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MINERAL RESOURCES TO DISCOVER

Proceedings
Volume 3
Mineral Resources to Discover
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**Set of 4 volumes**
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Cover photograph: Dumagami gold mine open pit with the Bousquet 2 mine headframe in the foreground and the Doyon mine waste rock pile in the background. Doyon-Bousquet-LaRonde mining camp, Québec, Canada. (Photo: P. Mercier-Langevin, Geological Survey of Canada).
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SY03 – IOCG-IOA ore systems and their magmatic-hydrothermal continuum: A family reunion?

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Abstract. The Olympic Dam Cu-U-Au-Ag deposit remains the single largest iron oxide Cu-Au deposit, even after over forty years since its discovery. The deposit is part of the spectrum of IOA-IOCG deposits which are distinguished from other metalliferous deposit types (e.g. porphyry Cu, sediment hosted Cu, volcanogenic massive sulphides, etc) by the presence of iron oxide-alkali metasomatism (Na-Ca-Fe, high temperature Fe$^{2+}$-K, and low temperature Fe$^{3+}$-K-H$_2$O-CO$_2$). At Olympic Dam, hematite-sericite-chalcopyrite-bornite-chalcocite-fluorite-barite has overprinted, and largely obliterated, an earlier assemblage of magnetite-apatite-carbonates-chlorite-pyrite within the deposit. Isochemical Na-Ca-Fe alteration occurs in the least altered parts of the host Roxby Downs Granite. Remnants of Fe$^{2+}$-K alteration (magnetite-K-feldspar) are present in altered Roxby Downs Granite distal to texturally destructive hematite-sericite alteration. Similar to other IOA-IOCG ore deposits, porosity generating albitization also affected the region surrounding Olympic Dam.

1 Introduction

Iron oxide-alkali-alteration produces a wide spectrum of mineralization styles: iron oxide-apatite (IOA), iron oxide Cu-Au-U, polymetallic skarns, and epithermal deposits (Porter 2010; Corriveau et al. 2016; Day et al. 2016; and references therein). Regional clusters of these iron oxide-alkali altered deposits and prospects include, but are not limited to, the Olympic Cu-Au Province (South Australia; Fig. 1), Cloncurry district (Queensland), Great Bear magmatic zone (Canada), St. Francois Mountains Terrane (Missouri), Kiruna district (Sweden), etc. Alteration facies present in these districts systematically change from the regional to deposit scale. Four metasomatic types are recognized in these districts: 1) Na to Ca-Fe, 2) high temperature Fe$^{2+}$-K, 3) low temperature Fe$^{3+}$-K-H$_2$O-CO$_2$, and 4) quartz veins/silicification (e.g. Skirrow et al. 2007; Corriveau et al. 2016; Montreuil et al. 2016).

The importance of albitization as a prerequisite for formation of iron oxide copper gold (IOCG) deposits is mentioned by many authors (e.g. Hitzman et al. 1992; Haynes et al. 1995). Albitization within the Olympic Dam district was briefly mentioned by Creaser (1989) and Davidson et al. (2007). Even though magnetite is present on the peripheries of the Olympic Dam (OD) deposit, hematite-sericite-chlorite-carbonate is the dominant alteration assemblage. The presence of earlier high temperature alteration assemblages (such as Na-Ca-Fe or Fe$^{2+}$-K) has only recently been documented until recently (Mauger et al. 2016; Kontonikas-Charos et al. 2017).

The present study uses whole rock Fe, K and Na assays from diamond drill core samples to demonstrate the presence of albite alteration assemblages, in addition to hematite-sericite-chlorite-carbonate at OD and nearby prospects. Detailed petrographic studies (Apukhtina et al. 2017; Krneta et al. 2016; Kontonikas-Charos et al. 2017; and currently unpublished work) are briefly mentioned to show the widespread occurrence of paragenetically early IOA mineral assemblages associated with OD and nearby IOCG prospects.
2 Geological background

The OD breccia hosted Cu-U-Au-Ag deposit occurs in the central-northern part of the Olympic Cu-Au Province (e.g. Skirrow et al. 2007) which is located on the eastern margin of the Gawler Craton (Fig. 1). Other deposits in the region include the Prominent Hill Cu-Au and Carrapatena Cu-Au-Ag-U deposits. Numerous barren (Snake Gully, Horn Ridge, Phillips Ridge Opal Fields, Town, Burgoyne, Burden Hill) to subeconomic IOCG-related prospects (Acropolis, Wirrda Well, Oak Dam, Island Dam) are also present in the Olympic Dam district. Alteration and mineralization are linked to the ~1600 Ma Gawler Range Volcanics (GRV) and Hiltaba Suite (HS) event (e.g. Skirrow et al. 2007). All OD district prospects occur under a cover sequence of Neoproterozoic to Cambrian sedimentary formations varying in thickness from ~250 to >800 m.

The OD deposit is hosted within the Roxby Downs Granite (RDG, a member of the HIS) and subordinate bedded clastic facies (Fig. 2). Mafic-ultramafic dykes and lavas/sills are also present (Ehrig et al. 2012). The Acropolis prospect consists of magnetite-apatite±biotite±K-feldspar±quartz vein networks in sericite-hematite altered felsic GRV which overlies Donington (~1840 Ma) granitoids. Brecciation is weakly developed and occurs locally (Cross, 1993). The Wirrda Well prospect is hosted within sericite+chlorite altered Donington granitoids which are intruded by ~1840 Ma and GRV-aged mafic-ultramafic dykes. Hiltaba suite granitoids occur immediately to the NE and S of Wirrda Well. Brecciation is more extensive and widespread than the RDG. At Acropolis, a magnetite-apatite±biotite±K-feldspar±calcite±quartz is partly to completely replaced by hematite-sericite-chlorite. Pyrite and chalcopyrite are the principal sulphide minerals, while bornite-chalcocite are present but at low concentrations in both Acropolis and Wirrda Well. The Island Dam prospect is discussed by Keyser et al. (this volume). The barren prospects consist of either Donington and/or HIS granitoids and associated mafic-ultramafic dykes.

3 Approach and results

To determine if the presence of albite-calcisilicate+ magnetite (Na-Ca-Fe) or magnetite-biotite-K-feldspar (Fe²⁺-K) alteration facies could be detected in whole rock assay data of samples from diamond drill holes, nine drill holes along two traverses were selected from OD (Fig. 2) which progress from the least-altered RDG into the ore deposit. Four drill holes from the barren prospects (Phillips Ridge and Opal Fields), all drill holes from Acropolis, two Donington Suite and four HS drill holes from Wirrda Well were also selected for graphical analysis of Fe, K, Na. Alteration styles defined by whole rock K-Na-Fe assays for the selected drill holes are shown in Figures 3-6.

