wt.%; Gro₇₀₋₈₄And₁₄₋₂₀Spess₀₋₄) with variable Fe³⁺-content (generally within two ranges 3.3-5.45 wt. % and 11-12 wt. % Fe₂O₃). The BSE images of the irregular garnet grains (Fig. 1G) reveals compositional inhomogeneity due to the changing Al³⁺/Fe³⁺ ratio (2.4-6.4). TiO₂ incorporation up to 1.12 wt. % is typical. The associated diopside shows variations in Fe²⁺-content. The rims of the crystals are Fe-enriched (5-6.42 wt. % FeO, 0.07-0.09 apfu) while the cores have ~ 1.6 wt. % FeO (0.02 apfu). The idiomorphic shape of diopside crystals in the garnet matrix suggests formation prior to grossular (Fig. 1H).

The chemical composition of the contact garnets (type 2) also reveals grossular-dominated members of the grandite series (14.75-18.83 wt. % Al₂O₃; Gro₆₃And₃₄Spess₃), but with significant Fe₂O₃ (9.8-12.2 wt. % Fe₂O₃; 1.90-1.92 apfu Al³⁺) overgrows Fe-grossular in some places. The type 2 garnet has lower TiO₂ content (up to 0.5 wt. %). The associated diopside (Fig. 1D) is ferroan (0.2 apfu Fe₂⁺) in accordance with the increased iron input in the contact skarns (garnet, epidote).

Apart from the general Al³⁺/Fe³⁺ substitution in the octahedral site of the grandite structure, the calcium concentration and replacements in the dodecahedral position are important. Ca-incorporation is mainly within the 2.5-2.8 apfu in the studied garnets, utilizing the accommodation of Mn, Mg, REE and U. A significant manganese concentration reaching 2.12 wt. % MnO is typical for both garnet types (0.07-0.14 apfu Mn²⁺). Some analyses show Mn-content reaching ~ 5 wt. % MnO. These points correspond to the lowest U-content measured. The Mg incorporation remains mainly below 0.3 wt. % MgO in type 1, and ≤0.2 wt. % MgO in the contact type.

### 4.2 Geochemistry of the grandites

The geochemical patterns of the studied garnets suggest a general trend of trace elements enrichment in the contact garnets compared to the porphyroblastic ones (Table 1). Among the most important traces are V, Cr, Zn, Ga, Ge, Y, Zr, Nb, Sn, incorporated isomorphically in the garnet structure (Grew et al. 2013), evidenced by the smooth ablation profiles. Apart from the Mn and Mg, whose content is in inverse proportion with Ca, only Y is considered to be accommodated in the dodecahedral Ca-position together with REE and U. A trend of positive correlation between the concentrations of V, Cr, Zn, Ga, Ge, Zr, Nb, Sn from one side and Fe³⁺ content from another is observed.

The chondrite-normalized patterns of the REE with low L-REE and higher content of M-HREE (Sm-Lu) are typical in both garnet types. The negative anomalies of Eu and Ce in the contact skarn grossular may be due to the concurrent growth of epidote.

**Table 1. Major characteristics of the two distinct garnet types**

<table>
<thead>
<tr>
<th>Garnet characteristics/type</th>
<th>Type 1</th>
<th>Type 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Occurrence</strong></td>
<td>lense-like 1-2 to 5-6 cm garnet-diopside porphyroblasts within marbles</td>
<td>massive aggregates in marbles on the contact with pegmatite veins</td>
</tr>
<tr>
<td><strong>Mineral association</strong></td>
<td>diopside, plagioclase, carbonates, quartz</td>
<td>epidote, Fe-diopside, quartz, albite</td>
</tr>
<tr>
<td>main minerals</td>
<td>titanite, pyrite ± scapolite</td>
<td>apatite</td>
</tr>
<tr>
<td>accessories</td>
<td>grossular (Gro₇₀₋₈₄And₁₄₋₂₀Spess₀₋₄)</td>
<td>Fe-rich grossular (Gro₆₃And₃₄Spess₃)</td>
</tr>
<tr>
<td><strong>Selected trace elements, ppm</strong></td>
<td>Ti (~ 1 wt. % TiO₂), Na (23-76), P (6-10), Sc (3-10), V (17-420), Cr (14-104), Zn (13-58), Ga (20-45), Ge (2-8), Y (21-98), Zr (10-66), Nb (1-3), Sn (3-7), U (1.2-1.7)</td>
<td>Ti (up to 0.5 wt. % TiO₂), Na (30-45), P (7-10), Sc (2-14), V (314-914), Cr (15-117), Zn (7-118), Ga (45-70), Ge (40-81), Y (30-172), Zr (7-31), Nb (25-47), Sn (8-57), U (1.7-3.05)</td>
</tr>
<tr>
<td><strong>Genesis</strong></td>
<td>metasomatic diffusion catalyzed by tectonic deformation in the metamorphic sequence</td>
<td>contact skarns and infiltration-dominated reactions onto the host marbles</td>
</tr>
<tr>
<td><strong>Timing, U-Pb age</strong></td>
<td>88±26 Ma</td>
<td>42.97±0.66 Ma</td>
</tr>
</tbody>
</table>
4.3 U-Pb dating

The low uranium content (up to 1.7 ppm) and relatively high Pb content of the grossulars from type 1 hampers precise LA-ICP-MS U-Pb age dating. The acquired age is 86 ± 26 Ma. However, Late Cretaceous-Paleocene (62–114 Ma, including the 2 sigma uncertainties) tectono-metamorphic events are known in the Rhodopes (Cherneva et al. 2006). Undoubtedly the formation of these garnets is somehow connected with the magmatic processes of the synmetamorphic granodiorites of the Unit 1 of the RWRB which took place at ~ 80 Ma (Kamenov et al. 1999).

Type 2 grossulars from the contact with pegmatite dykes are dated at 42.97±0.66 Ma suggesting a genetic link to the 43-37 Ma Cenozoic granites of the Rila-West Rhodope batholiths (Peytcheva et al. 1998, Kamenov et al. 1999, Cherneva et al. 2006, Von Quadt and Peytcheva 2005).

5 Discussion and concluding remarks

The age results strongly depend on the U-contents in the garnet structure, but also on inclusions of other (Pb-bearing) phases (plagioclase), and probably on overprinting processes that can lead to garnet alteration and new garnet growth. The precise dating record in the garnets is proportional to the U-content, which is considered to replace Ca in the dodecahedral position of the garnet structure. Thus, the concentration of elements which are likely to substitute for Ca (e.g. Mn, Mg, Y) could influence the precise U-Pb garnet dating.

The formation of type 1 garnets is interpreted as syntectonic porphyroblasts, according to their position in the host marble (Fig. 1A). Considering the catalyzing effect of the deformation on the mineral nucleation, these aggregates are product of increased diffusion rate due to the magmatogetic events in the metamorphic sequence. Formation of the contact massive skarn garnets along the pegmatite dykes is strongly influenced by infiltration-driven reactions onto the marble stratrum.

Compositionally the mineral association in the contact skarns compared to porphyroblasts reveals increased role of Fe in the garnet and diopside, evidenced also by epidote occurrence. The Ca/Mn substitution is well expressed, showing inverse concentration between their concentrations. Manganese incorporation is typical for both types, together with some Mg. The analyzed points with increased Mn are those with the lowest U-incorporation, influencing the dating record. However, the Mn-content show enchanced values in the contact garnet compared to that in porphyroblasts, suggesting that the U-incorporation depends not only on the chemical composition, but also on the possible trace element sources in the system (e.g. the direct contact with pegmatite dykes).

From a geochronometry standpoint the Fe-enriched grossular (type 2) gave better age results, although no direct correlation between Fe-incorporation and U-content is observed. The increased values for Ti, V, Cr, Zn, Ga, Ge, Zr, Nb, Sn do not influence the U-Pb dating accuracy as they are mainly accommodated in the octahedral site of the garnet structure.

The LA-ICP-MS U-Pb dating on grandite distinguishes two separate magmatic-hydrothermal events. We suggest that the deformational processes that type 1 garnets suffered, led to U-depletion, thus the acquired U-Pb age stays tentative. The abundant titanite crystals observed in the mineral assemblage of the porphyroblasts give excellent opportunity for crosschecking the timing of grossular formation. The contact-type skarn garnets (type 2) yield ages with low 2 sigma errors. Despite the unsatisfying age of garnet porphyroblasts they are undoubtedly older than type 1.

Acknowledgements

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Metamorphosed granite–greisen–skarn assemblage and related tin mineralization in Nedvědice, Bohemian Massif

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Abstract. The Nedvědice orthogneiss is located in the Svatka Crystalline Complex, eastern part of the Kutná Hora–Svatka Crystalline Unit, Bohemian Massif (Czech Republic). The orthogneiss is surrounded by a varied suite of rock types, such as mica schists, minor marbles, tourmalinites, amphibolites, serpentinites, quartzites and iron skarns. Its southeastern part is characterized by presence of tin mineralization, either associated with metapelites or in calc-silicate skarns, both in vicinity of the tourmaline-rich Nedvědice orthogneiss. Several tourmaline generations (magmatic, hydrothermal, metamorphic) were recorded in the tourmaline from the orthogneiss; together with metamorphic overprint of the tin mineralization in surrounding host rocks, the textures reflect Variscan metamorphic overprint of the Ordovician granite and its autochthonous (meta)sedimentary cover. The protolith of the Nedvědice orthogneiss is highly evolved, leucocratic, prealuminous granite rich in boron and fluorine.

1 Introduction

The Svatka Crystalline Complex of the Bohemian Massif (Fig. 1) consists of a complex and variable assemblage of metapelites, metagranites, skarns, tourmalinites, marbles, serpentinites and quartzites. Its southeastern part is characterized by presence of tin mineralization, either associated with metapelites or in calc-silicate skarns, both in vicinity of the tourmaline-rich Nedvědice orthogneiss. The studied area is located in the southern part of the Svatka Crystalline Complex (SCC), western Moravia, Bohemian massif (Czech Republic). It is bordered by the Moldanubian Zone in the S, by the Moravosilesian Zone in the E, and the Bohemicum in the W and N (Polička Unit).

The radiometric dating of metagranites in SCC revealed three stages of development of these rocks; (i) 1932 ± 7 Ma – indicating the granite protolith was probably derived from the melting of Late Paleoproterozoic basement, (ii) 515 ± 9 Ma – the granite crystallization in Ordovician, and (iii) ~340 Ma, reflecting the Variscan tecton metamorphic overprint (Schulmann et al. 2005; Buriánek et al. 2009). Typical rocks for this area are medium- to coarse-grained mica schist, orthogneiss, two-mica paragneiss, amphibolite, marble, migmatite, skarn, and tourmalinite (Fig. 2; Novák et al. 1998).

2 Skarns of SCC

The most frequent type of skarn is garnet-pyroxene skarn (± magnetite) with transitions to pyroxene skarns, pyroxene skarns with magnetite and garnet-amphibole (Pertoldová et al. 1998). Skarn protoliths were most probably heterogeneous sedimentary rocks with a component of exhalites deposited on the sea floor and endured all the metamorphic events together with the surrounding sedimentary/volcano-sedimentary sequences in the SCC (Pertoldová et al. 2009). Skarn-forming fluids reacting with the carbonates were probably derived from surrounding orthogneiss - former peraluminous granites rich in F, B, Sn, As (Houzar et al. 2006). Contents of Sn in whole rock analyses of Pertoldová et al. (2009) did not exceed 160 ppm.

The main skarn tin-bearing minerals are andradite and accessory malayaite; cassiterite is very rare (Hrazdil et al. 2009). The andradite forms medium- to coarse-grained aggregates with vesuvianite; the garnet contains ca. 1.2-2.4 wt. % SnO₂ (0.038-0.081 apfu Sn) and low F (<0.016 apfu), whereas the vesuvianite is rich in As. Malayaite (tin analogue of titanite) is a typical accessory Sn-mineral, with 54.50 – 56.27 wt.% SnO₂ (Hrazdil et al. 2009).

3 Tin mineralization in metapelites

Significant cassiterite anomalies were found in stream sediments in the region, however cassiterite was never confirmed in the Nedvědice orthogneiss. Placer prospecting revealed elevated contents of cassiterite in some samples (up to 0.75 wt.%) mainly in the vicinity of the orthogneiss and skarns. Other minerals recorded in small amounts were scheelite and zircon (Česneková 1968).
Tin mineralization was subsequently evaluated by the state exploration company Geoindustra (placer prospection, mapping, and drilling; Grym 1969); however, the exploration program did not reveal any significant ore accumulations.

Figure 2. Geological map of the studied Nedvědice area.

4 Nedvědice orthogneiss

Leucocratic orthogneiss at Nedvědice forms a N-S trending elongate body about 100 m thick and up to 1 km long, enclosed in mica schists (Fig. 2). The protolith of the Nedvědice orthogneiss is a highly evolved, leucocratic, peraluminous granite, depleted in Sr, Zr, Cr, and REE but enriched in Rb, B, Ga and F (Novák et al. 1998). The Nedvědice orthogneiss is special by the presence of tourmaline-bearing hydrothermal veins of fluorite which underwent regional metamorphism.

Two types of tourmaline were distinguished at the locality. The first one includes metamorphosed magmatic tourmalines with preserved magmatic cores and younger, recrystallized rims (Fig. 3). This tourmaline contains brecciated primary magmatic cores enriched in Fe, contain high X-site vacancies and variable F-content. The younger rim is enriched in Mg and F caused by probable breakdown of early tourmaline, biotite and plagioclase in the rock. The youngest rim has elevated Ca, Fe and lower F due to fractional crystallization of residual melt. The second type of tourmaline is present in metamorphosed fluorite layers. This coarse-grained tourmaline has patchy zoning where we can distinguish core and rim zones. The core is rich in F, Mg and Na while rim has relatively lower content of F and is enriched in Fe compared to the core. We interpret the core as primary hydrothermal and rim as metamorphic. Similarly to the rims of the magmatic tourmaline, the rims of tourmaline from fluorite layers are rich in Ca and Fe; this may indicate recrystallization under the same metamorphic fluids with elevated Ca and Mg contents.

Figure 3. BSE image of metamorphosed magmatic tourmaline (top) and hydrothermal tourmaline in fluorite layer (bottom). Letters in the top image represent: A – preserved brecciated magmatic core, B – metamorphic zone 1, C – metamorphic zone 2. Letters in the bottom image represent: D – primary zone 1, E – metamorphic zone 2.
5 Metamorphosed greisens in the SCC?

Some of the studied rocks feature elevated contents of rare elements and fluxes (Li, B, F) which suggests they may represent metamorphosed greisens. The topic was earlier studied by Němec (1986) who concluded that the identification of regionally metamorphosed greisens is not a simple task. Granitic rocks are usually homogeneous, and their overprint to orthogneisses does not result in significant mineralogical changes. Sometimes they host “greisen” layers; however, these are also present in surrounding mica schists and could form through greisenization of paragranites (Němec 1986). At the Kovářová locality, Němec (1986) described cassiterite-bearing greisens in mica schist near the Nedvědice orthogneiss and suggested that the original greisens formed by greisenization of paragranites.

Our data from the first type of “greisens” (enclosed in the orthogneiss) support their magmatic-metasomatic origin (Tab. 1), as they contain high F contents of 0.22–1.33 wt. % and show enrichment in Li (73 – 640 ppm). The mica in the “greisens” is unusually F-rich, with up to 3.37 wt. % F; this composition suggests formation from highly evolved acidic fluids.

Table 1. Whole rock analysis of selected samples; 1 and 2 – orthogneiss, 3 and 4 – metamorphosed fluorite layer

<table>
<thead>
<tr>
<th>sample no.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tbody>
<tr>
<td>SiO₂ Wt.%</td>
<td>76.06</td>
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<td>64.24</td>
<td>51.97</td>
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<td>1.84</td>
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<tr>
<td>MgO Wt.%</td>
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<td>0.14</td>
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<tr>
<td>CaO Wt.%</td>
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<td>0.53</td>
<td>0.31</td>
<td>0.34</td>
</tr>
<tr>
<td>Na₂O Wt.%</td>
<td>2.57</td>
<td>2.22</td>
<td>1.26</td>
<td>1.99</td>
</tr>
<tr>
<td>K₂O Wt.%</td>
<td>5.04</td>
<td>4.95</td>
<td>5.02</td>
<td>2.66</td>
</tr>
<tr>
<td>TiO₂ Wt.%</td>
<td>0.14</td>
<td>0.12</td>
<td>0.54</td>
<td>0.79</td>
</tr>
<tr>
<td>P₂O₅ Wt.%</td>
<td>0.25</td>
<td>0.23</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>MnO Wt.%</td>
<td>0.02</td>
<td>0.03</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Cr₂O₃ Wt.%</td>
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<td>&lt;0.002</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
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<tr>
<td>Sum %</td>
<td>99.11</td>
<td>99.05</td>
<td>95.87</td>
<td>92.16</td>
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<tr>
<td>Sn ppm</td>
<td>11</td>
<td>9</td>
<td>34</td>
<td>20</td>
</tr>
<tr>
<td>F ppm</td>
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<td>Li ppm</td>
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<td>211</td>
<td>640</td>
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Acknowledgements

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References


Mineralogy, geochemistry and U-Pb geochronology of grandite from the Martinovo Fe-skarn deposit, Western Balkanides, Bulgaria

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Abstract. Grossular-andradite (grandite) bearing skarns are a favorable environment for deposition of magnetite ore with economic importance in the Martinovo deposit, W Balkanides, NW Bulgaria. Ore mineralization results from hydrothermal activity related to the Carboniferous Sveti Nikola granite emplaced in the Cambrian-Ordovician low grade metamorphics of the Diabase-Phyllitoid complex. Skarns, composed of primary clinopyroxene and garnet, form massive aggregates at the subvertical contacts of schists and calcite/siderite marbles with clear lateral zonality. Distal garnets reveal andraditic composition, while proximal are grossular-dominated. The mineral association includes molybdenite, scheelite and scarce uraninite. Compositionally, the grandites have oscillatory zonation due to the changing Fe/Al ratios. Garnet trace element analyses reveal incorporation of significant amounts of V, Cr, Ga, Ge, As, Mo, Sn, and W. Precise HR LA-ICP-MS U-Pb dating of grandite yields 306.2±1.9 Ma that is in prefect agreement with the ID-TIMS Concordia Age = 306.6 ±1.4 Ma. High U content (10-70 ppm) results in a possibility to apply LA-quadrupole ICP-MS dating that yields a lower intercept age of 303.7±5.2 Ma. The age record does not depend on the major element chemical inhomogeneity of the crystals as the main variation is in the octahedral position, occupied by Fe³⁺ and Al³⁺.