Unaltered RDG (i.e. post-magmatic isochemical alteration or no net hydrothermal addition-subtraction of elements) plots within the dashed box at K ~4.6 wt% and Na ~2.6 wt% (Fig. 3, upper graph). Progressive alteration of plagioclase to sericite has produced a trend towards ~6.5 wt% K. Albitization can be correlated with a trend towards ~5-6 wt % Na. Rocks in which hydrothermal K-feldspar is dominant plot ~>6.5 wt% K. Weakly to intensely hematite-sericite and then hematite altered samples show a trends from ~6.5 wt% K towards the origin. Albitized alteration has affected the RDG and is also indicated where K/Na ratios (Fig. 3, lower graph) are <1.76. Weakly to intensely Fe-oxide altered samples plots along the arc from >5 to >60 wt% Fe.

Albitization (without significant overprinting Fe-oxide metasomatism) occurs in the unmineralized HIS granites at PR and OF (Fig. 4).

At Acropolis, a magnetite-apatite±K-feldspar+biotite (Fe²⁺-K) alteration assemblage has been extensively overprinted by an assemblage of hematite-sericite-chlorite-carbonate (Fe³⁺-K-H₂O-CO₂). The felsic-mafic GRV and Donington Suite granitoids have been affected by weak albite alteration (Fig. 5).

The HIS granites (WRD3 and WRD6) located east of Wirrda Well are weakly albitized (Fig. 6). Plagioclase in the Donington Suite granitoids (WRD46 and WRD33) at Wirrda Well is replaced by K-feldspar as well as sericite and minor albite altered to sericite. Hydrothermal K-feldspar occurs in HIS granites intruding Donington Suite granitoids (WRD19) along the NE margin of the prospect.

Figure 2. Simplified geological plan showing the basement (at -350 mRL) rock/alteration types. The outer limit of the Olympic Dam Breccia Complex (ODBC) is gradational with the Roxby Downs Granite (RDG) and is defined by the last occurrence of magmatic biotite, when progressing from the RDG into the ODBC (modified from Ehrig et al. 2012).
Figure 3. Whole rock analyses K vs Na (upper graph) and Fe vs K:Na ratio (lower graph) alteration trends for the RDG and ODBC. RD2274 is likely a hybrid of the RDG and HR granite in which weak albite alteration is present. Inset is a photograph (image ~50 mm wide) of least altered RDG.

Figure 4. Whole rock analyses K vs Na and Fe vs K:Na ratio alteration trends for barren, albitized HIS felsic intrusions at PR (PD4) and OF (OFD1,2,3). Inset photos (width ~ 47 mm).

Figure 5. Whole rock analyses (n = 5075) K vs Na and Fe vs K:Na ratio alteration trends for all of the drilling within the Acropolis IOA-IOCG prospect. The red dots are the data from ACD12, a HS granite. Inset photos (width = 47mm) magnetite+apatite+K-feldspar+quartz vein cutting intensely sericite altered felsic GRV lava.

4 Discussion and implications

Albitization (Na-Ca-Fe alteration) creates porosity, enhances permeability, and can lead to element remobilization (e.g. Haynes 1972; Hitzman et al. 1992; Haynes et al. 1995; Kontonikas-Charos et al. 2017, and references therein). It is clearly a precursor alteration style required for the formation of IOCG-IOA deposits (e.g. Williams et al. 2005; Porter 2010; Corriveau et al. 2016). Na-Ca-Fe alteration occurs in the Olympic Cu-Au Province (e.g. Skirrow et al. 2007), but, until recently, has been mentioned only rarely in the Olympic Dam district (e.g. Creaser 1989; Davidson et al. 2007). Kontonikas-Charos et al. (2017) detailed petrographic study of the RDG was the first to describe the isochemical formation of hydrothermal albite and K-feldspar within apparently geochemically unaltered RDG. During albization of the RDG, porosity was created and coarsening of minerals occurred due to the release of metals. Krneta et al. (2016) linked albrite alteration to the transition of magmatic apatite to hydrothermal apatite at OD. Remnants of early magnetite-apatite associated mineral assemblage were described in the deepest drill hole far from hematite-sericite dominated altered facies at OD (Apukhtina et al. 2017).

Albitization (without significant overprinting Fe-oxide metasomatism) affected the unmineralized HIS granites at
PR and OF prospects, as well as the subeconomic Acropolis and Wirrda Well prospects. High temperature Fe$^{2+}$-K followed by Fe$^{3+}$-K alteration at Acropolis and Wirrda Well partially overprint the Na-Ca-Fe altered facies and early magnetite apatite vein networks.

Simple K-Na-Fe scatterplots supported by detailed petrography can be used to identify various iron-oxide-alkali alteration types which are often difficult to recognize when logging and mapping.

Figure 6. Whole rock analyses (n =3245) K vs Na and Fe vs K:Na ratio alteration trends for the Wirrda Well IOA-IOCG prospect. Drill holes WRD33 (mineralized) and WRD46 (unmineralized Donington Suite granitoids) are extensively altered and located within the prospect. The other drill holes (WRD3, 5, 6, 19) are HS granitoids. WRD 3 and 6 are located -22 km NE and -14 km E of the prospect center, respectively. WRD 6 and 19 are on the SE and NE edges of the prospect. The upper inset is a BSE image (~200 µm wide) showing magnetite, apatite, chalcopyrite and uraninite. The lower photograph (height ~47 mm) shows apatite-calcite veins which cuts chalcopyrite+pyrite-bearing magnetite+hematite+apatite breccias.

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A magmatic flotation model that genetically links iron oxide – apatite and iron oxide – copper – gold deposits

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Abstract. Trace element concentrations in magnetite, hematite, pyrite and apatite, Fe and O stable isotope abundances of magnetite and hematite, and H isotopes of magnetite and actinolite from IOA and IOCG deposits in the Chilean Iron Belt are used to develop a new genetic model that explains IOA and IOCG deposits as a continuum produced by a combination of magmatic and magmatic-hydrothermal processes. Together, the data are consistent with a model where 1) magnetite and apatite crystallize as near-liquidus phases from silicate melt; 2) magnetite and apatite crystals serve as nucleation sites for gas bubbles and promote volatile saturation of the melt; 3) the volatile phase coalesces and encapsulates magnetite and apatite, and scavenges metals, S and P from the melt; 4) the magnetite-apatite-fluid suspension ascends from the host magma during regional extension; 5) as the suspension ascends, magnetite and apatite grow from the fluid and record an evolving magmatic-hydrothermal composition; 6) during ascent, magnetite and apatite are deposited to form IOA deposits; 7) the further ascending fluid transports Fe, Cu, Au, S where hematite, magnetite and sulfides precipitate to form IOCG deposits. The model explains the globally observed temporal and spatial relationship between magmatism and IOA and IOCG deposits.

1 Introduction

Iron oxide – apatite (IOA) and iron oxide – copper – gold (IOCG) deposits are commonly spatially and temporally related to each other and magmatism in subduction zone environments, and commonly hosted in magmatic rocks. Iron-oxides in both deposit types are Ti-poor relative to Fe-oxides in igneous rocks. Sulfides enriched in Cu and Au are present in both deposit types, although modally are more abundant in IOCGs. Mineralization is structurally controlled, notably in the Chilean Iron Belt (CIB) where mineralization occurred in regional-scale, trench-parallel faults. In general, temperatures of mineralization are 500 to >650 °C for magnetite and apatite in IOAs, and 400 – 550 °C and 300 – 400 °C, respectively, for Fe-oxides and sulfides in IOCGs. In this study, we interrogate the chemistry of magnetite, hematite, apatite, actinolite and pyrite from the Los Colorados IOA deposit, and magnetite and hematite from the Mantoverde IOCG deposit in the CIB to develop a new model that explains the formation of IOA and IOCG deposits as a continuum resulting from combined magmatic and magmatic-hydrothermal processes.

2 Samples

Thirteen samples from two drill cores were collected from the western ore body of the Los Colorados IOA deposit, and twenty samples from the Mantoverde IOCG deposit were collected from one drill core just north of the Mantoverde Norte pit.

3 Methodology

We used electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS) to quantify the composition of magnetite, apatite, actinolite and pyrite in samples from Los Colorados, and magnetite and hematite from Mantoverde. Solution MC-ICP-MS following the double-spike method of Millet et al. (2012) was used to measure Fe isotopes in magnetite and hematite. Laser fluorination gas isotope ratio mass spectrometry in dual inlet mode was used to measure O isotopes in magnetite and hematite (Bilenker et al. 2016).

4 Chemistry of magnetite, actinolite, apatite and pyrite

4.1 Magnetite chemical zoning

EPMA X-ray mapping reveals that magnetite grains are strongly zoned (Fig. 1). The concentrations of Ti V, Al, and Mn are the highest in magnetite cores and
progressively decrease toward the magnetite rims (zones 2 and 3), a trend that is consistent with magnetite that crystallized at progressively cooler temperatures. When plotted on the magnetite discriminant diagram from Nadoll et al. (2014), the trace element signature of magnetite is consistent with growth from an evolving magmatic-hydrothermal fluid.

Figure 1. a Ti concentration map reveals highest Ti in magnetite cores. b Ti, V, Al and Mn in magnetite progressively decrease from core (Zone 1) to rim (Zones 2, 3). The green star in the porphyry field represents the average [Al+Mn] vs. [Ti+V] composition of all magnetite analyses. The colored arrow in b indicates expected change in [Al+Mn] vs. [Ti+V] for magnetite growing from a cooling magmatic-hydrothermal fluid.

4.2 Comparison of magnetite chemistry with igneous and hydrothermal magnetite

Nadoll et al. (2015) proposed that the concentrations of Ti and V in magnetite can be used to discriminate magnetite from among igneous, magmatic-hydrothermal and low-temperature hydrothermal sources. Magnetite from Los Colorados overlaps with igneous and magmatic-hydrothermal magnetite (Fig. 2).

Figure 2. V and Ti concentrations in magnetite from Los Colorados are plotted against global fields for magnetite from igneous rocks and low-temperature hydrothermal environments based on data from Nadoll et al. (2014).

4.3 Iron and oxygen stable isotopes

The ratios of $^{56}$Fe/$^{54}$Fe ($\delta^{56}$Fe relative to IRMM-14) and $^{18}$O/$^{16}$O ($\delta^{18}$O relative to SMOW) for magnetite samples from Los Colorados and Mantoverde plot within the global range for magnetite from igneous rocks, indicating that Fe and O in both deposits are derived from a magmatic source reservoir (Fig. 3).

Figure 3. Fe and O stable isotopes data for magnetite indicate a magmatic source for Fe and O. The pink box represents the global range for igneous magnetite.

4.4 Trace element abundances in pyrite

Pyrite from Los Colorados contains elevated concentrations of Co, Ni, Cu, Au, Ag, and As, and is compositionally similar to pyrite from the Mantoverde and Ernest Henry IOCG deposits, and Aguablanca magmatic Cu-Ni sulfide deposit (Fig. 4). The trace element characteristics of pyrite from Los Colorados are consistent with an intermediate to mafic magma source for metals in pyrite (Fig. 4).

Figure 4. Co and Ni concentrations in pyrite from Los Colorados shown as triangle and square symbols in both panels (triangle = pyrite in main ore body; square = pyrite in host diorite). The colored fields in each panel correspond to the pyrite data for Mantoverde, Ernest Henry, and Aguablanca. See Reich et al. (2016) for data sources.

4.5 O and H isotopes in magnetite and actinolite

The difference in $\delta^{18}$O for magnetite and actinolite ($\Delta^{18}$O actinolite-magnetite) from Los Colorados is 4.10‰, which yields a calculated minimum formation temperature of
630 °C. The δD (H/D relative to VSMOW) of magnetite and actinolite are -53.5 ±1.5‰ and -59.3 ±1.7‰, respectively, which indicate a mantle source for H. Published fractionation factors between magnetite-andesite and magnetite-water (Δ18O magnetite-andesite = -4.0‰ and Δ18O magnetite-water = -4.5‰) yield δ18O values of 6.60‰ and 7.10‰ for the parent magma and co-existing water, respectively. These values are consistent with subduction zone magmas and magmatic-hydrothermal fluids (Taylor 1968; Bindeman 2008).