1 Introduction

Grossular-andradite garnets (Ca₃Al₂Si₃O₁₂–Ca₃Fe₂Si₃O₁₂), commonly known as grandites, are primary skarn minerals formed by metasomatic processes in carbonate environments. The recent advances in the U-Pb LA-ICP-MS geochronology (Seaman et al. 2017, Salnikova et al. 2017, Wafforn et al. 2018) have shown the ability of the Ca-garnets from the grandite series to record the timing of the hydrothermal processes in ore deposits.

Here we present mineralogical, geochemical and LA-ICP-MS U-Pb dating results of skarn garnets from the Martinovo iron deposit in Western Balkans, NW Bulgaria. We use them to constrain the favorable conditions for timing of iron skarns and discuss the main possible mechanisms for trace element incorporation.

2 Geological background

The Martinovo iron ore deposit is part of the Chiprovtsi ore district, located in the westernmost part of the Balkanides, NW Bulgaria. It is hosted by the Cambrian-Ordovician Diabase-Phyllitoid Complex (DFC; Haydoutov 1991). The DFC is composed of various schists, calcsilicate rocks, ophiolite and volcanic materials which suffered low grade metamorphism. Skarn formation processes in the calcite and siderite marbles and economic magnetite ore mineralization is suggested to be genetically related to the intrusion of the Sveti Nikola granite with Late Carboniferous age (313.8 ± 3.5 Ma, Carrigan et al. 2005). The primary skarns are composed by clinopyroxene and garnet, developed on the subvertical schist/marble contacts with the granite. The exoskarns reveal clear mineral and compositional lateral zonality with proximal pyroxene, intermediate garnet-pyroxene and distal garnet zones (Tarassova and Tarassov 1988), due to the bimetasomatic processes in the thermal aureole of the pluton. The magnetite ore, occurring as irregular, columnar, pipe-like bodies is mainly related and hosted by the distal garnet zone, although its formation has also been interpreted as thermometamorphic alteration of siderite (Dragov, 1992).

3 Analytical techniques

The mineral relationships were studied by optical microscopy and BSE on SEM-EDS. Major element garnet compositions were determined by Jeol JSM-6610LV SEM-EDS at the University of Belgrade. Trace element and REE concentrations in garnets and associated minerals were measured by LA-ICP-MS, using the New Wave UP193FX laser ablation system attached to Perkin-Elmer Sciex ELAN DRC-e ICP-MS at the Geological Institute, BAS, Sofia, with 75 μm laser craters, 8 Hz repetition rate and ca. 6 J/cm² energy density on sample.

U-Pb isotope and additional trace element composition of the garnets were defined at the Institute of Geochemistry and Petrology of ETH Zurich, Switzerland and the Geological Institute of the Bulgarian...
Academy of Sciences. At ETHZ a Resonetics Resolution 155 laser ablation system coupled to a Thermo Element XR Sector-field ICP-MS was used equipped with some improvements compared to similar systems previously described. Energy density on sample was ca. 3 J/cm², repetition rate of 5, and ablation craters of 40 μm were applied as standard conditions. Mali garnet (Seaman et al. 2017) was used as primary external standard for dating and NIST 612 for tracing. Analytical protocols include the two SRM in the beginning, every 10-15 analyses and at the end. At GIBAS UP193FX New Wave LA system and Elan DRCe quadrupole ICP-MS and Dashkesan garnet SRM (Stifeeva et al. 2018) are used for dating, together with NIST 610 as an SRM for tracing. Repetition rate of 8, and ablation craters of 50-75 μm were applied. The results were calculated using Iolite combined with Visual Age to obtain ages and ratios corrected for instrumental drift and down-hole fractionation. The plots were processed using ISOPLOT 3.0 or ISOPLOT 4.15. Iolite and SILLS programs and the SiO₂ content in garnet (as internal standard from EPMA and mineral stoichiometry) were used for calculation of the chemical composition (48 major and trace elements).

4 Results

4.1 Mineralogy

Garnet occurs mostly as fine grained, massive aggregates, extensively cracked, intergrown with diopside-hedenbergite in the pyroxene-garnet zone (Fig. 1A). Euhedral garnet crystals are rarely observed. The primary mineral assemblage includes also titanite, plagioclase, K-feldspar, apatite, and allanite. Titanite, apatite, and allanite occur as euhedral to subhedral crystals.

Oscillatory zonation is apparent in the analyzed samples in transmitted light microscopy and in back-scattered SEM images (Fig.1B). It shows variation in Al and Fe content that leans towards intermediate grossular-andradite composition (Al₂O₃ - 8.3-13.0 wt.%, Fe₂O₃ - 15-17 wt.%) of the garnets in the garnet-pyroxene zone; and to andradite composition of the garnets (Al₂O₃ - 0.4-4.0 wt.%, Fe₂O₃ - 15-17 wt.%) in the distal garnet zone. The Mn-content is slightly higher in Al-rich garnets (MnO - 2.5-4.1 wt.%) compared to Fe-rich (MnO - 0.6-1.1 wt. %). The correlation between Mn and Al (0.70) is better than between Mn and Ca, thus suggesting an octahedral incorporation in the structure (Mn³⁺). Small quantities of Mg (120-1000 ppm) and Ti (10-160 ppm) were detected. The CaO content is within the range 30-35 wt.%.

The skarns underwent retrograde metasomatic alteration with formation of chlorite, amphibole, quartz, calcite, scheelite, molybdenite, uraninite, magnetite, pyrite and other sulfides. The ore mineralization spatially associates with the garnet-pyroxene - garnet zone.

The skarns can be classified as Mo±W according to the abundant molybdenite-scheelite mineralization associated with the garnet (grossular-andradite) – pyroxene skarns (Meinert 1992).

4.2 Geochemistry

Apart from major elements in the grandite, trace element signatures in the studied garnets reveal incorporation of V (44-256), Cr (8-16), Ga (28-32), Ge (23-29), As (5-44), Sr (1-14), Y (up to 4), Mo (1-30), Sn (24-128), La (2-11), Ce (4-13), ²⁰⁶Pb (below 13 ppm). The W-content is significant, reaching more than 2000 ppm in most of the analyzed points (n=24). Among the important trace elements in the garnet structure is U, directly influencing the age record of their formation. All above mentioned elements are presented in the garnet structure as isomorphic substitutions, evidenced by the flat and stable depth ablation profiles.

The ²³⁸U incorporation in the studied grandite grains is high, ranging from 10 to 70 ppm. Well expressed positive correlations of U with the following elements are observed: W (0.69), La (0.92), Ce (0.70), As (0.53), and Mo (0.59). Positive correlations exists among these elements as well (Fig. 2). Uranium content correlates positively with total REE (0.75) and LREE (0.76), thus
suggesting incorporation by substitution for divalent cations (Ca²⁺) in the dodecahedral position (Smith et al. 2004, Gaspar et al. 2008). Correlation with total HREE becomes only positive (0.62) when the analyses with U concentrations below 25 ppm are excluded implying probably late partial extraction of U in some areas of the garnets during retrograde process. This apparently does not affect the U-Pb dating.

The garnets are generally depleted in REE (11.0-48.6 ppm), especially in MREE and HREE, as the latter are hardly detected. The chondrite-normalized patterns of garnet also display LREE enrichment and MREE-HREE depletion, with well expressed positive Eu anomaly (Eu/Eu⁺ =2.5-18.3). This is consistent with the typical chondrite-normalized patterns for andradite garnets outlined by Gaspar et al (2008).

4.3 U-Pb dating

Precise HR LA-ICP-MS U-Pb dating of grandite yields 306.2±1.9 Ma which is in agreement with the ID-TIMS Concordia Age = 306.6 ±1.4 Ma. High U content (10-70 ppm) provides an opportunity to apply LA-quadrupole ICP-MS dating that defines an lower intercept age of 303.7±5.2Ma. All age results support the genetic link to the Sveti Nikola granite intrusion (313.8 ± 3.5 Ma, Carrigan et al. 2005).

5 Discussion

The precision of the HR LA-ICP-MS U-Pb dating of the Martinovo grandites is comparable with the precision of the age obtained by the ID-TIMS techniques. As the skarns are acting as a host environment for the magnetite bodies, their age 306.2±1.9 Ma directly records the hydrothermal activity in the vicinity of the granite and defines the maximum age limit for the economic ore mineralization in Martinovo deposit.

The age record in garnets is directly influenced by the U-content in their structure. The Sveti Nikola granite, as well as some other Carboniferous granites in the Balkans (in Bulgaria and Serbia, Jovanović et al. 2019) are known as enriched in uranium and the latter obviously influences the U-content of the skarn granites. High U content (10-70 ppm) results in a possibility to apply not only HR LA-ICP-MS dating but also the more common quadrupole-MS technique. Despite the small inclusions of scheelite and molybdenite, we suggest that the garnets from the Martinovo deposit could be used successfully as a standard reference material for garnet dating.

Acknowledgements

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Mineral-chemical characterization of the schist-hosted veinlet-style Sn-bearing mineralization of the Pöhla-Hämmerlein skarn deposit, Westerzgebirge, Germany

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Abstract. The Pöhla-Hämmerlein Sn-In-polymetallic deposit comprises mainly skarn lithologies (Schuppan et al. 2012). Besides, it features cassiterite-bearing quartz-fluorite-tourmaline veinlets that penetrate the two-mica-schist country-rock. They have been observed at three localities (Hauptstolln, Querschlag 2, Chamber 7543) to occur only below the skarn body where they crosscut the schist in about 15° to the schistosity. The typical mineral association consists of cassiterite, quartz, fluorite, and minor tourmaline. A second occurrence reveals minor amounts of sulfides (arsenopyrite, chalcopyrite, pyrite, pyrrhotite) next to cassiterite. Bulk ore geochemistry reveals grades of up to 3.3 wt.% Sn.

Tin-grades correlate with the frequency of veinlets, and country rock shows only a slight enrichment in Sn, which occurs there as impregnation. Accordingly, possibly economic mineralization is entirely caused by veinlet-style mineralization with cassiterite as the Sn-bearing mineral phase. The mineral assemblage of the veinlets shows homogenization temperatures in the mesothermal range (238–344 °C).

The crosscutting of the late-Variscan country-rock (metamorphose age c. 340 Ma, Kröner and Willner 1998) and the enrichment of incompatible elements are indications for a magmatic influence of the cassiterite-quartz-fluorite-tourmaline veinlets, possibly related to an unidentified granite intrusion stage at the eastern rim of the Eibenstock granite massif.

1 Introduction

The Pöhla-Hämmerlein skarn deposit was discovered in 1969 during uranium exploration in the W-Erzgebirge by the Soviet-German company SDAG Wismut. In the following years, several exploration campaigns were established to bring the deposit into production, however all operations were unsuccessful. New exploration efforts started in 2014, and the whole resource has been estimated to contain ca. 22.1 Mt @ 0.2 wt.% Sn and 15.9 Mt @ ~130 ppm In (Anglo Saxony Minerals Ltd. 2018). In the footwall of the skarn ore bodies, some cassiterite-bearing veinlets occur in the two-mica-schist country rock. These veinlets were firstly described as “Schiefererz” (cf. Schuppan et al. 2012) and present possibly economic Sn-mineralization in stringer zones that are likely associated with the skarn genesis (Fig. 1). This mineralization type has not received intense attendance. With this study, we want to provide new detailed insights into the mineralogy of the veinlets and also deliver new constraints for the genesis.

2 Geological background

The Hämmerlein deposit is hosted by Variscan metamorphic rock units of the western Erzgebirge (cf. Baumann et al. 2000) which belongs to the Saxo-Thuringian zone and is situated at the northern margin of the Bohemian Massif. The metamorphic units consist mainly of schists (greenschist to amphibolite facies), gneisses, and metacarbonates (Rötzler and Plessen 2010). The peak of metamorphic conditions was reached at around 340 Ma (Kröner and Willner 1998).
different types of magmatic-hydrothermal ore deposits like greisen, skarn, and polymetallic veins occur (Baumann et al. 2000). The units are crosscut by networks of local to regional faults, the most prominent being the NW-SE striking Gera-Jáchymov Fault Zone.

The veinlet-hosted “Schiefererz” ore type presents itself as part of a series of two-mica-schist, which is situated below the elongated skarn body of calc-silicates from the Hämmerlein Sn-In-polymetallic skarn. The schist belongs to the Jáchimov group. The whole deposit lies above a granite body of type Eibenstock (Schuppan et al. 2012).

3 Methodology

For this study, underground mapping was performed 2016 and 2017. We gathered a total of 63 samples from the “Hauptstolln”, “Querschlag 2”, and “Tin Chamber 7543”. On these, light microscopy and SEM/MLA (scanning electron microscope/mineral liberation analysis), as well as bulk ore geochemistry (ALS Global), and fluid inclusion analysis (Flin Lab of the Institute of Mineralogy at TUBAF) was performed.

4 Results

Results provide an overview of the distribution of the Sn-bearing “Schiefererz” ore type and the mineral association of the veinlets. “Schiefererz” was sampled at three locations (Fig. 2). Bulk ore geochemistry outlines enrichment of certain elements related to the veinlets and fluid inclusion microthermometry further shows the formation conditions.

4.1 Mapping

Mapping of two adits shows how veinlets are all crosscutting the two-mica schist host-rock with a slight angle of 10–30° towards N to NE. Furthermore, cassiterite mineralization often disappears at the hanging wall contact to the overlying skarn body. A set of subvertically dipping veinlets occurring NW of “Tin Chamber 7453” shows no cassiterite.

4.2 Petrography

Microscopy revealed that the “Schiefererz”-cassiterite occurs in two major habits: discrete subhedral crystals (c. 50–3,400 µm) or acicular cassiterite (needle tin; <100 µm). Discrete crystals reach up to a few mm and are the predominant crystal habit found in the “Hauptstollin” and “Tin Chamber 7453”. Cassiterite from “Querschlag 2” consists of needle tin and smaller grain-sizes of discrete crystals. Discrete crystals show zoning and twinning, while needle tin aggregates only show zoning (Fig. 3).

MLA analyses reveal the association of minerals. Cassiterite predominantly occurs together with quartz, tourmaline, and mica, and minor feldspar, chlorite, fluoride, and rutile. In a second type close to the overlying skarn body, additional sulfides (arsenopyrite, chalcopyrite, pyrrhotite) occur (cf. Fig. 3).

4.3 Fluid inclusion microthermometry

Microthermometry was performed on eight double polished sections (c. 200 µm) using fluid inclusions in cassiterite, fluorite, and quartz (Fig. 4). Homogenization temperatures are 313–344 °C, 238–347 °C, and 263–310 °C, respectively. Salinity is relatively low with 0.6-6.9 equiv. wt.% NaCl, with only some fluid inclusions in fluorite of sample “SOH-2.2” showing 12-19 equiv. wt.% NaCl and a homogenization temperature of 238–274 °C (Fig. 5).

4.4 Bulk ore geochemistry

Bulk ore geochemistry shows an increase of incompatible elements in zones with crosscutting veinlets. Concentrations of Rb, Cs, Li, B, Sn, and W are typically around 3–7-times increased compared to seemingly barren samples (Tab. 1) but can reach up to ~16,000-times enrichment (e.g. for Sn).
Figure 4 Photos and photomicrographs of the veinlet-style mineralization. Top: Qz-Cst-Tur-mineralization from the Hauptstolln. Bottom: Sulfide-bearing veinlets adjacent to skarn lithologies in Querschlag 2. (Apy=arsenopyrite, Ba=baryte, Ccp=chalcopyrite, Cst=cassiterite, Po=pyrrhotite, Py=pyrite, Qz=quartz, Sp=sphalerite, Tur=tourmaline).
5 Discussion

The more or less uniform mineral assemblage and the relatively homogenous values of homogenization temperature and salinity suggest a single event for the formation of the veinlets.

The variation of crystal habits of cassiterite with the occurrence of larger single crystals and needle tin indicates mesothermal formation conditions (Ramdohr 1975). Furthermore, zonations show that the fluid was heterogeneous in all areas where “Schiefererz” was observed. This is also supported by variations in homogenization temperatures from 263–347 °C and relatively low salinity (<5 equiv. wt.% NaCl). The slightly enriched salinity in five fluid inclusions in fluorite probably reflects mixing.

The elevated contents of incompatible elements like Rb, Cs, Li, B, F, Sn, and W in samples with mineralized veinlets and homogenization temperatures of up to c. 350 °C support a magmatic origin of the “schist ore” mineralization.