4.6 Halogen zoning in apatite

Apatite grains from Los Colorados are zoned with respect to halogens and water. The highest F concentrations are in grain cores, and systematically the Cl/F ratio increases toward grain boundaries. Chlorine is also enriched proximal to cracks. The highest F concentrations overlap F-rich apatite crystallized from silicate melt, and the highest Cl concentrations overlap apatite crystallized from magmatic-hydrothermal fluid.

5 Inclusions in magnetite

5.1 Fluid inclusions in magnetite

Halite-saturated fluid inclusions are present in zone 2 rims of magnetite grains from Los Colorados (Fig. 4). The inclusions are small, typically <5µm, and indicate that magnetite zone 2 grew in equilibrium with a brine.

5.2 Mineral inclusions in magnetite

Transmission electron microscope (TEM) analyses reveal nanometer-sized inclusions of diopside (MgCaSi2O6), richterite (Na(Ca,Na)(Mg,Fe)5[Si8O22](OH)2), and Ti-rich magnetite (mangetite-ulvöspinel), and domains of hercynite (FeAl2O4) in magnetite zone 1 cores from Los Colorados. These observations require that magnetite zone 1 cores crystallized at ≥860 ±15 °C.

6 Magnetite chemistry from Los Colorados IOA and Mantoverde IOCG deposits

The concentrations of [Al + Mn] vs. [Ti + V] in magnetite from Los Colorados and Mantoverde are plotted on the magnetite discriminant diagram in Fig. 6. The scatter among samples from Mantoverde is consistent with δ56Fe and δ18O data that indicate a small degree of dissolution-reprecipitation of magnetite. Despite the scatter, the combined data are consistent with magnetite crystallization from a cooling magmatic-hydrothermal fluid in both deposits.

Figure 6. Magnetite from Los Colorados and Mantoverde plotted on the magnetite discriminant diagram from Nadoll et al. (2014). Arrow indicates expected change in [Al+Mn] vs. [Ti+V] for magnetite growing from a cooling magmatic-hydrothermal fluid.

7 A new genetic model that links IOA and IOCG deposits

Here we present a new genetic model that explains iron oxide – apatite and iron oxide – copper – gold deposits as a single continuum that forms by a combination of magmatic and magmatic-hydrothermal processes.

1) Magnetite and apatite microlites crystallize as near-liquidus phases in oxidized, intermediate-mafic silicate melts. Magmatic magnetite will be enriched in trace elements such as Ti, V, Mn and Al. The magmatic apatite will be enriched in F, having a high F/Cl ratio.

2) During magma decompression, magnetite and apatite surfaces promote nucleation of gas bubbles from the silicate melt, and bubbles nucleate on the surface of these crystals (Hurwitz and Navon 1994) (experiments demonstrate that bubbles do not nucleate on silicate minerals; Gualda and Ghiorso 2007). As volatile exsolution proceeds during decompression, the bubbles coalesce and sweep up magnetite and apatite microlites, forming a crystal-fluid suspension. The bulk density of the fluid suspension is less than the density of the surrounding magma as long as the suspension is ≤37 vol% magnetite, and the suspension will ascend buoyantly via channels that develop as the magma solidifies.

3) Chlorine, S, P and metals (Cu, Au, Co, Ni) partition...
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efficiently from the silicate melt to the fluid. Experiments show that the fluid will have a high Co/Ni ratio. The magmatic-hydrothermal fluid chemistry will be dominated by FeCl₂, KCl and NaCl. Experiments show that at 800 °C and 140 MPa the fluid contains ~6 wt% Na, ~11 wt% K and ~7 wt% Fe (Simon et al. 2004). Model calculations show that as the fluid ascends and decompresses from 140 to 110 MPa, the concentrations of Na and K increase to 14.0 ± 0.8 wt% and 15.0 ± 1.6 wt%, whereas Fe decreases to 6.4 ± 0.6 wt%. Thus, during ascent, magnetite microlites continue to grow, sourcing Fe from the decompressing and cooling magmatic-hydrothermal fluid. Likewise, apatite continues to grow, becoming more Cl-rich as it grows from the magmatic-hydrothermal brine. This is consistent with the presence of brine inclusions and decreasing concentrations of Ti, V, Mn and Al in magnetite zone 2, and increasing core-to-rim Cl/F ratios of apatite at Los Colorados. Increasing Na and K concentrations of the brine during decompression reduce the potential for sodic and potassic alteration, neither of which is observed at Los Colorados.

4) During ascent along pre-existing faults, magnetite and apatite will reach neutral buoyancy and drop out of the fluid suspension to form a magnetite-apatite ore body that is concordant with the fault, and depending on the local porosity and permeability of the host rock, the fluid suspension may percolate laterally into the host rock forming disseminated mineralization, which is commonly observed in IOAs.

5) The fluid that cools at this level of neutral buoyancy can precipitate sulfides, notably pyrite that will scavenge metals from the fluid, resulting in pyrite with a high Co/Ni ratio.

6) For a rapidly ascending fluid, a significant amount of the suspension will continue to ascend. As the fluid evolves to lower pressure and temperature, it saturates with magnetite and sulfides to form an IOCG deposit.

Conclusions

The chemistry of magnetite, apatite, actinolite and pyrite from the Los Colorados iron oxide – apatite deposit, and magnetite and hematite from the Mantoverde iron oxide – copper – gold deposit fingerprint a magma source for the ore fluids responsible for mineralization. Together, the chemical signature of the modally dominant minerals from both deposits is consistent with IOA and IOCG deposits forming from a single evolving (decompressing, cooling) magmatic-hydrothermal ore fluid. The model presented requires rapid decompression of the ore fluid and plausibly explains the textures and chemistry of the enigmatic ore bodies at El Laco, Chile.

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The roots and tops of magnetite-apatite mineralization: evolving magmatic-hydrothermal systems

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Abstract. Magnetite-apatite deposits form a well-defined type of mineralization characterized by the presence of a core of massive magnetite ± apatite with an extensive aureole of alkali-calcic alteration hosting a low grade mineralization. Geology and geochemistry suggest that these deposits are the product of the crystallization of oxidized water-bearing iron-rich melts that separated from a parental silicate magma. The temporal and vertical evolution of these systems is controlled by the timing and depth of separation of large amounts of aqueous fluids, a process that leads to the formation of complex magmatic-hydrothermal systems. These magnetite-apatite systems grade upwards into bodies of massive apatite or an extrusive magnetite-apatite mineralization. A key feature of this style of mineralization is the formation of large breccia pipes and diatremes that are related to melt degassing at shallow depths.

1 Magnetite-apatite deposits

Magnetite-apatite (MtAp) rocks form a well-defined group of ore deposits characterized by the presence of massive magnetite with variable amounts of F-apatite, diopside/actinolite, and scapolite; this type of massive orebody has sharp non-replacive contacts with the host rocks, which are usually affected by a large aureole of alkali-calcic hydrothermal alteration that is zoned around the massive mineralization. They typically have a characteristic mineral assemblage including K-feldspar/albite, diopside/actinolite and scapolite with a low grade-mineralization in breccias, stockworks or disseminated ore. All these deposits are poor in sulphides and quartz but have variable amounts of anhydrite. In detail, the massive magnetite mineralization form vertical ellipsoidal pipes or lenses controlled by major transcrustal faults; only when located at or near the surface form stratiform deposits.

Despite not being as economically significant as banded iron formations (BIF), they can form large deposits such as Kiruna (Sweden) and as well as several other medium-sized ones clustered in the Coastal Cordillera of the Andes, Missouri, the Urals, China, and Iran. Furthermore, some of them are potential sources of Co and REE. Despite grouped within the Iron Oxide-Copper-Gold (IOCG) style of mineralization (Williams et al. 2005), MtAp deposits form an independent group that is easily discernible from the dominantly replacive sensu stricto IOCG deposits.

The existence of melt inclusions and crystallized magmas (nelsonite) with a composition similar to MtAp deposits, the high temperature of formation, the geologic relationships and the common presence of structures similar to that of crystallized igneous rocks suggest that these rocks are the product of the crystallization of iron-rich melts (Frietsch 1978; Naslund et al. 2002; Tornos et al. 2016).

2 The roots of the system: Immiscible iron-rich melts

There is widespread evidence that immiscible P-bearing iron-rich melts are present in different magmatic systems within the Earth’s crust (e.g., Clark and Kontak 2004; Jakobsen et al. 2005). Recent work (Kamenetsky et al. 2013) shows that there is a solvus surface between Fe-rich melts enriched in Ca, Mg, Ti and P, and silica-rich melts enriched in Al, Na and K. Water and volatiles are strongly fractionated into the Fe-rich end member (Lester et al. 2013). The ultimate cause of melt immiscibility can be crustal contamination by P-, Fe- or silica-rich rocks (Philpotts 1967). In the Andes, the Sr-Nd isotope geochemistry of MtAp ores tracks the composition of the underlying basement and in several sites it is likely that the primitive andesitic magmatism interacted with P-rich evaporite-bearing sedimentary rocks.

The shape of the solvus is critical for the formation of the MtAp mineralization; only systems crystallizing at decreasing temperatures or with high degrees of crustal contamination will form immiscible iron-rich and rhyolite
Magnetite occurring as microphenocrysts or in melt inclusions in the parental rocks, as well as sometimes in the alkali-calcic hydrothermal assemblage, are enriched in Ti (≈2 wt%), commonly containing exsolution lamelae of Ti-rich oxides (Velasco et al. 2016). These major differences cannot be due solely to changes in the temperature-fO2 but are interpreted as controlled by the Kd between the iron-rich melt and the exsolving volatile (P- or F-rich) hydrothermal fluids or by mineral equilibria involving Ti-bearing magnetite, titanite or rutile. The last two minerals are widespread in the massive MtAp mineralization and the host rock hydrothermal alteration.

![Figure 1. Drops of magnetite showing no chemical zonation and enclosed in an aureole of hydrothermal (alkali-calcic) alteration with the host microdiorite. Magnetite shows abundant exsolution lamelae of ulvöspinel and is intergrown with titanite (Los Colorados Mine, Chile).](image)

### 3 Water separation and melt crystallization

The solidus temperature of an iron-rich melt strongly depends on the phosphorous, fluorine, and water contents, which significantly lower the temperature of crystallization from ca. 1600°C to less than 1000°C. The crystallization of an almost monomineralic magnetite rock is due to the high oxygen fugacity and low aSiO2 of the melt, something that inhibits the formation of most iron-bearing silicates; when present, they often form an external zone of coarse-grained actinolite accompanied by interstitial magnetite. After the crystallization of magnetite, only apatite and small amounts of actinolite/diopside can crystallize.

One of the most striking features of these deposits is the highly variable Ti content of the magnetite. While the classical nelsonite has Ti-rich magnetite, magnetite of the MtAp mineralization is usually regarded as impoverished in Ti (<=5000 µg/g) (Dare et al. 2015; Knipping et al. 2015; Velasco et al. 2016; Broughm et al. 2017; Kołodziejczyk et al. 2017). Despite that is generally true, the Ti content of magnetite crystallized from immiscible melts can be very low as has been described in several localities. In MtAp deposits it varies significantly between the different generations of magnetite crystallization.

If iron-rich melts behave similar to silicate melts, the ascent and later crystallization of the magnetite rock should promote the exsolution of large amounts of aqueous fluids enriched in incompatible elements (Na, K), volatiles and abundant Fe. As in other magmatic-hydrothermal systems, when water exsolution takes place at intermediate to shallow depths (i.e., <4 km) and above the two-phase surface, it will separate in two immiscible phases, a dominant low density vapour carrying most of the volatiles and a residual relatively immobile brine enriched in elements that form chloride complexes (Driesner and Heinrich 2007); the relative proportion, and the salinity, of the immiscible fluids depends on the depth but in very shallow environments this process can form small amounts of an (hydro)-saline melt as has been described in El Laco by Broman et al (1999) accompanied by large amounts (>99 wt%) of a low density gas. Reaction of the high density chloride-rich brine with the host rock would produce the alkali-calcic alteration observed around the massive magnetite-apatite zone and associated low grade mineralization while low-density gas would tend to flow upward. A mixture of gas with the melt would ascend in a form similar to that described by Woods and Cardoso.
(1997) and promote the formation of flows of vesiculated magnetite and explosive volcanism as observed at El Laco or Cerro del Mercado (Mexico); this mechanism is predicted to be more important and efficient for the upflow of the iron-rich melts than tectonic stress in shallow systems. Eventual reaction of this gas with surficial waters would produce large zones of steam heated alteration such as is observed at El Laco (Tornos et al 2016).