Figure 5 Homogenization temperatures and salinity (equiv. wt.% NaCl) of fluid inclusions in cassiterite (Cst), fluorite (Fl), and quartz (Qz).

Table 1 Bulk ore geochemical composition of unmineralized samples and mineralized samples from Hauptstolln, Querschlag 2, and Tin Chamber 7543.

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<thead>
<tr>
<th>Element</th>
<th>Unmineralized (ppm)</th>
<th>Querschlag 2 (n=25)</th>
<th>Hauptstolln (n=13)</th>
<th>Kammer 7543 (n=22)</th>
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<tbody>
<tr>
<td>B</td>
<td>34</td>
<td>54</td>
<td>115</td>
<td>109</td>
</tr>
<tr>
<td>Cs</td>
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<td>249</td>
<td>17</td>
<td>8</td>
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<tr>
<td>F</td>
<td>625</td>
<td>2120</td>
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<td>15</td>
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<tr>
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<td>42</td>
<td>47</td>
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<td>100</td>
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<td>6271</td>
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<td>18700</td>
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<tr>
<td>W</td>
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Acknowledgements

This research is carried out as part of ResErVar project in the national r4 program (grant number 033R129 to TS). The BMBF is gratefully acknowledged for funding. Further gratitude goes to the Sample Preparation Lab at Helmholtz Institute Freiberg for Resource Technology. We highly appreciate the support by Saxore Bergbau GmbH and Zinnkammern Pöhla e.V. during underground mapping and sampling. Final gratitude to Tom Járóka for helping with the manuscript.

References

Mineral paragenesis and zoning of the Hashim Abad magnetite-skarn, Isfahan Province, Central Iran

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Abstract. The Hashim Abad magnetite-skarn occurrence is situated in the Urumieh-Dokhtar-Magmatic-Arc, Central Iran. It is located in a transition zone of Cretaceous, dolomitic limestone and a Miocene, dioritic intrusion along a NW-SE striking fault. A contact metamorphic influence of the wall rock is marked by the formation of green amphiboles in the magmatic rock and the recrystallisation of calcite to marble. The metadioritic wall rock is additionally affected by alteration zones, preferentially towards the contact zone. Massive magnetite replaces the marble. Associated with the lens-shaped magnetite load are green calc-silicates. They consist mainly of diopsidic pyroxenes and minor chlorite, actinolite and titanite. Magnetite is locally associated with chalcopyrite and shows an anomalous gold concentration. Several indicators suggest that the Hashim Abad deposit can be assigned to the Fe-Cu-Au-skarn class. Hydrothermal influence is visible by sericitisation of feldspar and due to SWIR analysis indicating the presence of saponite, sepiolite and palygorskite. Furthermore, veins of calcite, ankerite and quartz are present in the whole contact zone, locally associated with epidote. They transect also magnetite and calc-silicate rocks and are themselves influenced by brittle faults.

1 Introduction

The Tethyan belt is a major porphyry-epithermal-skarn related mineralized belt that extends across central and southeast Europe, Turkey, Iran, Pakistan, through the Himalayan region and SE Asia. The less explored Iran, located in the central part of the Tethyan belt, is recognized as hosting world class deposits such as Sar-Cheshmeh porphyry (1.2 Gt @ 0.7% Cu) and Sungun porphyry-skarn (500 Mt @ 0.75% Cu). These porphyry and skarn deposits are related to the evolution and closure of the Neo-Tethys Ocean and then the collision of the Afro-Arabian and Eurasian plates. Zagros orogenic belt (ZOB) in Iran, formed as part of these geodynamic processes, is the most important porphyry copper and skarn belt in Iran. The ZOB is part of the central Tethyan belt, which extends about 2000 km in NW-SE direction in Iran, and consists of three parallel NW–SE-trending tectonic segments including Urumieh Dokhtar magmatic arc (UDMA), Sanandaj-Sirjan zone (SSZ) and Zagros fold and thrust belt (Fig. 1).

The Hashim Abad skarn deposit is located in the central part of the UDMA. The occurrence was mined in an open pit with an extent of about 50 m NW-SE and 400 m SW-NE.

2 Samples & methods

Our study comprised a sampling campaign with geological mapping of an open pit mine and the surrounding area at a magnetite skarn near Hashim Abad, 20 km south of Nain, Isfahan Province. In the open pit, different levels of the contact zone of the magnetite-body between magmatic rock and a marble unit were sampled along a traverse, perpendicular to the strike of the magnetite-load. The sampling of hard rocks covered the contact zones from magnetite to the different wall rocks in order to trace changes in mineralogy, characteristic mineral textures, as well as ore and rock fabrics.

Optical microscopy on thin and thick sections was carried out for mineral identification and to determine the paragenesis of the different rocks and alteration minerals. Additionally, SEM-imaging and semi-quantitative EDX-analyses were performed to detect mineral compositions more precisely and to identify
geochemical trends of distinct mineral groups (e.g. pyroxene).

For identification of typical alteration minerals (e.g. clay minerals) reflectance spectroscopy in the wavelength range 350 to 2500 nm was conducted on hand specimen, using a TerraSpec spectrometer (ASD Inc.).

3 Geological Framework

The study area is marked by a mountain range with about 2000 m elevation. Lithologically, this area is dominated by Cretaceous limestone, which is associated with dioritic intrusive rocks situated along a major fault.

The wall rock consists of a greenish meta-diorite and a light grey marble. The magmatic rocks show an alteration-zoning towards the magnetite front, indicated by different rock colours (Fig. 2) and mineral assemblages. The contact between the meta-granodiorite and the marble was influenced by tectonic processes, indicated by shear bands, slickensides, and the slight lamination of minerals. Due to field observations, the relative timing of the formation of calc-silicates and magnetite seems to be syngenetic to the emplacement of the diorite.

The lens-shaped magnetite load follows the marble-meta-diorite-contact. The strike of the contact follows the general strike of the Urumieh-Dokhtar-Magmatic-Arc, i.e. NW-SE.

Figure 2. Simplified schematic cross-section across the contact between meta-diorite and marble (not to scale).

4 Results

4.1 Mineralogical characterisation of the wall rocks

The meta-diorite mainly consists of feldspar, amphibole, chlorite, quartz, and subordinate magnetite.

The mineral paragenesis changes continuously towards the marble contact. Distal to the contact, the rocks are green coloured and show a slightly preferred orientation of the amphiboles. These rocks commonly exhibit poikiloblastic growth of amphiboles that contain small quartz inclusions. Chlorite is commonly green-coloured, indicating a high iron content and has replaced pyroxene. Feldspar is the most abundant mineral in the meta-diorite and commonly shows twinning as well as growth-zonation. EDX-measurements show that the feldspar is sodium-rich with albite composition. Fine-crystalline alkali feldspar occurs locally, filling interstices of albite feldspar-crystals. The latter show tight lamellae and were internally partly converted to sericite. Interstitial quartz shows indications of recrystallisation. Furthermore, magnetite crystals, as small as tens of µm, display minor martitisation along the crystallographically preferred cleavage. SWIR-spectra of fresh meta-diorite hand specimens are predominantly marked by absorption features of palygorskite with subordinate spectral signatures of chamosite bands.

In an intermediate zone (Fig. 2, alteration zone 1), the meta-diorite tends to be less greenish and is more of white colour. The colour change starts along joints cross-cutting the rock. Microscopic observations revealed that the colour of amphiboles changes from deep green to lighter brown and pale green, respectively. Titanite and epidote occur in small amounts. Euhedral to subhedral feldspars were slightly altered by sericisitisation within the centre of the crystals. Additionally, between individual feldspar crystals recrystallised, interstitial quartz represents late fillings. Reflectance spectra of meta-diorite of the intermediate zone contain absorption bands caused by a mixture of SWIR-active minerals comprising mainly palygorskite as well as minor smectite and calcite.

Additionally, small, dark aplite veins transect the meta-diorite of the intermediate zone and these consist of lath-shaped, green to brown coloured amphiboles, which are embedded in a feldspar-quartz groundmass and are accompanied by fine-crystalline euhedral magnetite. Feldspars are commonly lath-shaped and show slightly growth zoning. TerraSpec-analyses of the aplite veins show a mixture of actinolite and chlorite.

Meta-diorite of the proximal zone (Fig. 2, alteration zone 2) consists of feldspar, quartz, amphiboles, pyroxenes, and in some veins occur epidote in other calcite and quartz. This zone shows shear bands, which transect feldspar and epidote, whereas the quartz seems to be recrystallized. Feldspar crystals are more intensely altered by sericitisation and show a pale brown colour. In some feldspars, small muscovite flakes but also carbonates document advanced alteration in the centre of the feldspar. Recrystallised quartz is partly intimately overgrown by clinopyroxene on crystal boundaries. Reflectance spectroscopy carried out on meta-diorite hand specimens taken proximal to the magnetite ore body revealed characteristic absorption bands of palygorskite and illite/smectite. Veins cross-cutting this zone are spectrally marked by absorption features caused by vermiculite and calcite.

The marble is generally light grey coloured and appears to be tectonically folded. Some areas near magnetite lenses contain subordinate amphibole and chlorite, thus forming locally a calc-silicate marble. SWIR-analyses of marble samples show strong
absorption by calcite and subordinate spectral absorption bands from saponite. Reflectance spectroscopy on samples from the magnetite ore body showed generally a mixture of absorption features caused by chlorite, actinolite, and minor goethite. Brownish joint coatings within the magnetite contain spectral evidence for the occurrence of sepiolite, a Mg-phyllosilicate, and tilleyite, which represents a characteristic calc-silicate mineral containing additionally a carbonate complex, typical for contact metamorphic zones in the transition from igneous rocks to limestones. SWIR-analyses of samples from the greenish-yellow areas within the magnetite document chlorite-type minerals such as chamosite and sheridanite as well as some chrysotile.

### 4.2 Mineralogical characterisation of the skarn assemblage

The occurrence of the green rock units is spatially related to magnetite lenses, which are enveloped by a calc-silicate mineral association. The magnetite itself locally contains greenish calc-silicates, which mostly occur as inclusions within the magnetite bodies or at the immediate contact with the marble unit. Generally, magnetite replaced marble and the spatial boundaries are characterized by sharp contacts. Occasionally, larger spherical marble inclusions occur within magnetite lenses. Locally, magnetite contains small, sharp-edged marble clasts, which appear brecciated. Locally, magnetite also replaces marble on a smaller scale along veins within the marble.

Sulphide minerals such as chalcopyrite and pyrite are associated with the magnetite (Fig. 3). Pyrite is partly intergrown with magnetite and chalcopyrite or occurs as individual particles surrounded by carbonates. In some cases, magnetite encloses chalcopyrite completely. It can be assumed, that the sulphide ore minerals occur only on the marble-side of the magnetite lens to marble contact. Chalcopyrite locally occurs together with small amounts of covellite, which might be an indication for a supergene origin of this sulphide mineral. Other green to greenish-blue secondary copper minerals as well as red to brown secondary iron minerals are abundant along joints, supporting the interpretation of a supergene alteration zone near surface. Apatite and titanite occur also intergrown with magnetite.

The magnetite ore lenses show a tectonic overprint and magnetite but also pyrite and chalcopyrite show signs of brecciation, particularly along faults or shear bands. In these areas, the joints are filled with haematite or other secondary iron oxy-hydroxide minerals. Generally, sulphides occur only, where magnetite is closely associated with dark green minerals, which are typically calc-silicates.

The green rocks consist of calc-silicates and the most abundant minerals of these are clinopyroxenes, but also actinolite, titanite and a mixture of carbonates and chlorite. This zone is crosscut by small veinlets of calcite, calcite with quartz, or quartz only. SWIR-spectra of the green calc-silicates display spectral features of actinolite, saponite, and talc. Additionally, on joint coatings, absorption bands caused by sepiolite dominate the reflectance spectra.

![Figure 3. Sulphide minerals as chalcopyrite (yellow) and pyrite (white) are intergrown with magnetite (medium grey). Magnetite shows a slight martitisation along crystallographically preferred cleavage.](image)

### 4.3 Geochemical trends and skarn formation

The magnetite locally contains small amounts of vanadium. Some pyrites contain small amounts of arsenic, nickel, and cobalt. Analyses revealed that one sample of a hand specimen of magnetite contains an anomalous concentration of 500 ppb gold. The elemental composition of zoned epidote indicate small amounts of REE were substituted preferentially in outer growth zones.

The clinopyroxenes contain magnesium and iron, but no manganese. Some diopsidic pyroxenes show a slight zonation towards more iron-rich rims. The compositional trend is clearly notable between hedenbergite (Fe-rich clinopyroxene) and diopside (Mg-rich clinopyroxene), but a diopsidic composition is more common. The magnesium content of the measured pyroxenes increases from the magmatic side of the magnetite body to the marble side.

Based on field observations, microscopy, and pyroxene composition it can be assumed that the exoskarn portion exceeds the portion of the endoskarn in this particular system.

### 4.4 Skarn classification

In order to classify skarn deposits, Einaudi and Burt (1962) and Meinert (1992) created a diagram for clinopyroxenes based on microprobe analyses. In this study, we use EDX-data to delineate the trend of the pyroxene composition typical for the Hashim Abad skarn occurrence (Fig. 4). The data show a trend between diopside and hedenbergite, both commonly associated with Fe-, Cu- and Au-skarns. The occurrence of magnetite, intergrown with some chalcopyrite support this classification.
Figure 4. Ternary diagram of clinopyroxene compositions, showing the correlation between composition and skarn-related metal content (after Einaudi and Burt 1962 and Meinert 1992). The EDX-data of samples from Hashim Abad show a trend to magnesium-rich pyroxenes between the endmembers diopside and hedenbergite. The hedenbergitic trend of the pyroxenes can be interpreted as an indicator for a Fe-, Cu- and Au-skarn.

4.5 Hydrothermal alteration

A marked hydrothermal influence is documented by small veins and veinlets throughout the entire contact zone. These veins consist predominantly of carbonates, dominated by calcite with minor ankerite. Some veins are composed of quartz and carbonates or are composed just of quartz. The minerals within the veins are euhedral to subhedral and commonly larger than the surrounding carbonates or quartz crystals. Some vein minerals show typical growth structures from rim to centre. Some of the veins show also brittle deformation with some mm offset by micro-faults.

Saponite and sepiolite/palygorskite can be regarded as alteration minerals formed under hydrothermal conditions by replacement of primary skarn-related magnesium silicates.

Additionally, feldspars show sericitisation, which is also an effect of hydrothermal influence of the wall rock.

5 Conclusions

The formation of skarn deposits and their metal association is strongly controlled by the plate tectonic environment. In case of the Hashim Abad skarn occurrence, the tectonic setting within the subduction-related back-arc of the Urumieh-Dokhtar-Magmatic-Arc is a typical situation for copper and gold skarns.

Fault zones are areas of crustal weakness, in which magma can ascend and intrude more easily and can locally form skarn deposits in contact with limestone or marble.

The amphiboles in the meta-diorite are considered to have formed under metamorphic greenschist facies conditions. Therefore, the emplacement of the plutonic rock seems to have occurred before or during the last orogenic events in this region. Additionally, the tectonically induced faulting and associated recrystallisation of limestone to marble accompanied this event.

The ores at Hashim Abad were also affected by shear-bands and faults, indicating a later phase of tectonic activity from transitional ductile to brittle conditions. This event could have been associated with hydrothermal activity as indicated by the occurrence of cross-cutting carbonate veins, locally associated with quartz. The emplacement of veins have been related to extension caused by plutonic crustal uplift and erosion to the recent surface level.

The Hashim Abad exoskarn mainly consists of green, diopsidic pyroxene, which indicates, that magnesium completely derived from dolomitic marble and was incorporate into typical skarn minerals. As a result of the increasing magnesium content of calc-silicates towards the marble front, the reaction front replaces the dolomitic marble and consequently Mg-rich calcisilicatic minerals were formed during prograde skarn formation. In magnesium-rich skarn systems, it is more common to form forsterite than garnets. The only evidence for this could be the presence of talc as supergene alteration product of Mg-rich olivine, particularly along fractures.

The retrograde mineral assemblage of actinolite, epidote, and chlorite replaced magnetite and could have overprinted the initial zoning of the skarn system.

Endoskarn might be present in small amounts where pyroxenes have grown along crystal boundaries in the altered meta-diorite. Depending on the temperature, pH, and Eh conditions, different minerals were formed during that alteration and these are most commonly saponite and sepiolite. More distal to the magnetite body, the fluids altered the meta-diorite as well. Here, the alteration zone 1 was influenced by Mg-bearing fluids, which caused changes in amphibole chemistry and led additionally to the formation of clay minerals.

Alteration zone 2 within the meta-diorite documents a strong fluid-host rock interaction causing the alteration of the wall rock with extensive sericitisation of feldspar phenocrysts.

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References


EPMA analysis on epidote-group minerals from the LREE-bearing Fe-Polymetallic Skarn-Type Deposit Vesser/Schmiedefeld, Thuringia, Germany

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Stefan Kiefer
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Abstract. The LREE-bearing garnet-magnetite-skarn deposit Vesser/Schmiedefeld is located in southern Thuringia.

Bulk rock analyses from the ‘Schwarzer Crux’ mine show high contents of light rare earth elements (LREE), e.g. 1025 ppm La and 737 ppm Ce, hosted mainly by epidote group members. The LREE-bearing epidote group minerals from the ‘Schwarzer Crux’ mine are members of the solid solution system epidote–ferriallanite, respectively ferriallanite-(La). Some of the electron microprobe analysis (EPMA) on epidote group minerals show REE cation levels up to 1.24 atoms per formula unit (apfu) which is more than members of epidote group minerals can regularly incorporate.