The extent of the hydrothermal alteration zone accompanying the MtAp mineralization is significantly large, up to 5-10 times the size of the massive ore. In the Coastal Cordillera of the Andes, the alkali-calcic alteration shows a marked but gradual zonation with an internal zone in which actinolite, biotite, K feldspar and variable proportions of scapolite coexisting with stockwork- and breccia-like magnetite mineralization; locally, there are zones enriched in granite and epidote that likely reflect the existence of more oxidizing fluids. The proportion of calc-silicates and the K/Na ratio of the feldspars decrease outwards. In the outermost part of the aureole of hydrothermal alteration, the magnetite occurs disseminated in the altered groundmass. This alteration is similar to that found in IOCG deposits but the major difference is the lack of sulphides other than rare pyrite. The outmost hydrothermal zone consists of propylitic alteration.

Sulphur is abundant in these systems but in the oxidized form of anhydrite. Anhydrite is found in the melt inclusions within the parental andesite-diorite but also makes up a significant part of the mineral assemblage in several of the deposits. This suggests that the lack of sulphides in these rocks is due to the oxidized nature of the iron-rich melts which inhibits the formation of sulphides.

**Figure 2.** Breccia with oriented fragments of andesite with alkali-calcic alteration supported by apatite (Maria Ignacia Mine, Chile).

Magnetite-apatite deposits show a marked vertical continuum; the deep part of the systems is dominated by massive magnetite poor in vesicles and with the fluor-apatite in irregularly distributed pods or finely disseminated, or absent. The upper zones are characterized by the presence of up to meter-sized crystals of fluor-apatite in bands or veins – usually in the selvage of the bodies - showing unidirectional growth structures. These textures as well as the presence of melt and high and low density fluid inclusions recording complex processes of silicate and water immiscibility (Velasco and Tornos 2009). This suggests that these rocks formed during the separation of aqueous fluids from a melt in genesis similar to that of pegmatite in felsic magmatic-hydrothermal systems.

### 3 The tops of the system

The crystallization at depth of the magnetite ± apatite rock leave a volatile-rich residual melt that crystallizes in the massive apatite ± actinolite rocks that sometimes cap sub-outcropping mineralization (Fig. 2). Here, coarse grained apatite coexists with actinolite and minor amounts of ilmenite and hematite and forms homogeneous bodies along fractures or forms the groundmass of large magmatic-hydrothermal breccia pipes. The presence of these massive apatite-rich bodies suggest that here the system never reached the surface.

However, the high fluid pressure generated during the upflow and crystallization of MtAp rocks allows many magnetite-apatite systems to reach the surface, producing local extrusive magnetite lava flows, such as those described in El Laco and Cerro del Mercado, or breccia-diatreme complexes. Along with the well-described example of Olympic Dam there are abundant examples of magnetite-apatite deposits forming part of diatreme breccia complexes including Abovian (Armenia), Gushan (China), Bafq (Iran), Artilleri and Peña Colorado (Mexico), Tunguska basin (Russia), El Laco and perhaps the Per Geiger deposit (Kiruna). Since these breccias are located in the top part of MtAp mineralizing systems it is very likely that many of them have been eroded away. At El Laco and Artilleri the tops of the systems are well preserved as possible maars or crater lakes. At Artillo, the subaqueous pyroclastic deposits include welded fragments of the immiscible silicate melt (Levresse et al, this volume). In some of these extrusive deposits the amount of apatite is quite low, something probably related to degassing of the melt in the atmosphere.

### 4 Superimposed alterations

Downward crystallization and cooling of the magnetite-apatite rocks lead to the collapse of the magmatic-hydrothermal system and the hydrothermal alteration of the massive MtAp ores. This widespread phenomenon has sometimes produced a pervasive disturbance of the earliest rocks, masking the original magmatic features. In some localities, the MtAp rocks are crosscut by stockwork-like veins of hydrothermal magnetite and the early fluor-
apatite is replaced by Cl- and CO3-rich apatite. Later, calc-silicates and feldspars are locally replaced by chlorite, carbonates, quartz and clays, and magnetite by hematite.

In the deposits studied there are no evidences of transition from MtAp mineralization to coeval IOCG mineralization. Some of the MtAp rock, as well as other magnetite-rich rocks, act as a trap for later superimposed genetically unrelated hematite-rich Cu-Au (IOCG) mineralization, as can be observed in some of the major hematite-rich Cu-Au deposits of the Coastal Cordillera of Chile such as Mantoverde, Sierra Norte or Cero Negro Norte.

5 Conclusions

The geology and geochemistry of several MtAp deposits reveal some common features that suggest that these deposits represent complex and unusual magmatic-hydrothermal systems related to the crystallization of immiscible iron-rich melts that separated from parental intermediate to mafic silicate melts. Only systems showing a significant degree of melt immiscibility can form large volumes of iron-rich melts that locally flow upwards along major faults and produce large volumes of aqueous fluids that are responsible of the formation of pegmatite-like rocks and large maar-diatreme complexes and lava flows when extruding in subaerial environments. Reaction of these fluids with the host rock also produces large volumes of a characteristic alkali-calcic hydrothermal alteration.

These systems are perhaps broadly equivalent to magmatic Cu-Ni deposits in mafic-ultramafic rocks. In both cases, the ultimate cause of melt separation has been interpreted to be crustal contamination. However, in MtAp systems contamination by oxidized crustal rocks produces highly oxidized systems that favour the formation of sulphide-poor magnetite and apatite rocks instead.

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Genetic models of IOCG and IOA deposits from China: Implications for ore genesis and their possible links

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Abstract. Ore genesis of iron oxide-copper-gold (IOCG) and iron oxide-apatite (IOA) is controversial, and different models have been proposed. However, those models have rarely considered the deposits from China. Mesozoic IOA deposits from Eastern China are spatially and temporally associated with subvolcanic dioritic intrusions. The orebodies are mainly hosted within the apical zones of the intrusions and along the contacts between intrusions and overlying volcanic rocks. They are commonly associated with extensive brecciation, Na and Ca-Fe alteration types, and spatial zonation of alteration. The magnetite-apatite assemblages were considered to form from an extremely high-temperature saline magmatic-hydrothermal system, which interacted with the country rocks, of the subvolcanic intrusions. IOCG deposits from Southwest China are hosted in late Paleoproterozoic meta-sedimentary and meta-volcanic rocks in a rift-related basin at the continental margin of the Yangtze Block. Orebodies are generally stratabound and/or structurally controlled. Some deposits contain both true IOCG and magnetite-only orebodies. The ore-forming fluids at the iron-oxide stage are dominantly magmatic in origin, possibly derived from deep-seated magmas, whereas non-magmatic fluids were involved at various degrees during the Cu-sulfide stage. IOA deposits are proximal magmatic-hydrothermal systems formed at a specific condition, whereas IOCG deposits are derived from magmatic fluids that have significantly circulated in country rocks.