However, preliminary results of study show that the LREE enrichment in epidote and the existence of ferriallanite strongly depends on the distance to contact of the granite intrusion. The increasing LREE contents in epidote and the occurrence of ferriallanite in relation to the granite contact as well as elevated F contents and MoS₂ mineralization indicate that the ore bodies in the Vesser/Schmiedefeld area belong to a Fe-polymetallic skarn-type deposit, which show a spatial and temporal relationship to a Variscan granite intrusion.

1 Introduction

The REE-bearing Fe-polymetallic skarn-type deposit Vesser/Schmiedefeld is located in southern Thuringia in the Variscan unit of the Thüringer Wald (Thuringian Forest).

The object of study is the old mining site ‘Schwarzer Crux’. It was one of the most important Fe-mines around the town Suhl. From the 19th century it belonged to the mining company ‘Vereinigte Cruxzechen’, a pit field about one square kilometer in size. The company mined magnetite and hematite as well as secondary pyrite. The mining activities finished in 1924. Today, a part of the ‘Schwarzer Crux’ mine is opened to the public as visitor mine, but the most of the underground mining work was safely closed, filled or is collapsed today.

The deposit consists of westerly fifty degree dipping and few centimeters to meters thick layers of massive magnetite, which is associated with fluorite (F in bulk ore up to 18.10 wt.%), calcite and barite at different levels (Figs. 1, 2 and 3). The magnetite ore bodies are related to a granite contact and hosted by a garnet skarn. The granite intrusion is probably related to the ‘Thuringian main granite’ with an intrusion age of 337 ±4 Ma (Zeh et al. 2000).

Figure 1. Layered magnetite (Mgt) intergrowing with garnet (Grt) and calcite-fluorite-barite (Cal-Fl-Brt) (sample: 042-a S-heading ‘Schwarzer Crux’ mine)

Figure 2. MLA-false colour image (sample: 038-g ‘Schwarzer Crux’ mine S-heading) Legend: red: magnetite (Mgt); dark-gray: quartz (Qtz); gray: calcite (Cal); blue: fluorite (Fl); pink: bario (Brt); lime green: ferriallanite (Aln); light-blue: apatite (Ap); green: chamosite (Chm); blue green: orthoclase (base of image: 6 mm)
The main mineral phases are magnetite, calcite (partially enriched in manganese up to 7.83 wt.% MnO), fluorite, barite, rough masses of grossularite-andradite, orthoclase, barite-bearing orthoclase (up to 11.56 wt.% BaO), quartz, chamosite, biotite, stilpnomelane, pyrite, hematite and a great variety of accessory minerals e.g. ferriallanite, epidote, muscovite, ilmenite, chalcopyrite, apatite, monazite, molybdenite, titanite, pyrophanite, zircon and chalcedony.

Bauer (1872) described a two centimeter allanite crystal from the 'Schwarzer Crux' mine. The locality east of the visitor mine is no longer accessible today. But in collected and in archive samples REE-enriched epidote group minerals are very common, with a size up to 3 millimeters (Fig. 2).

2 EPMA analyses on epidote group minerals

The main LREE host minerals are part of the epidote-group. To determine the epidote group and respectively the allanite subgroup by LREE content, we analyzed epidote group minerals by EPMA (Figs. 4 and 5).

For best accuracy, we set at least three measurement spots for each mineral and formed the mean. Several measurements were not suitable for stoichiometry and were selected.

For stoichiometric calculations, the cations where calculated on the basis of 8 cations for 2.97 to 3.03 Si apfu and for 3.03 to 3.05 Si apfu, on a basis of 3 Si apfu respectively (Franz & Liebscher 2004; Armbuster et al. 2006).

Table 1. Exemplary samples of EPMA analyses calculated to numbers of cations (apfu), (023b: NE-heading; 036c and 038g: S-heading; 050-III: S-transverse-heading, 'Schwarzer Crux' mine)

<table>
<thead>
<tr>
<th></th>
<th>023-b</th>
<th>023-b</th>
<th>036-c</th>
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<td>0.003</td>
<td>-</td>
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</table>

La is the main LREE. The ratio to Ce is nearly constant for all analyzed LREE hosting minerals (Fig. 6).
ThO₂ does not correlate with LREE in general. High contents of Th (given as ThO₂ up to 22.5 wt.%) and REE total (given as sum of La₂O₃, Ce₂O₃, Pr₂O₃, Nd₂O₃, Sm₂O₃ and Dy₂O₃ up to 64.9 wt.%) where detected in fractures and grain boundaries as amorphous phases, with anomalous stoichiometry. In most analyses, ThO₂ correlates with Y₂O₃.

3 Stoichiometric calculations

A general formula for epidote is Ca₂Al₂Fe³⁺Si₃O₁₂(OH). The structural formula for epidote-group minerals is A1A2M1M2M3(SiO₄)(Si₂O₇)(O,F)(OH) and simplified A₂M₂Si₂O₁₁(O,F)(OH). The A-site position contains divalent cations, e.g. Ca²⁺, Sr²⁺, Pb²⁺, Mn²⁺, Ba²⁺ but also REE³⁺ and Th⁴⁺. The A site where divided into A(1) and A(2), because of different coordination numbers. A(1) is mostly occupied by Ca²⁺, whereas A(2) site also contains REE³⁺ and Th⁴⁺ (Fig. 7). M site positions where occupied by trivalent cations M: Al³⁺, Fe³⁺, Mn³⁺, Cr³⁺, V³⁺ and as charge balance for A site by divalent Fe²⁺, Mn²⁺ and Mg²⁺, especially in M(3) site. (Wilson et al. 2013, Armbruster et al. 2006, Franz & Liebscher 2004, Gieré & Sorensen 2004, Dollase 1971).

4 Preliminary results and further work

LREE bearing epidote group minerals from the ‘Schwarzer Crux’ mine are part of the solid solution system epidote–ferriallanite, with ferriallanite-(La) as endmember (Figs. 7 and 8). In this study we found a significant relation between the LREE content of the epidote group minerals and the distance to the granite intrusion contact. Probably the LREE enrichment of epidote members are a function of the distance to the granite contact. We plan to confirm these results with additional measurements by EPMA and LA-ICPMS in the future.

Former investigations tried to explain the ore formation as a pre-Variscian VMS deposit formed by black smoker activity in a Cambrian back arc basin, which was later oxidized by a granite intrusion during the Variscan orogeny (Bankwitz and Bau 1997).

The significant dependency of the content of LREE and the Fe³⁺/Fe²⁺-ratio to the distance of the granite contact is maybe an indicator that the REE enrichment is associated with the granite intrusion. The increasing REE contents in epidote and the occurrence of ferriallanite in relation to the granite contact as well as elevated F contents and MoS₂ mineralization indicate that the ore bodies in the Vesser/Schmiedefeld area belong to a Fe-polymetallic skarn-type deposit which show indications for a spatial and temporal relationship to the Variscan granite magmatism in the area.

Our new results reinforce the assumption that the Vesser/Schmiedefeld deposit is associated with metasomatic mineralization in calcareous rock units (Schlegel 1902), i.e. as Fe-polymetallic skarn-type mineralization which is possibly related to a granite intrusion.
References


Mineralization processes of the Carboniferous Malkansu large scale manganese metallogenic belt in Western Kunlun Mountain

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Abstract. The large scale Carboniferous Malkansu manganese carbonate metallogenic belt was a recent discovery newly found in Western Kunlun Mountain. This belt is hosted by a marine sedimentary sequence of the Upper Carboniferous Kalaatehe Formation. Based on trace element and S-C isotopic features of this formation, an oxic-suboxic stratified water system is proposed for the Maerkansu basin. The 1st and the 2nd Member non-mineralized wall rocks display modern seawater-like REEs+Y profiles that are characterized by negative Ce anomalies and HREEs enrichment relative to LREEs in AUCC-normalized diagrams, suggesting an oxic surface water condition. While the absence of a Ce anomaly in non-mineralized rock samples from the 3rd Member argues for relative reducing conditions. Low values of enrichment factors for the redox-sensitive trace elements (U, V, Cr and Mo) in the non-mineralized wall rocks (particularly the 3rd Member) indicate a suboxic rather than an anoxic (precludes euxinic) bottom water conditions. Collectively, it is suggested that ore-forming conditions of the Maerkansu manganese metallogenic belt is a relatively open rather than a strictly restricted basin system.

1 Introduction

The large scale Carboniferous Malkansu manganese carbonate metallogenic belt was recently found in the Western Kunlun Mountain of Xinjiang Province (Fig. 1a). The manganese-mineralized beds are stratigraphically continuous, with 60 km in length and high grade (average Mn contents is 35%). It is expected to be a new manganese resource base in China, with defined manganese-carbonate-rich ore reserves (shallower than 300m) up to 45 million tons by the end of 2017 (Gao et al. 2016). Since little work has been done with the manganese belt and its associated rocks, limited information is available for manganese mineralization mechanisms as well as its depositional environment. In this paper, we present petrologic and geochemical results of both manganese ore and the associated rocks, in order to study the depositional environment of the Carboniferous Maerkansu large scale manganese metallogenic belt in West Kunlun Mountain.

2 Geology of manganese metallogenic belt

2.1 Geological setting

As one of the major tectonic units forming the northern boundary of the western Tibetan Plateau, West Kunlun Orogenic Belt (WKOB) underwent long-term crustal assemblage and accretion between early Paleozoic and Mesozoic in response to the evolution of the Proto- to Palaeo-Tethys ocean (Robinson et al. 2016; Zhang et al. 2018), and overprinted by Cenozoic tectonism as well as volcanism accompanying India-Asia convergence (Zhang et al. 2008; Jiang et al. 2013). Tectonically, the Malkansu manganese metallogenic belt is situated at the junction of the western margin of the Tarim block and the western section of the WKOB, belonging to the north Kunlun terrane (Fig. 1a and 1b) (Gao et al. 2016; Zhang et al. 2018). Recent studies suggested that these shallow marine carbonate and clastic rocks are possibly representative of a late Paleozoic to early Mesozoic back-arc basin sequence, which formed in response to the northward subduction of the Paleo-Tethys Ocean in western Kunlun (Zhang et al. 2018).

Figure 1. (a) Tectonic sketch map of China, also showing the spatial and temporal distribution of major sedimentary manganese ore deposits. (b) Simplified tectonic units of the West Kunlun Orogenic Belt (modified after Robinson et al. 2004; Zhang et al. 2018). (c) Simplified geological map of the giant Malkansu manganese belt, northwestern portion of the West Kunlun Orogenic Belt (modified after No.2 Geological Bureau, Xinjiang BGMR, 2018).
In addition, geochemistry studies on the Carboniferous volcanic rocks revealed that they display typical characteristics of E-BABB, indicating that the north Kunlun terrane was in a back-arc extensional environment during the early Carboniferous (Yun et al. 2015). Thus, the Carboniferous-Permian sequence in the Malkansu area represents sedimentary occurrences of an extensional back-arc basin.

2.2 Geology of manganese deposits

The Malkansu manganese metallogenic belt is distributed in an approximately west-east orientation, extending more than 60 km (west to east) in length but less than 2 km (north to south) in width (Fig. 1c). Exposed strata include Carboniferous manganese-bearing sedimentary rocks of the Kalaatehe Formation, Permian volcano-sedimentary rocks of the Maerkanque Formation and Cretaceous terrigenous sedimentary rocks of the Kukebai Formation (Fig. 1c). The Kalaatehe Formation is subdivided, from bottom to top, into three members (Fig. 2), with the 1st Member (C2k1) consisting of sedimentary breccia, the 2nd Member (C2k2) of calcarenite, and the 3rd Member (C2k3) of organic-rich calcareous mudstone with one or two manganese-mineralized intervals (Gao et al. 2016; Zhang et al. 2018).

Overall, the rock assemblages of the Upper Carboniferous Kalaatehe Formation, from the sedimentary breccia and calcarenite at the bottom to the calcareous mudstone (including manganese ore belt) at the top, and then grade into the calcarenite and micrite at the uppermost, consist a complete transgression-regression cycle. The manganese-mineralized intervals occur in organic-rich calcareous mudstone, together with the black shale nearby the ore zone, suggesting that the occurrence of manganese mineralization occurred during the highstand systems tract.

Figure 2. Stratigraphic column of the Kalaatehe Formation.

The presence of dark gray to black well-developed horizontal bedding, organic carbon-rich, and pyritiferous calcareous mudstone indicates that it was deposited in a relatively stable, possibly with minimal hydrodynamic energy environment (Zhang et al. 2018).

Generally, two to three manganese-rich layers occurred in the mining area. The principal ore body, more than 5 km in length, occurs stably and continuously with no branch. However, the thickness varies greatly, ranging from less than 1m to more than 10 m, with an average manganese grade of more than 35% (Gao et al. 2016).

More than ten different minerals are present in the manganese-rich ore and associated host rocks, which can be divided into silicate, carbonate, oxide, sulfide, and graphite and/or organic materials (Fig. 3). Organic materials, or sometime in the form of graphite, were mostly observed in the calcareous mudstone and the manganese-rich rocks. Besides, minor borates (mainly sussexite), in some cases, are also present in the manganese ore zone based on XRD analysis (Zhang et al. 2018).

Figure 3. Photomicrographs showing typical textures of manganese carbonate ore. (a) Thin sections of massive manganese carbonate ore, displaying laminated structure. (b) Isolated fragments of micrite showing characteristic of “dropstones” within finer-grained sedimentary rocks (plane-polarized light). (c) Crenulated to wavy laminations in manganese carbonate ore, noting minor manganese calcite veins also occurred (plane-polarized light). (d) Manganese carbonate (rhodochrosite) is the predominant mineral in the manganese ore, while Mn-rich silicate (frieldite) and Mn-rich aluminosilicate (chlorite) are also common (backscattered electron image). (e) At least two generations of
rhodochrosite occur in the manganese ore with the early one containing minor calcium and magnesium, while the later one incorporating iron (backscattered electron image). (f) Rhombohedral (top) and stromatolitic (bottom) rhodochrosite generally occurred in some cases (backscattered electron image). (g) Minor Mn-Fe oxides (left) are deduced to be the primary precipitates that enter the sediments, while most fibrous manganese oxides (right) are thought to be the results of manganese carbonate surface weathering (backscattered electron image). (h) Alabandite coexisting with rhodochrosite (left) or “floating” on the manganese carbonate (right) is the only sulfide in the manganese ore (backscattered electron image).

3 Geochemistry of the Mn metallogenic belt

The 1st and the 2nd members non-mineralized wall rocks display modern seawater-like REEs+Y profiles that are characterized by negative Ce anomalies and HREEs enrichment relative to LREEs in AUCC-normalized diagrams, suggesting an oxic surface water condition. While slight Ce/Ce⁺ (close to 1) in the non-mineralized rock samples from the 3rd Member argues for a relative reducing conditions (Zhang et al., 2018).

Despite the variability in the absolute concentration of these redox sensitive elements, however, their enrichment factors show little change through the whole studied profile (Fig.4), which means that there is no obvious enrichment on these elements. For example, the U and the enrichment factor of U (UEF) are constant in all non-ore rocks from the 1st to 3rd Member of the Kalaatehe Formation (0.54-4.01 ppm and 0.26-5.18, respectively). Same regularities were also occurred on the V and VEF (48-243 ppm and 1.19-4.15, respectively), Cr and CrEF (31-484 ppm and 0.82-9.48, respectively) in wall rock samples of all three Members. The low values of enrichment factors of the redox sensitive elements that are observed in the non-mineralized rocks indicate that the enrichment mechanism for these elements mentioned above were not achieved under the depositional conditions of the Kalaatehe Formation, which further argues for a suboxic (unlikely anoxic and cannot be euxinic) conditions during the sedimentation. Intriguingly, it seems that the Mo and the enrichment factor of Mo (MoEF) values increase upward through the studied profile (except for several higher values in the 2nd Member, 0.08-4.30 ppm and 0.08-3.97, respectively) with peak values in the calcareous shale of the 3rd Member (4.42-23.22 ppm and 6.58-21.09, respectively) (Fig. 4), suggesting that the depositional conditions of the first two members and the 3rd Member are somewhat different. Nevertheless, a good relationship between the contents of Mo and the TOC (R²=0.62) suggests that this Mo enrichment is mainly resulting from the absorption of organic materials.

Additionally, large fractionation of sulfur isotope (δ34S values from -16.18 to -1.40‰, with an average of -8.36‰) indicates a relative high sulfate concentration in the water column, and the rate of sulfate replenishment exceeded that of sulfate reduction. The 13C-depleted stable carbon isotopes in manganese carbonate ores further confirmed that Mn-carbonates are precipitated from the reduction of Mn(IV) oxides precursor by organic matter in the sediments during the diagenesis rather than directly precipitate in the anoxic water column (Zhang et al. 2018).

Based on trace elements, Mo concentration and total organic carbon (TOC) content (ranges from 0.08 to 1.83 wt % with an average of 0.65 wt %), suggests in somewhat a relative open rather than a strictly restricted basin system.

4 Discussion

4.1 Depositional environment

Petrographic and geochemical studies on the manganese ore reveals that the first precipitates to concentrate manganese in the sediments were Mn(IV) dominated oxides, and the Mn(II)-bearing carbonates in the Malkansu area have undergone Mn(IV) oxide precursor reduction processes. The consistently large positive Ce anomalies, negative Y anomalies, low Y/Ho ratios, and no obvious fractionation between LREEs and HREEs of the manganese carbonate ores, are features typical of modern marine hydrogenic ferro-manganese oxide precipitates. The 13C-depleted stable carbon isotopes in manganese carbonate ores further confirmed that Mn-carbonates are precipitated from the reduction of precursor Mn(IV) oxides by organic matter in the sediments during diagenesis rather than form as a chemical sediment directly in an anoxic water column.