1 Introduction

When Hitzman et al. (1992) proposed the first synthesis of the Proterozoic Fe-(Cu-U-Au-REE) deposits, an initial concept of iron oxide-copper-gold (IOCG) deposits, iron oxide-apatite (IOA) deposits were included as the iron-rich end member of this group. A key question is whether a magmatic-hydrothermal fluid that precipitates massive magnetite (IOA ores) will continue transporting significant amounts of dissolved Fe, Cu, and Au to form true IOCG ores, a model recently illustrated for IOA and IOCG deposits in the Great Bear magmatic zone of Canada (Corriveau et al. 2016). However, such possible genetic links between the two deposit types have only been documented in a few settings. In most cases, they remain obscure and controversial (Williams 2010). In the Central Andes and the Great Bear magmatic zone, several studies proposed that IOA deposits may represent the deeper roots of IOCG systems (e.g., Sillitoe 2003; Mumin et al. 2010; Barton 2014; Corriveau et al. 2016; Reich et al. 2016). However, Groves et al. (2010) have suggested that IOCG deposits have different temporal distribution and tectonic settings from IOCG deposits, although both types of deposits are characterized by Na-Ca alteration zones and common association with brecciated rocks. In addition, IOA deposits have also been considered to form from a volatile-rich iron-oxide melt (Tornos et al. 2016) or magnetite-bubble pairs (Knipping et al. 2015) separated from conjugate silicate melts, which were subsequently overprinted by hydrothermal alteration.

Here we present genetic models based on the studies of the IOA and IOCG deposits from China, including the Mesozoic IOA deposits in Ningwu district of Eastern China and the Proterozoic IOCG deposits in the Kangdian district of Southwest China (Fig. 1). We compare them with published genetic models worldwide, and give some constraints on the ore genesis of the two types of deposits.

Figure 1. A simplified geotectonic map of China with locations of Proterozoic IOCG deposits in the Kangdian belt and Mesozoic IOA deposits in the middle and lower Yangtze River belt.
2 Mesozoic IOA deposits in Eastern China

2.1 Geological background

Tens of IOA deposits are hosted within the early Cretaceous volcanic basins of Ningwu and Luzong, along the Yangtze River, Eastern China (Fig. 1). The orebodies are mainly hosted within the apical zones of subvolcanic intermediate to slightly mafic intrusions and/or along the contacts between these intrusions and the overlying country rocks. They are commonly associated with extensively albitized breccias and Na-Ca alteration zones.

Alteration zones commonly extend hundreds of meters to a few kilometers with both vertical and horizontal zonation around the ore-hosting intrusion (Fig. 2; Ningwu Research Group 1978). The inner zone I within the intrusion is characterized by incipient to pervasive albite and possible scapolite. It grades toward an intermediate zone II dominated by actinolite, albite, epidote, apatite, and chlorite. The outer zone III is marked by abundant carbonate, pyrite, and chlorite. Orebodies are mainly hosted within the zone II, where magnetite is spatially associated with actinolite-apatite and/or diopside-anhydrite assemblages. Pyrite ore bodies may occur in zone III in some deposits.

All the deposits have consistent isotopic ages at 131-130 Ma, which are contemporaneous with the emplacement of the shoshonitic subvolcanic intrusions (Mao et al. 2011; Zhou et al. 2013). They are interpreted to have formed under regional lithospheric extension and thinning, and ore metals were derived from basaltic melts sourced from enriched lithospheric mantle (Zhou et al. 2013). The regional extensional event was possibly related to the roll-back and the rotation of the Izanagi plate (Mao et al. 2011).

2.2 Proposed genetic model

These deposits have been mined actively early in the 20th century and have been extensively studied by Chinese geologists. Among them, a synthesis of research outputs was summarized in a book of the Ningwu Research Group (1978) that proposed an integrated genetic model for these deposits (Fig. 2). The key point of this model attributes the ore-forming processes to the evolution of the subvolcanic intrusions. Most of the ore bodies are considered to form by magmatic-hydrothermal processes. These deposits have many similarities to skarn-type Fe deposits. Skarn assemblages of garnet and diopside have been preserved in some deposits. But in most cases, the deposits are characterized by mineral assemblages of magnetite-apatite-actinolite. Ore bodies are mainly hosted along the albitized alteration zones along the contact between the intrusion and country rocks (Fig. 2). It is thus concluded that the IOA deposits in Ningwu most likely formed from an incipient high temperature magmatic fluids (Ningwu Research Group 1978), which is similar to the models proposed by Hildebrand (1986), Mumin et al. (2010) and Montreuil et al. (2016) for the IOA to IOCG systems of the Great Bear mafic magmatic zone, Canada.

Recent studies on fluid inclusions and stable isotopes have shown that the earliest ore fluids were highly saline and extremely high temperature (740-840°C; e.g., Li et al. 2015). Therefore, magnetite was likely precipitated from a volatile-rich salt system during magmatic-hydrothermal transition (Zhao et al. 2016). This interpretation is consistent with field and textural data that magnetite formed slightly later than albitization but coeval withapatite and actinolite which is typical of IOA deposits in many settings (see also Corriveau et al. 2016). However, the exact properties of such a salt system and how it forms are still not well understood at the moment.

Figure 2. A conceptually integrated genetic model for the IOA deposits in Eastern China proposed by the Ningwu Research Group (1978). Note the orebodies mainly occur at the apical zones of the intrusion and/or at the contact zones between the intrusion and country rocks. I, II, and III indicate alteration zonation, see text for details.