4.2 Mineralization model of Mn carbonates

Thus, according to the proposed redox-stratified water column (with oxic surface water and suboxic bottom water) for the Malkansu basin, a pool of abundant dissolved manganese (Mn2+) can be envisaged for the
deep suboxic water. During the transgression, upwelling allowed the dissolved manganese to be precipitated in the form of manganese (hydroxide) oxides at or near the oxic-suboxic chemocline where it intersects with the basin substrate. Moreover, this process may also lead to a relative high surface water primary productivity, which ascribes to the nutrients contained in the deep water column been carried to the surface water mass resulting in the thriving of organisms. Manganese (hydroxide) oxide precipitates together with the net productivity (excess organic matter) were rapidly buried due to the continuous transgression. In the sediments, dissimilatory reduction of manganese (hydroxide) oxides in combination with the oxidation of organic matter, resulting in extremely high dissolved manganese (Mn²⁺) concentration and creating relative high alkalinity condition in pore-waters, which is suitable for the precipitation of manganese carbonates (Fig. 5). The ultimate source of the manganese is uncertain but may have been fluvial-sediment loads of hydrothermal activity associated with the extensional back-arc basin system.

Figure 5. Mineralization model of Malkansu manganese carbonate metallogenic belt.

5 Summary

1) Based on petrographic and lithologic studies, it is suggested that the Upper Carboniferous Kalaratehe Formation represents sedimentary sequences of an extensional back-arc basin associating with the evolution of the Paleo-Tethys Ocean.

2) These rock assemblages, from the sedimentary breccia and calcarenite at the bottom to the calcareous mudstone (including manganese ore zone) at the top, and then the calcarenite and micrite at the uppermost, consist a complete transgression-regression cycle, while the manganese precipitation occurred during the highstand systems tract.

3) Low values of enrichment factors for the redox-sensitive trace elements (U, V, Cr and Mo) in the non-mineralized wall rocks indicate a suboxic rather than an anoxic environment.

4) Based on trace elements, S-C isotopes and TOC content, it is suggested that ore-forming condition of the Carboniferous Maerkansu large scale manganese metallogenic belt is a relative open rather than a strictly restricted basin system.

Acknowledgements

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References


Textural evolution of the Lovisa Zn-Pb-(Ag) deposit, Bergslagen, Sweden: insights from microscopy and 3D X-ray tomography

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Abstract. The presently mined Lovisa deposit constitutes a c. 1.9 Ga, stratiform Zn-Pb-(Ag) sulphide mineralisation hosted by rhyolite-dominated metavolcanic rocks in the Bergslagen ore province, south central Sweden. The mineralised rock sequence at Lovisa has been subjected to polyphase ductile deformation, amphibolite facies regional metamorphism, and late-stage brittle deformation. The combined effects of these processes have produced a diversity of post-genetic ore textures within the sulphide horizons, including metablastic growth, piercements, ductile and brittle sulphide deformation, and durchbewegung and 'ball ore' textures. Here we report on the character and textural evolution of the Lovisa deposit in conjunction with regional metamorphism and deformation, utilising new data from ore- and electron microscopy combined with 3D tomography by means of novel XRT-XRF drill core scanning technique.

1 Introduction

Over the past half-century, there has been an increasing understanding that sulphide ores hosted in orogenic belts exhibit post-genetic textures attributable to mechanical and chemical processes during later metamorphism and deformation (e.g. Ramdohr 1955; Vokes 1969; Marshall and Gilligan 1993; Cook et al. 1993). Such textures have been described from several deposits in the Palaeoproterozoic Bergslagen ore province in south central Sweden (Andersson et al. 2016, and references therein; Fig. 1). A notable example is the case of rotated, rounded silicate clasts occurring within matrices of extensively deformed sulphides; the so-called 'ball ores' (Geijer 1971; Vokes 1973). One of the sulphide deposits in Bergslagen observed to have been significantly affected by metamorphism and deformation is the Lovisa Zn-Pb-(Ag) deposit (Fig. 1). The currently exploited mineralisation at Lovisa comprises stratiform sulphides that occur interbedded with fine-grained, originally rhyolitic rocks, all of which have been overprinted by polyphase ductile deformation, amphibolite facies regional metamorphism, and later stages of brittle deformation. Here we report results from the on-going, EU-funded X-Mine project, on the textural evolution of the Lovisa deposit. This specifically includes the use of 3D tomography by means of novel XRT-XRF drill core scanning technology to provide new insights in such studies, yet also providing input for further method development.

Figure 1. Bedrock geology map of the Bergslagen ore province, showing the location of Lovisagruvan (the Lovisa mine) and other active mines and known mineral occurrences (modified from Stephens et al. 2009). Inset shows location of map in Sweden.
2 Bergslagen and the Lovisa deposit

The extensively mined Bergslagen ore province is situated within the Swedish part of the Fennoscandian Shield and contains a highly diverse array of ore types, of which base metal and iron oxide mineralisation predominate (Fig. 1; e.g. Tegengren 1924; Geijer and Magnusson 1944; Stephens et al. 2009). The main ore-bearing rock sequence in Bergslagen comprises mainly dacitic to rhyolitic, pyroclastic-dominated metavolcanic rocks with local marble interlayers that were originally deposited within an evolving, continental back-arc basin (Allen et al. 1996). This c. 1.90-1.87 Ga metasupracrustal succession occurs as inliers in intrusive rocks that are penecontemporaneous or younger than the metavolcanic rocks. During the Svecokarelian orogeny, these rocks and their mineralisation were subjected to polyphase ductile deformation and amphibolite-facies regional metamorphism featuring peak conditions between c. 1.87 and 1.80 Ga (e.g. Stephens et al. 2009).

The Lovisa Zn-Pb-(Ag) deposit is located in the northern part of the Guldsmedshyttan syncline in western Bergslagen (Fig. 1). The exploited Zn-Pb mineralisation, as well as a stratigraphically lower, Pb-Ag sulphide-bearing iron formation (Lovisa Iron Formation), are mainly hosted by rhyolithic metavolcaniclastic rocks (Lundström 1983; Carlzon and Bleeker 1988). These stratiform sulphide ores have been interpreted to originally have formed syn-genetically in a vent-distal, seafloor exhalative setting in which the Zn-Pb mineralisation was confined to a c. 5-10 m thick stratigraphic interval and concentrated in two distinct ore horizons. The stratigraphically lower ‘Sphalerite Ore’ (Jansson et al. 2018) comprises fine (generally c. 10-50 mm thick) layers of sphalerite-dominated sulphides that occur interbedded with rhyolitic ash-siltstone and minor chloritic schist. In contrast, the stratigraphically upper ‘Main Ore’ of Jansson et al. (2018) consists of a tabular body of massive sphalerite-galena, locally up to c. 1 m thick, with minor sulphides also being present in a laminated facies that occurs peripheral to the massive ore.

3 Textural evolution of the Lovisa sulphide mineralisation

The different textures resulting from the metamorphism and deformation of sulphide mineralisation at the Lovisa deposit were investigated using a combination of drill core study, reflected polarised light- and electron microscopy, as well as energy-dispersive X-ray spectrometry (EDS) and wavelength-dispersive X-ray spectrometry (WDS) with a Zeiss Supra 36VP SEM and a JEOL JXA-8530F electron microprobe (Department of Earth Sciences, Uppsala University), respectively, and 3D X-ray drill core scanning in a GeoCore X10 device (Orexplore AB, Kista, Sweden). The GeoCore X10 uses a novel technique; X-ray tomography (XRT) and X-ray fluorescence (XRF) combined measurement together with automatic weight measurement to scan drill cores up to a diameter of 50.6 mm. It produces a 3D tomographical visualisation of the distribution of contrasting minerals in the core with a resolution of down to 200 µm, along with density data as well as concentration data for most major and trace elements (Orexplore, 2019). We here primarily focus on ore textures developed within the two Zn-Pb-rich sulphide horizons (Sphalerite Ore and Main Ore, respectively) and within the Lovisa Iron Formation.

3.1 Primary ore textures

The oldest generation of sulphides at Lovisa is best preserved within the Sphalerite Ore in what is presumed to be relict, essentially syn-genetic sedimentary layering (Figs. 2A-B, 2E-F). The sulphide-enriched layers are dominated by fine-grained, anhedral sphalerite with minor intergrown pyrite and galena. This sphalerite generally carries minute inclusions of chalcopyrite (‘chalcopyrite disease’). Such finely-layered sphalerite mineralisation, which is generally difficult to distinguish from the surrounding silicate-rich rock during drill core inspection, can be visualised in great detail using the XRT-XRF scanning data (Figs. 2B, 2F).

3.2 Ore textures related to metablastic growth

Porphyroblastic pyrite is widespread throughout the stratigraphic sequence and has overgrown the primary sulphide assemblages (Fig. 3A). The crystals comprise an early generation of generally anhedral pyrite that contains abundant inclusions of sulphides (sphalerite and galena, locally chalcopyrite and pyrrhotite) and silicates, resulting in a poikilitic texture. Many pyrite porphyroblasts also exhibit a later generation of subhedral to euhedral, inclusion-poor pyrite that form rims around the earlier poikilitic pyrite (Fig. 3A).

Magnetite in the Lovisa Iron Formation generally occurs in aggregates of anhedral crystals. These typically exhibit a poikilitic texture with inclusions of sulphides, suggesting early magnetite blastesis.

3.3 Ore textures related to ductile deformation

Ductile deformation textures visible in the Sphalerite Ore include folding of the primary layering. Metarhyolite interbeds are commonly boudinaged and define Z-symmetric folds (Fig. 2A; Jansson et al. 2018), and related fabrics within the sulphide beds are evident in the XRT-XRF images (Fig. 2B). Locally, sulphide-rich piercement veins protrude from fold hinges (Fig. 2A). The XRT-XRF scanning data show that galena was preferentially remobilised into such veins, while sphalerite has largely remained in the pre-existing layers (Fig. 2B).

The more massive character of sulphides in the Main Ore compared to that in the Sphalerite Ore, and the higher galena:sphalerite ratio, led to partitioning of strain and development of more extreme forms of ductile deformation features (Jansson et al. 2018), such as the distinctive ‘ball ore’ texture of the Main Ore.
Advances in Understanding Hydrothermal Processes

In the ball ore, fragments of silicate-rich rock as well as milky vein quartz and pyrite blasts or clasts occur in a matrix of fine-grained, deformed sulphides dominated by sphalerite and galena. The silicate-rich fragments vary from decimeter-scale, ‘detached cores’ of folded host rock, to significantly smaller and increasingly rounded clasts (Figs. 2C, 3B). These features reflect the progressive breakup, rotation and ‘kneading’ of the fragments within the sulphide matrix during deformation (e.g. Vokes 1969, 1973). Rotational fabrics are defined by fine-grained silicates occurring in the sulphide matrix around silicate clasts (Fig. 3B), and locally as curved inclusion trails within porphyroblastic silicates and pyrite.

In the sulphide matrix of the ‘ball ore’, galena mainly occurs in zones of reduced strain, such as within the hinges of detached folds (as revealed by the XRT-XRF image in Figure 2D) or in strain shadows to silicate clasts and pyrite porphyroblasts (Figs. 3A-B), as well as in later veinlets and fractures.

Networks of sulphide veins and fracture fills crosscut the laminated facies peripheral to the Main Ore. The veins are generally dominated by galena over sphalerite and pyrite, and they locally exhibit a minute ‘ball ore’ texture similar to that observed in the Main Ore. The origin and timing of these veins remains ambiguous. Jansson et al. (2018) argued that they may have formed as piercement veins during shearing of the Main Ore, or by later sulphide remobilisation at the transition to more brittle conditions.
3.4 Ore textures related to brittle deformation

Later cataclastic features are superimposed on the early metablastic aggregates at Lovisa. In the case of pyrite porphyroblasts, brittle cataclastic deformation was accompanied by remobilisation of the more ductile galena and sphalerite into microfractures and corroded margins (Fig. 3A), as well as by remobilisation of sulphide inclusions within the pyrite.

Massive sphalerite locally displays some cataclastic fracturing with infilling of galena. This is consistent with galena entering the brittle field after sphalerite during cooling. Late-stage fractures infilled with calcite and local sphalerite are prevalent at the Lovisa deposit (Figs. 2E, 3D). The calcite in such veins exhibits extensive, deformation-related twinning. The XRT-XRF scanning data indicate a close spatial relationship between the late-stage, fracture-filling sphalerite and early, layered sphalerite (Fig. 2F), suggesting that remobilisation of sphalerite also occurred during brittle deformation.

In the Lovisa Iron Formation, abundant galena-dominated veins crosscut the silicate groundmass as well as brittle-deformed magnetite aggregates. The sulphide assemblage locally also contains chalcopyrite, sphalerite, pyrrhotite and rare tetrahedrite, with the chalcopyrite typically having replaced galena. These galena-rich veins exhibit complex intergrowths with metamorphic micas (Fig. 3C), suggesting co-crystallisation during the retrograde stages of regional metamorphism (e.g. Cook et al. 1993). The galena-rich veins are in turn crossed by later fractures hosting a more complex sulphide-sulphosalt assemblage carrying minerals that are otherwise sparsely occurring or previously unknown in the Lovisa deposit, including chalcopyrite, galena, freibergite, tetrahedrite, pyrite, arsenopyrite, pyrargyrite, and several unidentified Ag-rich phases. These late-stage sulphide-sulphosalt fracture fillings in the Lovisa Iron Formation are in part comparable to remobilised, Pb-Ag-Sb-rich assemblages documented from other metamorphosed sulphide deposits in Bergslagen (e.g. Wagner et al. 2005) and in similar terranes elsewhere (Vokes 1969).

4 Conclusions

The Lovisa Zn-Pb-(Ag) sulphide mineralisation has recorded a diversity of post-genetic ore textures that can be attributed to polyphase ducitile deformation, amphibolite facies regional metamorphism, and late-stage brittle deformation, all affecting the original ore deposit and its host rocks. Key examples include multi-stage metablastic growth of pyrite; folding of interlayered sulphide and silicate beds and remobilisation of sulphides into piercement veins; rotation and kinking of silicate-rich fragments in a matrix of extensively deformed, in part duchbewegung-textured sphalerite and galena (‘ball ores’); intergrowths of sulphide veins and metamorphic micas; and brittle fracturing with local remobilisation of sulphides. Variations in primary depositional character between the sulphide-bearing horizons, and differences in the proportions of individual, variably competent sulphide minerals (mainly galena to sphalerite ratios) significantly influenced the ore textures that developed during subsequent metamorphism and deformation.

The use of XRT-XRF drill core scanning technology has proven to be a powerful tool in the on-going study of the Lovisa deposit. It allows for detailed 3D tomographic visualisation and chemical characterisation of a wide range of meso- to micro-scale textures related to metamorphism and deformation in both ores and host rocks, as well as – particularly when combined with traditional methods such as ore- and electron microscopy – new insights into the behaviour of specific sulphide minerals during such processes.

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References


LA-ICP-MS trace element study of sphalerites from the MVT Cracow-Silesia district, Poland

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Abstract. The Cracow-Silesia Zn-Pb district in Poland hosts classic examples of carbonate-hosted MVT deposits. Limited information about the distribution of trace elements in sphalerite has been available for this locality. Results of this LA-ICP-MS study show that trace element concentrations are quite typical for carbonate-hosted MVT deposits. Indium and gallium content is often below the detection limit while the median content of germanium in the dataset is 67 µg/g but varies significantly between samples. In schalenblende samples, a clear difference in Ge and Ga contents between dark and light-colored sphalerite bands has been noticed. This study also demonstrated very high contents of thallium in some samples, up to 3063 µg/g which are some of the highest Ti contents reported for sphalerite. The trace element measurements were used to apply the GGIMFis geothermometer and results are significantly higher than temperatures obtained for fluid inclusion studies of sphalerites from this district.

1 Introduction

Sphalerite in Zn-Pb deposits often contain trace elements at levels that are potentially economic or could pose an environmental threat. Progress in laser ablation inductively-coupled mass spectrometry (LA-ICP-MS) has led to a growing number of studies undertaken to assess differences in the trace element content of sphalerite from different types of Zn-Pb deposits (e.g. Cook et al. 2009; Ye et al. 2011; Mederski et al. 2017). Of special importance is the recent development of the matrix-matched sphalerite reference material MUL-ZnS 1 (Onuk et al. 2017) which improves accuracy and precision of the analyses.

The trace element contents of ore minerals in the Cracow-Silesia Mississippi Valley-type (MVT) district show large variations between different paragenetic stages and vary from mine to mine or even within parts of the same deposit. Compared to other MVT deposits worldwide, the Cracow-Silesian ores contain sphalerites with one of the largest ranges in Ag, Fe and Cd content and early studies identified substantial variations in trace element concentrations in banded sphalerite (Viets et al. 1996, Kucha et al. 2001). To our best knowledge, after early semi-quantitative attempts in the 1990s (Leach and Viets 1992, Mayer and Sass-Gustkiewicz 1998) only limited LA-ICP-MS data for this locality, measured for a single sample, has been available (Ridley et al. 2015). Therefore, the aim of this investigation is to provide trace element data in the main textural types of sphalerites from this classic MVT district. An additional goal is to apply and test the GGIMFis geothermometer proposed by Frenzel et al. (2016), on compositionally zoned banded sphalerites.

2 Geological setting and samples

The Cracow-Silesia ore deposits, located in southern Poland (Fig. 1) are commonly considered a classic example of MVT deposits. Zn-Pb mineralization occurs in the Mesozoic sedimentary cover of the Paleozoic basement of the Central European Platform and is mainly hosted by the epigenetic ore-bearing dolomite of the Muschelkalk Group (Middle Triassic) (Leach et al. 2003). The average content of metals in sulfide ores usually ranges from 2 to 4% Zn and 1 to 2% Pb. The initial total ore resources are estimated to be ca. 700 Mt of Zn+Pb ores at 4 to 6% and are considered one of the richest known MVT Zn-Pb deposits in the world (Leach et al. 2003). After 800 years of continuous mining, current demonstrated resources of zinc and lead ores in Poland are 84.4 Mt of sulfide ores containing 3.63 Mt of Zn and 1.43 Mt of Pb.

The mineralogy is simple: sphalerite, galena, marcasite and pyrite with rarely occurring Fe-Pb and Fe-Pb-As sulphosalts (Mayer and Sass-Gustkiewicz 1998). Gangue minerals include dolomite, barite, calcite and ankerite. Five clusters of mainly stratatobound or nest-like karst breccia ore-bodies are present in the region: Olkusz, Chrzanów, Bytom, Zawiercie and Tarnowskie Góry (Fig. 1) with exploitation currently carried out only in the Pomorzany mine. Undeveloped ore deposits are located in the areas of Klucz, Laski and Zawiercie.

Sphalerite samples from the Pomorzany mine, Trzebionka mine and Orzel Bialy mine, representing different textural types, were analysed (Fig. 2). Samples from Pomorzany and Trzebionka are characterized by sulfides replacing host carbonates and commonly mimicking the original host rock fabric. Additionally, they contain colloform and banded ores, consisting of an alternation of colored bands or spherulitic aggregates of colloform sphalerite. Orzel Bialy samples are composed of banded sphalerite. Sporadically, sphalerite, galena, and iron sulfides are found in a variety of speleothems (stalactites and stalagmites). Commonly, these features are composed of iron sulfides but in some cases, the dripstone-like forms also contain sphalerite and occasionally galena (sample Röt from the Pomorzany mine).
4 Results

4.1 Trace elements

Table 1 presents results of LA-ICP-MS analyses for selected elements. The Fe content can be as low as 90 µg/g and as high as 5.6%. Cadmium is usually present at levels of several hundred to several thousand µg/g but some exceptional spots gave values up to 1.2%. Arsenic content varies between a few µg/g and 1.9% while the Pb concentration is between tens of µg/g up to 2.2%. Very high contents of Tl were measured, especially in samples from the Orzel Bialy mine. Some spots yielded as much as 3063 µg/g Tl, ranking among the highest reported in the literature so far. It is important to stress that all elements mentioned earlier seem to be present in the sphalerite structure and do not form micro inclusions of other minerals (Fig. 3).

Strong correlations (R² = 0.8-0.9) between As and Tl as well as As and Pb were found. Xiong (2007) proposed the substitution of Tl in a low-temperature environment (up to 150°C) in terms of Tl+0.5As3+0.5S solid solution; this might explain the observed Tl-As correlation.

Indium, as expected from MVT deposits is very low, usually below detection limit. Gallium content is often below the detection limit and in general does not exceed 12.3 µg/g. The median content of germanium in the whole dataset is 7 µg/g but varies significantly between samples. Measurements of sphalerite from the Trzebionka and the Pomorzany mine has given tens of µg/g of Ge, while in the case of the Orzel Bialy - hundreds of µg/g, up to 384 µg/g. These values are typical for MVT deposits (Frenzel et al. 2016). Belissont et al. (2016) described the coupled substitution 3Zn2+ ↔ Ge4+ + 2 monovalent cations as the main mechanism of Ge incorporation. This explains correlations observed in some samples between Ge-Mn and Ge-Fe. In some cases, germanium shows also a strong correlation (R² > 0.8) with As, Tl, Pb, but this phenomenon is not universal for the whole dataset.
Table 1. The results of LA-ICP-MS measurements in µg/g.

|       | Mn  | Fe  | Ga  | Ge  | As  | Ag  | Cd  | In  | Hg  | Tl  | Pb  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| **Orzel Bialy** |     |     |     |     |     |     |     |     |     |     |     |     |
| MEDIAN (38) | 29  | 6 172 | 0.6 | 66  | 4 209 | 0.2 | 1 672 | -  | 1   | 552 | 8 654 |
| MIN   | 13  | 2 212 | <0.1 | 14  | 710  | <0.1 | 415  | <0.1 | 0.6 | 62  | 3 348 |
| MAX   | 65  | 56 619 | 1.1 | 382 | 19 294 | 329 | 12 739 | <0.1 | 1.9 | 3063 | 22 747 |
| **Trzebieńka** |     |     |     |     |     |     |     |     |     |     |     |     |
| MEDIAN (12) | 9.1 | 4 987 | -  | 14  | 879  | -  | 763  | -  | 1   | 77  | 1 740 |
| MIN   | 5.4 | 2 558 | <0.1 | 7.1 | 457  | <0.1 | 332  | <0.1 | 0.8 | 39  | 917  |
| MAX   | 282 | 12 321 | 12  | 24  | 2 006 | 41  | 2 234 | <0.1 | 2.3 | 136 | 3 452 |
| **Pomorzany** |     |     |     |     |     |     |     |     |     |     |     |     |
| MEDIAN (13) | 6.9 | 1 107 | 0.2 | 92  | 261  | 0.8 | 1 637 | -  | 2   | 19  | 1 110 |
| MIN   | <0.1 | 91   | <0.1 | 1.2 | <0.1 | <0.1 | 349  | <0.1 | 1   | 0.2 | 20   |
| MAX   | 141 | 39 491 | 2.5 | 384 | 5 405 | 64  | 6 600 | 0.1 | 5.7 | 485 | 7 447 |

Figure 3. Depth profiles indicating that Pb and Tl are present in the sphalerite and not as a minute inclusions.

In schalenblende samples, a clear difference in Ge and Ga contents between dark and light-colored sphalerite bands have been noticed (Fig. 4). With the exception of the speleothem sample, all light bands have low (max. 12.3 µg/g) but measurable Ga contents, while Ge concentrations remain below 100 µg/g. On the other hand, the dark bands tend to have higher Ge content and usually undetectable Ga concentrations.

4.2 GGIMFis geothermometer

The trace element measurements were used in an attempt to test the GGIMFis geothermometer proposed by Frenzel et al. (2016). Obtained results (Tab. 2) are significantly higher than temperatures collected by fluid inclusion studies of sphalerites from this district (80 to 158°C, Kozłowski 1995) but they are within a 50–70 °C range in which mean (homogenization) temperature can be predicted by GGIMFis geothermometer (Frenzel et al. 2016). However, it is important to stress that homogenization temperatures should be considered minimum fluid temperatures and previous authors noted the extreme difficulty in investigating fluid inclusions due to their small size and strong internal reflections of the host mineral. Despite these difficulties, it would be
advisable to perform new fluid inclusions studies coupled with trace element determination by LA-ICP-MS in sphalerites, in order to calibrate the GGIMFis and homogenization temperatures in this ore district.

A characteristic feature is a significant change in GGIMFis temperature during the transition from the light to dark bands and vice versa (Tab. 2). It is not surprising given that the band color is mainly connected to the incorporation of different elements and it is believed that often, but not always, darker color is caused by Fe (e.g. Barton and Bethke 1987) which is utilized in the GGIMFis. Minor elements, the presence of organic matter and nano-inclusions of other minerals may also influence sphalerite color. Contents of two other elements of the geothermometer, Ge and Ga, also influence sphalerite color. Contents of two other elements of the geothermometer, Ge and Ga, also

Table 2. Calculated GGIMFis temperatures.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>GGIMFis temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orzel Bialy 2 (n=16)</td>
<td>179-217°C</td>
</tr>
<tr>
<td>Trzebionka dark band (n=9)</td>
<td>195-240°C</td>
</tr>
<tr>
<td>Trzebionka light band (n=3)</td>
<td>100-142°C</td>
</tr>
<tr>
<td>Pomorzany (n=12)</td>
<td>113-182°C</td>
</tr>
<tr>
<td>Röt (n=28)</td>
<td>34-246°C</td>
</tr>
<tr>
<td>Orzel Bialy 1 light bands (n=18)</td>
<td>146-170°C</td>
</tr>
<tr>
<td>Orzel Bialy 1 dark bands (n=6)</td>
<td>191-218°C</td>
</tr>
</tbody>
</table>

5 Conclusions

Trace element contents in sphalerites from the Cracow-Silesia district measured by LA-ICP-MS are quite typical for carbonate-hosted MVT deposits. The most interesting result of this study is the extremely high content of thallium in samples from the Orzel Bialy mine. Enrichment in Tl in this ore district has long been known and is illustrated by the presence of rare Pb-As sulphasalts such as gratonite and jordanite that have been found to be enriched in Tl (Paulo et al. 2002). Mayer and Sass-Gustkiewicz (1998) reported that marcassite from the Pomorzany mine may contain up to 1000 µg/g Tl and in Olkusz up to 2300 µg/g. The available literature for Tl content in sphalerites from this district usually lists values up to 100 µg/g but several papers reported higher values (e.g. sphalerites from the Klucze deposit up to 500 µg/g, Górecka 1996).

This study demonstrates values up to 3063 µg/g which are among the highest Tl contents in sphalerite reported in the literature. These results indicate a need for a closer investigation of the effects of sphalerite on thallium environmental hazards in the Cracow-Silesia mining district.

References


Advances in Understanding Hydrothermal Processes

Magmatic hydrothermal overprinting in the super large Dajiangping S(Pb-Zn) SEDEX deposit, Guangdong Province

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Abstract. The Dajiangping deposit is the largest SEDEX pyrite deposit in South China Block. The pyritic sulphides occur in the Sinian metamorphic rocks as laminated sulphides and massive lenses. Recently, new veins and layered lead-zinc orebodies underlying the pyritic orebodies have been discovered. Sphalerite in Pb-Zn orebodies provided an Rb-Sr isochron age of 88.5±3.9Ma, indicating that it is not contemporaneous with pyrite sulphide bodies. The petrographic and microthermometric analysis of fluid inclusions from the two types of mineralization implies that they have different fluid homogenization temperatures and salinities. Sulfur isotope evidence indicates that the Pb-Zn orebody was formed by magmatic hydrothermal mineralization in the Cretaceous, and the pyrite orebody was probably overprinted by Cretaceous magmatic-hydrothermal activity.

1 Introduction

The Dajiangping deposit in the southwestern Cathaysia Block, is the largest SEDEX-type pyrite deposit in China and contains >200 million tons of pyritic sulphides (Yang et al. 1997). The deposit consists of stratiform orebodies and ubiquitous laminated ores, and recently, Pb-Zn orebodies (prospective reserves Pb+Zn 1.54Mt) were discovered underlying the pyrite orebody (Luo et al. 2004). Although some studies on the genesis and sources of pyrite orebodies from Dajiangping deposit are available (Chen et al. 1998; Zhang et al. 1992; Li et al. 2006; Qiu et al. 2018), the genesis of Pb-Zn orebody and its relationship with the pyrite are still not clear. Sedex deposit is an important source of lead-zinc resources in the world. It accounts for about 50% of the total reserves lead-zinc deposits (Sangster, 2002), whereas, the number of this type pyrite deposits in the world is relatively small, only were reported in the Chinese literature, such as Dongshengmiao from Inner Mongolia.

SEDEX deposits generally have stratabound characteristics, with some developing a "double-layer" structure, in which the upper part consists of layered sulphides, and the lower part is veinlet and vent complex ore-bearing alteration body (Goodfellow et al. 1993; Leach et al. 2005). Regionally, the Dajiangping deposit is located in the core part of Daganshan ore field, which shows clear metal zoning possibly related to hydrothermal (magmatic source) mineralization. However, the role of magmatism is not clear during the formation of the Dajiangping deposit (Song et al. 2011). In this study, we contrast the characteristics of fluids from the lead-zinc orebody with pyrite orebody, the sulfur isotope composition, in order to discuss the genesis of Pb-Zn orebody and its relationship with pyrite orebody.

2 Geologic setting

The Dajiangping deposit is located in the northeast margin of the Luoding fault-bounded basins, southwest of Qin-Hang (Qinzhou Bay to Hangzhou) belt, which is a suture zone between the Yangtze and Cathaysia Blocks (Mao et al. 2010, 2011; Yuan et al. 2011, 2015, 2018).

The oldest strata exposed in the Luoding basin is the Proterozoic Shapingwan Formation (Ptsh). The Sinian Daganshan Formation (Zd) including quartz-mica schist,
siliceous rock, crystalline limestone and tuff is the main pyrite-bearing strata. Younger Ordovician and Silurian strata consist of sedimentary flysch deposits. The Devonian and Carboniferous rocks are mainly sedimentary clastics and carbonate rocks. They are key skarm Cu-Pb-Zn orebody bearing strata in this area (Cai et al. 2002). The Triassic conglomerate, sandstone, siltstone and shale are present. The Cretaceous is mainly made of sandstone. The NE-trending structures including Guizihu arc fault and the Wuchuan-Sihui deep fault are developed which was caused by many periods of tectonic movements, and control the develop of rocks and deposits in this area (Yang et al. 2012). The magmatic activity is strongest in Caledonian and Yanshanian, mainly including granite and monzonitic granite (Fu et al. 2010), example is the Dajinshan granite, which has the SHRIMP Zircon U-Pb isotopic age of 84.17±0.34 Ma (Yu et al. 2013).

Luoding basin is a NE-trending Mesozoic fault-bounded basin. A set of Ag-Zn-Pb-Au-Sn deposits are distributed surrounding it, including Xinrong-Lianzhou Au-Ag-Mn ore field in the southern margin (Huang et al. 2002) and Daganshan W-Sn-Ag-Zn-Pb-S ore field in the northern margin. The Daganshan polymetallic ore field is controlled by Daganshan arc or ring structures including folds and faults surrounding the granite zone. It comprises Dajinshan large W-Sn deposit, Dajiangping large S(Pb-Zn), Gaocheng large Ag-Pb-Zn and Jiuqiling medium Sn deposit (Qin 2018), Chadoring medium Ag-polymetallic deposit and so on. The ore field is not only of a wide variety of mineralized elements, but also has a very clear mineralization element zonation associated with magmatic activities, showing the elements of W/Sn/Bi →Sn→Sn/Pb/Zn/Ag→Ag/Pb/Zn → Au from the granite rock inside to outside.

3 Ore deposit geology

The Dajiangping deposit is mainly exposed in the Sinian Daqishan Formation metamorphic suite. The lithologies consist mainly of metamorphic carbonaceous siltstone, crystalline limestone, quartzite, siltstone and black shales, which are host rocks of pyrite and lead-zinc orebodies. Folds and faults are well developed, especially the NW trending F4 fault, which controls the distribution of pyrite ore bodies (Fig. 1). The magmatic rocks in the mining area are not developed, and only small Yanshanian medium-fine-grained granite was found to the south of the mining area.

The Dajiangping pyrite deposit is composed of five pyrite orebodies, divided into the west and east parts by the F3 fault. The No. III stratiform orebody (Fig. 2a) in the west and the No. IV lens orebody in the east were relatively larger. Stratiform orebodies that are distributed within a 6 × 4 km-wide zone with a thickness of up to 170m, hosted by carbonaceous strata and black shales. The No. IV lens orebody can reach to 1.59 km in thickness and is 2.15 km in length. The pyrite orebody has conformable boundaries with the host wall rocks. Mineral assemblages consist of pyrite, pyrrhotite, and a small amount of sphalerite, galena and chalcopyrite.

Gangue minerals are mainly quartz, calcite, sericite and graphite.

Six newly discovered Pb-Zn orebodies all occur within the Daganshan Formation metamorphic rocks, with the larger No. 2 orebody controlled by a regional arc shape structure. Underlying the stratiform orebodies (Figure 2b), are calcareous siltstone and black shale. The length of Pb-Zn orebody >1.6km, with average thickness of 4.83 m. The average grade of mineralized elements is Pb: 0.106ppm, Zn: 0.107ppm, Sn: 0.025ppm, Ag: 21.78ppb, Au: 0.40ppb (Luo et al. 2004). Occurrences of part orebodies are consistent with the stratum. The wall rock alterations of V2 orebody composed of silicification, pyritization, sericitization, chloritization and fluorination.

4 Discussion

SEDEX deposits generally develop typical “double layer” structures, upper part is a massive sulfide orebody, and the lower part is vein, disseminated or veinlets, cylindrical sulfide orebody or altered ore-bearing body, which represented submarine hydrothermal replacement (Large et al. 1983; Goodfellow et al. 1993; Leach et al. 2005). Compositonally, the metal elements of the upper layered orebodies and the vein mineralization of the lower sections show the identical evolution regularity from bottom to up (Large et al.1999; Goodfellow et al. 2007). The two parts formed nearly simultaneously in theory. We compared the stratiform pyrite orebody with the vein Pb-Zn orebody in the following aspects.

Lead-zinc ore and pyrite bodies in the Dajiapng deposit have different mineral assemblages and alteration types. Mineral assemblages of the former are relatively diverse, including galena, sphalerite, pyrrhotite, calcite, fluorite, quartz, chloride, accompanied by sericitization, chloritization, silicification, carbonation and a small amount of epidote. Whereas, the later included only pyrite, pyrrhotite, quartz and calcite, corresponding to silicification and carbonation. The pyrite overgrowths with sphalerite and galena (Fig. 2d),
is bright or light yellow, often medium-coarse grained idiomorphic cubes, with occasional pentagonal dodecahedron crystal forms, and the size of grains ranging between 0.25 mm and 5 mm. Pyrite is white yellow, poor crystallized, irregular or rounded (Fig. 2c) in banded ores, with mostly size of 0.05~0.5 mm. These suggest that the metallogenetic environment of lead-zinc ore is different from that of banded ore. The petrographic and micro-thermometric analysis of fluid inclusions from the two types of ores indicate that mineralization-related fluids are both liquid-rich two-phase H2O-NaCl. The salinities of the fluids (w(NaCl)eqv) from vein Pb-Zn ores varies between 1.23% and 12.85%, with an average value of 7.81%, and peak values ranging from 6% to 9%, slightly higher than that of fluid from banded ore, which w(NaCl)eqv are between 3.71% to 9.08%, average and peak values are 5.90% and 4%~7%, respectively. There are various ranges of inclusion homogenization temperatures in vein Pb-Zn ore, varying from 118℃ to 410℃, average is 343℃, but showing two peak intervals of 220~300℃ and 380~400℃. The lower interval is comparative to that in the banded ore, which concentrate on 200~300℃, with an average of 255℃. This indicates that the two ores form in different fluid systems and there is a high-temperature fluid involved in the Pb-Zn mineralization process. Daughter-bearing mineral and melt inclusions were discovered in vein Pb-Zn ore support this.

The sulfur isotope compositions show that the layered orebody has the δ34S value of (-10.9‰ to -25.6‰), which represents bacterial sulfate reduction. The δ34S value of the lead-zinc orebody is -7.1‰ to 6.4‰, showing the influx of a deep source of sulfur.

Previous studies have reported a whole-rock Rb-Sr isochron age of 630 Ma for the Dajiangping deposit (Wang et al. 1997). But Qiu et al. (2018) thought the ore-hosting strata were deposited during the mid-late Devonian according to U-Pb ages of detrital zircons from sandstone interlayers within the stratiform orebodies. Sphalerite in Pb-Zn orebodies has a Rb-Sr isochron age of 88.5±3.9Ma (Zhao et al. 2016), implying it formed in various periods of pyrite body formation. The age of Pb-Zn ore vein coincides with the mineralized event in the same Daganshan polymetallic ore field, including Dajinshan W-Sn deposit of Re-Os isochron ages of 80.07±1.19 Ma and Gaocheng Ag-Zn-Pb deposit of Rb-Sr age of 89.7±4.6 Ma.

5 Conclusions

1. The laminated pyrite ore has different inclusion homogenization temperatures and salinities than the vein Pb-Zn ore. These later formed in high-temperature and salinity fluids, indicating that the two ores form in different fluid systems and evolution processes.

2. The age of the lead-zinc orebody has been determined by the Rb-Sr isochron method for sphalerite, yielding a Rb-Sr isochron age of 88.5±3.9 Ma.

3. The sulfur isotope compositions show that the layered orebody has the δ34S value of (-10.9‰ to -25.6‰), which represents of bacteria sulfate reduction. The δ34S value of the lead-zinc orebody is -7.1‰ to 6.4‰, showing the characteristics of a magmatic source of sulfur.

4. The newly discovered lead-zinc orebody was formed by magmatic hydrothermal mineralization in Cretaceous, and the SEDEX pyritic sulphides were probably overprinted by the magmatic-hydrothermal activity.

Acknowledgements

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References


Ag-Sb-Pb-Cd mineral paragenesis in the barite veins: Example from the Sowie Mountains, Poland.

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Abstract. An unusual association of various silver minerals was identified in a barite vein from Bystrzyca Góra, Sowie Mountains, Poland. The ore mineralization is disseminated in a fine-grained dark barite-quartz matrix. The main ore minerals are galena and sphalerite. They are accompanied by various Ag-Sb-Pb-(Cd) minerals. Silver minerals are represented by pyrargyrite, miargyrite, stephanite, argentite, freibergite and Ag-bearing tetrahedrite with AgPbSb sulphosalts as frieselebenite, andorite and zoubekite as well as native antimony, greenockite, dyscrasite, plagionite, boulangerite, bouroinite, and two unknown phases. Unknown phase X is chemically close to (Cu$_{3.9}$Ag$_{0.1}$)$_{4.00}$Fe$_{2.5}$Sb$_{2}$Pb$_{7.5}$S$_{16}$ and phase Y is chemically close to (Cd$_{2.43}$Ag$_{4.46}$)$_{6.89}$Sb$_{3.06}$S$_{9.25}$. It is the first occurrence of Ag-Sb-Pb-(Cd) mineralization documented in Poland.

1 Introduction

Silver minerals are the main host of silver in the base metal mineralization in various mineralizing environments, however in barite veins these are not common. In Poland, silver minerals were identified in the LGOM district (Kozub-Budzyry and Piestrzyński 2018), the most common ones include native silver, silver amalgamates, cupropearceite, mackinstyrite. Additionally Ag-bearing bornite and chalcocite also occurs. Polymetallic mineralization in the Sudety Mountains, such as Radzimowice, Dziećmorowice, Kowary, Kletno, Miedzianka, contains Ag-Pb-Bi sulphosalts and Ag minerals/selenides with native Ag (Siuda 2012; and many others). Silver mineralization in sulposalts and Ag minerals/selenides with native Ag occurs. Polymetallic mineralization in the Sudety Mountains Block, the oldest Precambrian structural element of Middle-Sudetes. The Sowie Mountains Belt is a NW-SE elongated horst composed mostly of Archaic and Proterozoic high grade metamorphosed rocks, including gneisses, migmatites and amphibolites, with a predominance of Late-Proterozoic migmatitic gneiss of sedimentary origin. In the central part of the mountains, non-metamorphosed sediments of the Kulm Group, sit unconformably on the underlying complexes (Gunia 1985). Structurally controlled base-metal mineralization in this region is a result of complicated geological history involving magmatic processes and tectonic rearrangement. The ore mineralization is hydrothermal in origin and occurs in quartz-barite veins. The barite-base metal (±silver) veins were periodically mined over a few centuries, with the most intensive period of mining in the 16th century.

3 Methodology

Ore minerals with Ag mineralization were sampled in the old mine dumps close to Bystrzyca Góra, Sowie Góry Mountains. Silver minerals are disseminated in dark laminated barite. Ore minerals are small in size and macroscopically only galena is visible. Dark laminae, up to 1 cm thick are Ag-bearing but not all contain silver minerals. Silver minerals and sulphosalts were characterized in the Laboratory of Critical Elements at Faculty of Geology Geophysics and Environmental Protection, AGH-UST, Kraków Poland using a JEOL Super Probe 8230. 20 kV of accelerating voltage and beam current 20nA (for sulphosalts) or 10 nA (for silver minerals) were used for measurements with following standards natural: (pyrite, stibnite, chalcopyrite, galena, arsenopyrite, greenockite, cinnabar) or synthetic (native silver, Bi$_2$Se$_3$, Sb$_2$Se$_3$) and spectral lines: Ag(L$\alpha$), Pb(M$\alpha$), S(K$\alpha$), Sb(L$\alpha$), Cu(K$\alpha$), Fe(K$\alpha$), Bi(M$\alpha$), As(L$\alpha$) for sulphosalts, Ag (L$\alpha$), S(K$\alpha$), Sb(L$\alpha$), Cu(K$\alpha$), Bi(M$\alpha$), As(L$\alpha$), Se(L$\alpha$) for Ag minerals and Ag (L$\alpha$), S(K$\alpha$), Sb(L$\alpha$), Cd(L$\alpha$), Cu(K$\alpha$), Bi(M$\alpha$), Zn(K$\alpha$), Fe(K$\alpha$), Hg(M$\alpha$), As(L$\alpha$), Se(L$\alpha$) for tetrahedrite and Cd bearing phases.

4 Results

Various silver minerals and silver bearing sulphosalts were identified in the barite veins in Bystrzyca Góra. Ore minerals form individual crystals or intergrowths oriented in quartz veinlets cutting the barite. The main ore minerals are galena and sphalerite with a small amount of chalcopyrite, tetrahedrite, pyrite, bouronite and greenockite. Silver bearing mineralization forms early in the paragenesis, forming thin veinlets up to few hundred microns in size. The main silver minerals are...
pyrargyrite and stephanite with minor miargyrite and they are all replaced by younger sulphosalts with native antimony. Various Pb-Sb, Ag-Pb-Sb, Cu(Fe)-Pb-Sb sulphosalts were identified (Fig. 1).

4.1 Early stage – base metal mineralization

Minerals of the tetrahedrite group (TGM) occur as separate crystals in the barite matrix or they form inclusions in galena. They are usually not in connection with any silver minerals and seem to occur irrespective of the silver paragenesis. They are usually found in association with galena, sphalerite and bournonite. BSE imaging shows that crystals of the TGM are zoned (Fig. 2), cores have a lower content of silver while rims are enriched in silver with analyses falling in the field of freibergite (Fig. 3). Probably, the former Ag bearing tetrahedrite was corroded by silver rich fluids of younger paragenesis and freibergite domains were formed. Content of silver in TGM ranges from 8.11 wt.% up to 34.4 wt.% which indicate presence of Ag-bearing tetrahedrite and freibergite. Freibergite also occurs as separate idiomorphic crystals and is enriched in Fe - from 4.4 up to 5.8 wt.% with zinc up to 1.1 wt.% and As up to 0.17 wt..% Ag-bearing tetrahedrite has more variable chemical composition. Content of Zn vary between 0.4 up to 6.8 wt.% with small content of As up to 0.36 wt.% Content of Cd is similar for both members and it reaches maximum 0.33 wt.%.

Greenockite is very rare and forms only small crystals up to 50 microns, enclosed and replaced by galena. It exhibits a stoichiometric composition without any other trace impurities.

Bournonite is the only sulphosalt present in early assemblages of the paragenesis. It occurs with TGM and galena as well as sphalerite in the form of small crystals or inclusions in galena. It is stoichiometric without any other admixtures.

Figure 1. Compositional diagram Pb vs Sb vs Ag+Fe+Cu of sulphosalts and Sb rich phases from Bystrzyca Górna. Ideal phases were marked by cross.

4.2 Ag mineralization associated with Pb-Sb sulphosalts and native antimony

Pyrargyrite, stephanite and miargyrite are the main silver bearing phases in the samples. Acanthite/argentite are rare and occur as separate crystals in the ore bearing veinlets. They are sometimes replaced by Ag-Pb-Sb sulphosalts or they form intergrowths with plagionite, unknown sulphosalts, native antimony or galena. Argentite usually occurs as separate grains filling the vugs in pyrargyrite. It was probably formed during the decomposition of pyrargyrite. The chemical composition of pyrargyrite, stephanite and miargyrite is close to stoichiometric. Some analyses fall in the field between pyrargyrite and stephanite (Fig. 4). Low contents of Cu up to 0.5 wt.% and up to 0.1 wt.% of Bi were detected in pyrargyrite and miargyrite.
Ag-Pb-Sb sulphosalts are rare, occurring as intergrowths with silver minerals. Sometimes, they form veinlets replacing other minerals in the paragenesis. The size of the crystals is usually up to a few microns, only in the case of the veinlets could they reach up to 100 microns. The main sulphosalts is zoubekite, which occurs only in the form of thin veinlets. Andorite VI and freieslebenite are rare. They have higher contents of Ag in comparison to theoretical ones, which is due to small crystals enclosed by Ag minerals. Andorite VI could be characterized as $L_{97.95}$ which means 97.95 mol.% of AgSb substitution and $N=5.37$. Zoubekite has a stable chemical composition and the average formula could be written as: $(Ag_{0.68}Cu_{0.09})_{0.77}(Pb_{4.09}Fe_{0.04})_{4.13}(Sb_{4.06}Bi_{0.03})_{4.09}S_{10.59}$.

Pb-Sb sulphosalts are common, forming needle-like crystals or aggregates in association with other minerals for example unknown phase X, bouronite and Ag phases. The size of the aggregates is up to 100 microns. Only two phases were identified: boulangerite and plagionite. Their chemical compositions are nearly stoichiometric.

Native antimony is one of the most common phases in the Ag bearing paragenesis. Usually it replaces silver bearing minerals or sulphosalts and is replaced by galena. It also forms separate crystals disseminated in quartz and barite or intergrowths with dyscrasite which is always in the central part of the crystals. It is chemically pure with only minor arsenic content - up to 0.9 wt.% identified.

Unknown phase X is rare in the overall paragenesis. It occurs in the form of needle like crystals or intergrowths with another minerals (Fig. 5). It is commonly found with plagionite, pyargyrite, galena and native antimony. The size of the crystals is up to 100 microns and contain on average 0.5 wt.% of Ag, 0.4 wt.% of Bi, 5 wt.% of Fe, 8.7 wt.% of Cu, 9.1 wt.% of Sb, 57.8 wt.% of Pb and 18.76 wt.% of S which give the following formula calculated on the base of 16 cations:

$$(Cu_{3.72}Ag_{0.12})Fe_{2.44}(Sb_{2.06}Bi_{0.05})Pb_{7.61}S_{15.96}.$$
tetrahedrite by freibergite, replacement of previous sulphosalts paragenesis by native antimony and finally by galena. A similar paragenesis with Ag-minerals and various sulphosalts is typical for many barite deposits or base-metal deposits in Poland or in the world (Plumlee et al. 1994; Škacha et al. 2012; Megarskaya et al. 1986; Pršek unpublished and others). The presence of Ag-Pb-Sb, Pb-Sb, Ag-Sb, Ag-Cu-Fe-Pb-Sb sulphosalts with native antimony and dyscrasite together with Ag-Sb-Cd phase and greenockite as well as Ag rich tetrahedrite shows that the ore mineralization in barite veins forms under complex and changing hydrothermal conditions. Similar variability in mineralogy was identified in barite veins in the Apuan Alps (Italy) where many of new Pb-Sb (Ti, O, Cl, Hg, Ag, Cu) sulphosalts were described (Biagioni et al. 2014; Biagioni et al. 2016; Biagioni et al. 2018; and many others). TGM minerals are typical for many hydrothermal veins and mineralization, and they are often the main host of Ag in ores. Substitution of Ag for Cu is typical in base metal Ag bearing mineralization or in Au-Ag mineralization (Grammatikopoulos et al. 2005; Pršek et al. 2006; Gallego-Hernandez and Akasaka 2010; Kołodziejczyk et al. 2016; and many others).

The chemical composition of sulphosalts is usually close to stoichiometric, with only few variations. The main issue is Ag-Pb-Sb sulphosalts, especially andorite VI and frieseibenite which composition far from the theoretical one are shifted. Zoubekite from the Bystrzyca Górna deposit has lower Ag contents (4.6 wt.%) in comparison with Zoubekite from Pribram (5.8 wt.%) (Megarskaya et al. 1986) or from Silver King (6.58 wt.%) (Biagioni et al. 2014; Biagioni et al. 2016; Biagioni et al. 2018). Contents of Pb, Sb and Cu is similar to the theoretical one are shifted. Zoubekite from the Bystrzyca VI and frieslebenite which composition far from the main issue is Ag-Pb-Sb sulphosalts, especially andorite close to stoichiometric, with only few of variations. The paragenesis of silver minerals in the Pb-Zn Stan Terg deposit, Kosovo: an example of precious metal epithermal mineralization. Geol., Geoph. and Envir. 42:19-29.


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Clastic sediment-hosted Pb-Zn mineralization in the Selwyn Basin, Yukon, Canada and the relationship to alkaline magmatism

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Abstract. The Selwyn Basin in the Yukon Territory, Canada, is host to several Pb-Zn clastic sediment-hosted districts. Two of these districts, Anvil and MacMillan Pass, have alkaline magmatism in the same stratigraphic horizon as Pb-Zn mineralization. We have collected samples from these volcanics and begun to characterise volcanism in the Selwyn Basin. Samples are alkaline basalts and basaltic volcaniclastics produced through within plate magmatism. Samples from the Earn Group in Keno Hill are subalkaline metabasalts with tholeiitic compositions. Volcanism in MacMillan Pass was more explosive than within the Anvil District, where pillow lavas and lapilli tuffs represent periods of effusive and explosive subaqueous volcanism, respectively. Initial work on the thallium isotopes of volcanic rocks indicates that MacMillan Pass samples have a more negative $\varepsilon^{205\text{Tl}}$ range (-3.2 ± 1.8 to -14.2 ± 3.2) than those from the Anvil District (-0.9 ± 1.9 to -6.4 ± 1.2). Future work will expand upon initial Tl isotope data, constrain the age relationships between volcanism and mineralization and use Nd, Sr and Pb isotopes to characterise magma sources.

1 Introduction

Our understanding of the formation of Pb-Zn clastic sediment-hosted deposits has evolved over time. Historically, these deposits have been considered as purely hydrothermal, forming through exhalation of metal-rich brines onto the seafloor (Leach et al. 2010; Lydon 1983). However, deposits have been discovered where the ore did not form through exhalation but rather as sub-seafloor replacement (Gadd et al. 2016; Kelley et al. 2004; Magnall et al. 2016). Many deposits have volcanism present in the sedimentary package that hosts the Pb-Zn mineralization but this volcanism has generally been dismissed as unrelated to ore forming processes. The Selwyn Basin provides an ideal location to investigate volcanism in relation to Pb-Zn clastic sediment-hosted deposits. Paleozoic magmatism in the region occurs in spatial and temporal relation to two major Pb-Zn Districts (Goodfellow et al. 1995) (Fig. 1). This project will use a variety of geochemical techniques to characterise magmatism in the region, constrain age relationships and pinpoint linkages between magmatism and mineralization.

Regional geology

The Selwyn Basin formed on the passive margin of North America from the Late Proterozoic to the Early Carboniferous. Rift-fill and marine facies fill an
extensional sedimentary basin. Interbedded alkaline mafic volcanics from the Cambrian to late Devonian are scattered throughout the region (Goodfellow et al. 1995) (Fig. 1). Volcanic rocks were subdivided by Goodfellow et al. (1995) on the basis of different degrees of partial melting from either a metasomatized lithospheric mantle source or the asthenospheric mantle.

Clastic sedimentary hosted Pb-Zn deposits occur in three major districts within the Selwyn Basin; Howard’s Pass, Anvil district and MacMillan Pass (Fig. 1).

2 Methods

A total of 142 samples were sent to ALS Geochemistry in Vancouver, Canada for lithogeochemistry. Whole rock samples were crushed using a low Cr-Mo steel ring. Major elements were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and trace elements using inductively coupled plasma-mass spectrometry (ICP-MS) as outlined in Leybourne et al. (2018).

Thallium isotopes were measured at the Queen’s Facility for Isotope Research. The analytical methods used are outlined in Peter et al. (2018). Isotopes were measured using a Neptune multi-collector ICP-MS.

3 Results & discussion

3.1 Volcanic textures

Samples from the Anvil District were collected from the Menzie Creek Volcanics, which can be subdivided into three lithologies; 1) ash-rich tuffs, lapilli tuffs and volcanic breccias, 2) pillow and basalt flows, 3) gabbroic intrusives. Ash-rich tuffs typically contain no or little lapillus and are often graded. Lapilli tuffs contain relict glass shards with cuspate margins and pumice fragments that range from undeformed to flattened between samples (Fig 2a). Breccia fragments are typically basaltic. Volcaniclastic samples represent pyroclastic flows and fall deposits. Basalt pillows and flows indicate effusive subaqueous eruptions.

MacMillan Pass volcanics are dominantly volcaniclastic. These samples have a distinctive orange alteration in hand specimen. Lapilli tuffs and volcanic breccias are common, with heterolithic clasts. Ash-rich tuffs and a few intrusive samples were also collected. These samples have high carbonate contents. Most of this carbonate is present as coarse crystals comprising the matrix although some carbonate is present as clasts or replacing phenocrysts within clasts. Whereas a large proportion of this carbonate may be alteration, some is likely magmatic in origin. Breccias are poorly sorted and heterolithic, with clasts of basalt, pumice, chert, quartz and rare black shales. Clasts range from sub-mm to tens of cm. Clast boundaries vary from those that are angular and reflect little reworking to sub-rounded clasts. Pumice shows little deformation. Relict glass shards with cuspate margins are present in several lapilli tuffs. The size, sorting and heterolithology of breccias suggests that these samples formed in explosive eruptions and were likely close to the volcanic vent. Ash-rich tuffs are likely ash fall or surge deposits that formed distally from the vent.

Primary features in metavolcanics from the Earn Group in the Keno Hill region have been obscured by regional metamorphism up to the lower greenschist facies. These samples are crosscut by a series of Triassic dikes.

Misty Creek Embayment samples are dominantly basaltic, representing effusive eruptions. Several lapilli tuffs from this region contained mm to cm scale basalt clasts. No pumice or relict glass shards were observed.
3.2 Lithogeochemistry

Due to pervasive alteration of volcanic samples, typical sample classification schemes are not useful. A Zr/TiO₂ versus Nb/Y plot indicates that volcanics from the Keno Hill district are subalkaline whereas all other sample suites from the Selwyn Basin are alkali basalts, basanites or trachyandesite (Fig. 3a). Samples from MacMillan Pass, the Anvil District and the Misty Creek Embayment all plot as within plate alkaline basalts on the tectonic discrimination diagram of Wood (1980) (Fig. 3b).

All volcanic samples in the Selwyn Basin show an enrichment in Ba. Thallium shows a positive trend plotted against Ba, which is similar to mineralized samples from the Howard’s Pass deposit (Leybourne et al. 2018). Spider diagrams show that all samples have positive peaks in Ba with depletions in K, Sr, Ti, and Rb. Pb is commonly depleted in all samples except for those from Keno Hill.

3.3 Thallium isotopes

Five volcanic samples from the Anvil District give a ε²⁰⁵Tl range of -0.9 ± 1.9 to -6.4 ± 1.2. Six samples from MacMillan Pass range from -3.2 ± 1.8 to -14.2 ± 3.2 (Fig. 4). The value of -14.2 has a large error with it and is anomalously low, ~5 units from the second most negative MacMillan Pass sample (-9.5 ± 2.5). There is no clear trend when these results are plotted against Tl concentrations. However, plotted against Ba concentration, Ba concentration increases as ε²⁰⁵Tl values become more negative (Fig. 4).

MacMillan Pass and Anvil District volcanics both overlap with the Tl isotopic values of the Howard’s Pass Pb-Zn deposit (Fig. 5). However, these volcanic samples also overlap with the host rock of the Howard’s Pass deposit. When comparing the Tl isotopes to other geological settings, the one outlier from MacMillan Pass only overlaps with altered ocean crust. Tl isotopes from a larger sample suite in the Selwyn Basin will be analysed to investigate the potential of elements such as Ba and Tl in the Pb-Zn deposits to have been sourced from magmas.
4 Preliminary conclusions

Volcanism within the Selwyn Basin was varied, with different regions within the basin represented by differing eruption styles, geochemistry and alteration styles. Volcanic samples are alkaline in all regions except Keno Hill and were produced through within plate volcanism. Initial Tl isotopes are more negative for MacMillan Pass in comparison to those from the Anvil District and overlap with Tl values from the Howard’s Pass Pb-Zn clastic sedimentary-hosted deposits.

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References


Genetic links between Irish-type Zn-Pb deposits and related geochemical halos

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Abstract. A broad geochemical dispersion halo has been identified with a direct link to the underlying Tara Deep deposit at Navan, Ireland. In situ laser S isotope analyses have been performed on petrographically well-characterized samples from the halo. Four mineral assemblages have been identified. 1) In black shales, laminated pyrite comprising thin layers of framboidal low-$\delta^{34}$S pyrite with minor interstitial sphalerite. 2) Pyritized calcarenites are widely distributed and occur chiefly as biodebris replaced by low-$\delta^{34}$S pyrite. 3) A replacive assemblage occurs as late remobilizations exhibiting both crosscutting and bedding-parallel styles, overprinting the early laminated pyrite. It comprises mostly marcasite, with minor pyrite, sphalerite, chalcopyrite, galena, stibnite, arsenopyrite and pentlandite, with high $\delta^{34}$S values. 4) Hydrothermal cherts comprise thick microcrystalline quartz bands rimmed by dolomite, associated with marcasite, pyrite, sphalerite, chalcopyrite, galena, Ni-sulfosalts and stibnite with high $\delta^{34}$S values. These results indicate overlapping diagenetic and multi-phase hydrothermal sulfide mineralization. First, laminated pyrite and pyritized calcarenites suggests a bacterial origin within sediments during early diagenesis. Later, hydrothermal chert and replacive sulfides suggest hydrothermal exhalation during early-mid diagenesis. Similarities in mineralogy and S isotope compositions suggest genetic links between the halo and the underlying Tara Deep deposit.

1 Introduction

Irish-type Zn-Pb deposits are understood to have formed by replacement of Lower Carboniferous limestones. Networks of normal faults acted as pathways for ascending, warm, metal-bearing fluids which had scavenged metal from the underlying Lower Palaeozoic basement, to mix with cooler, hypersaline brine associated with dissolved bacteriogenic sulphide reduced bacteria (e.g. Ashton et al. 1986; 2003; 2015; Anderson et al. 1998; Fallick et al. 2001; Blakeman et al. 2002; Gagnevin et al. 2012). Almost all these studies are based on structural, petrologic and geochemical analyses of both the Main Orebody and South West Extension (SWEX). Following an extensive seismic survey in 2012 (Ashton et al. 2018), a new satellite deposit to the Navan orebody was discovered at ~1500m, known as Tara Deep, with an inferred resource of 18.2 Mt grading 7.6% Zn and 1.6% Pb (Ashton et al. 2019).

As discovery depths get deeper, the potential exploration importance of the overlying halos which surround many Irish-type deposits is becoming more important. Halos overlying the Navan deposit present geological features which suggest that here, the hydrothermal fluids that formed Navan replacive ore also reached the seafloor, forming sedimentary-exhalative (SEDEX) mineralisation (Altinok 2005; Yesares et al. 2019). Nevertheless, linkages between these halos and the economic Navan mineralization are poorly understood. Understanding these halos has the potential to significantly enhance mineral exploration strategies for deeply buried ores, and to strengthen genetic models of both replacive and SEDEX mineralization.

Here we focus on the genesis of the alteration halo of the recently discovered Tara Deep orebody associated with the Navan deposit. The geological record suggests that the halo mineralisation was formed close to the seafloor within the Upper Dark Limestone (UDL), linked to the underlying economic Tara Deep replacive ore.

2 Geological setting

The Irish Midlands are dominated by Lower Carboniferous limestones. These rocks were deposited in tropical seas, typically shallow but with sedimentary basins developing in response to crustal extension (Philcox 1984). They represent a marine transgression over clastic sedimentary rocks of late Devonian to Tournaisian age known as the Old Red Sandstone, a terrestrial red bed succession.

Irish-type Zn-Pb deposits consist primarily of stratabound sphalerite, galena and iron sulfides,
accompanied by dolomite, calcite and barite gangue, hosted in Tournaisian carbonate sedimentary rocks. They are concentrated near normal faults, which are often associated with development of Upper Palaeozoic sedimentary basins. These faults are probably inherited from the underlying complex Lower Palaeozoic basement geology that resulted from closure of the Iapetus Suture Zone during Late Caledonian continental collision (Leeder 1982; Murphy et al. 1991).

The Zn-Pb Navan orebody is located in the northern margin of the Dublin Basin and is hosted mainly by the Tournaisian Micrite Unit at the base of Pale Beds, of the Navan Group (Fig. 1).

Figure 1. Geology of the Navan orebody including the Tara Deep deposit (a) Map projection of the top surface of the Navan system, including the different deposits and main structural features; (b) Stratigraphic column of the Tara Deep area showing the different ore lenses and hosting rocks. (L.P. = Lower Palaeozoic). Taken from Yesares et al. 2019.

3 Tara Deep deposit and overlying halo

The Tara Deep orebody is located ~3 km SW of the SWEX of the Navan deposit, at a depth of 1.2-1.9 km (Fig. 1a). The current inferred resource, 1.5 x 0.7 km in plan, is mostly hosted by lower Micrite Unit, the Tournaisian basinal limestone sequence that hosts most of the Navan Main Orebody (Ashton et al. 2015). The Tara Deep deposit consists of a Zn-Pb semi-massive sulphide body up to 60 m thick. The Pale Beds comprise allochthonous slide units along with melange-like deposits of Shaley Pales, and/or Argillaceous Bioclastic Limestones. This allochthonous package is overlain by a polymict submarine debris-flow, currently considered to be equivalent to the Boulder Conglomerate of the Navan deposit (Fig. 1b).

Tara Deep is located between two major extensional structures. The G Fault forms the northern limit while the southern limit is defined by a larger structure, the ENE striking Navan Fault, which has a displacement of several kilometres. The structural terrace formed by the Navan and G faults is cut by the S fault, a NNW striking, steep westerly dipping structure (Fig. 1a).

As in the main Navan deposit, the majority of mineralization at Tara Deep occurs within a stratigraphic interval analogous to the 5-lens equivalent (lower Pale Beds). It comprises sphalerite and galena (5:1 ratio), with minor pyrite, marcasite, barite, stibnite and chalcopyrite. Tara Deep shows similar mineralogical compositions and textural relationships to the Navan main orebody and SWEX (Ashton et al. 2015).

The Tara Deep deposit is unconformably overlain by a deep marine succession, comprising Lower Visean-Visean basin fill, known as Upper Dark Limestones (UDL) (Fig. 1b; Fingal Group). In the Tara Deep area, the lower UDL includes the Thin-Bedded Unit (TBU) which comprises alternating sequences of black shales, silts and calcarenites (Figs 1b and 2). Here, uneconomic seafloor exhalative sulfide mineralization has been identified where the TBU overlies the Tara Deep deposit.

Figure 2. Main host facies and mineralization styles in the Upper Dark Limestone overlying the Tara Deep deposit. (a) Organic matter-rich black shales replaced by ~0.5 to 1.5 cm layers of fine-grained pyrite parallel to bedding; (b) alternating sequences of organic matter-rich black shales, silts and calcarenites including pyritized fossils; (c) Marcasite and pyrite filling fractures and interstices in both silts and calcareite; and (d) Centimetre-scale hydrothermal cherts, included in black shales which show a reddish Mn alteration.

4 Samples and methods

Samples from the sub-economic mineralization in the Thin Bedded Unit overlying Tara Deep were collected from drill core. Mineralogical, textural and paragenetic analyses were carried out by petrographic microscopy, SEM-EDS and EPMA.

Sulfur isotope analyses were carried out by in-situ laser combustion (Wagner et al 2002) of sulphides on polished blocks.

5 TBU Mineralogy

Petrographic analyses have revealed a texturally complex mineralogy composed mainly of pyrite and marcasite with subordinate sphalerite, galena, chalcopyrite, arsenopyrite, stibnite and undefined Ni-sulfosalts. Four different mineral assemblages have been identified from their mineralogical and textural features:

1) Laminated pyrite: is the major assemblage and is mostly composed of 0.5-15 cm thick bedding-parallel layers of frambooidal pyrite and subordinate interstitial sphalerite (Figs 2a and 3a). It is widely distributed in the
TBU, progressively decreasing upwards and is closely associated with black shales.

2) Pyritized fossils: calcarenite layers within the TBU show a high degree of pyritization including bioclast replacement (Figs 2b and 3b). It is widely distributed in the TBU, progressively decreasing upwards and closely associated with the laminated pyrite.

3) Hydrothermal chert: mainly comprises 0.5-2 cm thick microcrystalline quartz bands rimmed by euhedral coarse Mn-rich dolomite associated with bird’s eye marcasite, fine euhedral aggregates of pyrite, sphalerite, chalcopyrite, and galena which includes very fine exsolved Ni-sulfosalts and stibnite (Figs 2d, 3c and 3d). It is found systematically at higher stratigraphic levels in the TBU.

4) Replacive assemblage: is pervasively distributed throughout the TBU and occurs mainly in calcarenites. It occurs as late remobilizations both crosscutting, and parallel to, the bedding and overprinting the early laminated pyrite (Fig. 2c). It is formed by marcasite and pyrite, and minor sphalerite, chalcopyrite, galena and siegenite filling of open spaces (Figs 3e and 3f).

Figure 3. Reflected light and BSE images of the UDL-hosted mineralization overlying Tara Deep. (a) Laminated frambooidal pyrite (py) replaced by sphalerite (sl); (b) Pyritized fossils (mainly radiolaria) in a calcarenite layer; (c) Hydrothermal cherts included in black shales showing a sulfide rim formed by marcasite (mrc) and pyrite; (d) Sulfide rim on chert comprising by chalcopyrite (cp), galena (gn) and sphalerite; (e) Skeletal marcasite replacing a calcarenite; (f) Interstitial galena (gn) in pyrite.

6 Sulfur isotope data

Figure 4 shows S isotope analyses on sulfides hosted within the TBU overlying the Tara Deep deposit. The results show a wide range of δ34S values from -37.4 to +44.2‰.

Frambooidal laminated pyrite (Figs 2a, 3a and 3b) shows a wide range of low δ34S values from -37.4 to 3.3‰ (mean of -24%) (Fig. 4). The δ34S for interstitial sphalerite (Figs 2a and 3b) is also low, ranging from -32.8 to 7.1‰ (mean of -20.6‰) (Fig. 4).

Pyritized fossils in calcarenite (Figs 2b and 3c) have a broad range of δ34S values from -32.2 to 5.6‰ (mean of -13‰) (Fig. 4).

Marcasite associated with hydrothermal cherts (Figs 2d, 3d and 3e) exhibits higher δ34S values from 5.8 to 44.2‰ (mean of 17.2‰). The δ34S for sphalerite (Figs 2d and 3f) ranges from 7.0 to 15.2‰ (mean of 10.5‰), while chalcopyrite (Figs 2d and 3f) ranges from 17.5 to 36.8‰ (Fig. 4).

Marcasite included in the replacive assemblage (Figs 2c, 3g, 3h and 3i) shows a wide range of higher δ34S values from 0 to 24.5‰ (mean of 10.4‰) (Fig. 4).

7 Discussion and conclusions

Laminated pyrite (Fig. 2a) and pyritized fossils (Fig. 2b) show similar features to other mineral assemblages identified in the lower UDL (Altinok 2005). However, both hydrothermal chert (Fig. 2d) and the replacive assemblage (Fig. 2c) have not been described before.

The geological record (Fig. 2), detailed petrographic analysis (Fig 3) and S isotope compositions (Fig. 4) suggest overlapping of diagenetic and hydrothermal multi-phase sulphide mineralization in the TBU.

The close relationship between organic matter and negative δ34S values in both laminated pyrite and pyritized calcarenites (Figs 3a, 3b and 4) suggests that mineralization was generated by sulfate-reducing bacteria within soft sediments during early diagenesis, close to the seawater-sediment interface.

Marcasite included in the replacive association (Figs 2c, 3g, 3h and 3i) shows a wide range of higher δ34S values from 0 to 24.5‰ (mean of 10.4‰) (Fig. 4).
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Life with Ore Deposits on Earth