3 Proterozoic IOCG deposits in Kangdian

3.1 Geological background

The IOCG deposits in the Kangdian district, Southwest China, are hosted in late Paleoproterozoic (1.74 to 1.68 Ga) meta-sedimentary and meta-volcanic rocks (Zhao and Zhou 2011; Zhou et al. 2014). The ore-hosting rocks were formed in a rift-related basin at the continental margin of the Yangtze Block. Orebodies are generally stratabound and/or structurally controlled with thicknesses ranging from several to tens of meters. They are spatially associated with slightly younger 1.69 to 1.65 Ga mafic intrusions and various sizes of hydrothermal breccia bodies. The paragenetic sequence of the deposits includes pre-ore Na-(Ca-Fe) alteration (stage I), Fe-oxide mineralization dominated by magnetite and
siderite with subsidiary apatite (stage II), and Cu-(Au-REE) mineralization among K-Fe alteration with chalcopyrite, ankerite, biotite, chlorite, with possible bornite and REE minerals (stage III). In many deposits, except for the true IOCG ores, there are also massive and/or banded magnetite ores without Cu-sulfides. These magnetite-only ores commonly contain apatite, and are likely the earlier stage of the IOCG system but without significant overprint by sulfide assemblages.

Recent geochronological studies have shown that the Kangdian belt have multiple tectonothermal-hydrothermal events (Zhou et al. 2014). The late Paleoproterozoic (1.66-1.65 Ga) magmatism is the most important mineralization event to form the major deposits. A late Mesoproterozoic magmatic event (1.08-1.03 Ga) is possibly responsible for another significant mineralization/remobilization in the northern part of the district. These deposits have undergone widespread Neooproterozoic magmatic-metamorphic events, which are prominent for remobilization of Cu-(Au-REE) ores.

Figure 3. A conceptual genetic model of mixing magmatic fluids and basinal brines for the formation the IOCG deposits in the Kangdian district, Southwest China (Zhao et al. 2017).

3.2 A genetic model for Kangdian IOCG deposits

The Kangdian IOCG deposits have the following features: a significant volume of breccias, regional scale sodic alteration zones, and structurally controlled and/or stratabound orebodies. Fluid inclusions, stable and radiogenic isotopes studies have shown that the early stage ore fluids are dominantly magmatic in origin, possibly derived from deep-seated magmas (Fig. 3), however, non-magmatic fluids were involved at various degrees during the Cu-sulfide stage. We suggest that mixing of ascending hot magmatic fluids with cooler nonmagmatic fluids effectively led to the saturation and deposition of ore minerals. Iron first precipitated as magnetite, and locally as hematite, mainly within the brecciated zones or preferential structures of the hosting rocks; Cu-Au were more mobile and subsequently became saturated in the country rocks where sulfur saturation (e.g., externally derived sulfur) was available (Fig. 3). Orebodies of different metals may have complex controls in terms of their depth, ore-hosting country rocks, degree of fluid mixing, and at the location of alteration zones.

4 Discussion and implications

4.1 Ore genesis of IOA deposits

It has been shown that IOA deposits display remarkably similar styles of alteration and mineralization from district to district and throughout geologic time (Hitzman 2000). Many of the IOA deposits in eastern China display spatial, temporal, and hence genetic relationships to dioritic intrusions in shallow subvolcanic settings. This association is consistent with those typical of IOA deposits worldwide (Hildebrand 1986; Groves et al. 2010). Formation of an extremely high-temperature saline magmatic-hydrothermal system (>800ºC) that interacts with their country rocks in the vicinity of intermediate intrusions are required to form magnetite-apatite ores (Fig. 2), a similar model also proposed and illustrated by Corriveau et al. (2016). The consistent enrichment of Fe, P, and LREE in different locations argue for a common ore-forming process for IOA deposits. We hence suggest that IOA deposits form in a proximal magmatic-hydrothermal system of intermediate subvolcanic intrusions within a specific tectonic setting and/or condition. In Chinese, IOA deposits have been also termed as dioritic porphyry Fe deposits (Ningwu Research Group 1978).

4.2 A link between IOA and IOCG deposits?

There are many similarities between the two deposit types, in terms of high temperature Na-(Ca)-Fe alteration facies and common association with albited breccias (e.g., Corriveau et al. 2016; Montreuil et al. 2016). Many researchers have argued whether IOA deposits represent an iron-rich end member or they are the deep parts of a large IOCG system. However, in contrast to true IOCGs, typical IOA deposits lack economic copper and gold. It is proposed that Cu-sulfides are not saturated/precipitated at this stage of the systems (Corriveau et al. 2016; Reich et al. 2016). Alternatively, a specific high temperature (800-900ºC) saline magmatic-hydrothermal fluid, termed as magmatic hydrosaline liquid (Zhao et al. 2016) or volatile-rich iron-oxide melt (Tornos et al. 2016), fails to transport Cu and Au in IOA systems. In contrast, early stage ore-forming fluids for IOCG deposit may have temperatures of 500-600ºC or started at a slightly higher temperature but were effectively and quickly mixing with external low temperature fluids in a larger scale ore-forming system. In any cases, fluids that form IOCG deposits are significantly
lower than those recorded in IOA deposits. They can be derived from a deep-seated magma chamber (Fig. 3), therefore orebodies may not be spatially associated with igneous intrusions. Some IOCG deposits, e.g. the Dahongshan deposit in the Kangdian district, contain both Fe and Cu-Fe orebodies. A question arises as whether those massive magnetite-only ores should be considered IOA ores. In situ elemental analysis on magnetite show that their magnetite grains have Ti and V contents lower than typical IOA ore (unpublished data), implying they formed from hydrothermal fluids of relatively lower temperature. We hence suggest that IOA and IOCG deposits formed by somewhat similar processes from two related magmatic-hydrothermal systems, but may not be regularly parts of a single system transitional from IOA to IOCG deposits. Tectonic settings may have a first-order control on which types of deposits formed (Groves et al. 2010; Montreuil et al. 2016).

The central Andes metallogenic belt contains roughly contemporaneous large IOA and IOCG deposits (Sillitoe 2003), but there are still slightly different temporal distributions (Groves et al. 2010). Several other major IOCG metallogenic belts have both IOA and IOCG deposits, but they either contain large to small sized IOCG deposits with relatively small IOA deposits (e.g., Gawler, Cloncurry, Carajás, and Great Bear magmatic zone districts; Hitzman et al. 1992; Groves et al. 2010; Corriveau et al. 2016), or have large IOA deposits but small IOCG deposits/prospects (e.g., Norrbotten region; Groves et al. 2010; Martinsson et al. 2016). Besides, IOA deposits commonly predated IOCG deposits in those districts. It again implies a tectonic control on the two types of deposits (Groves et al. 2010; Montreuil et al. 2016).

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Two independent tectonic events controlling AIO and IOCG deposits in the Gällivare area, Sweden

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Abstract. As part of a multi-disciplinary project, the structural setting and evolution of AIO and IOCG mineralizations in the Gällivare area, northern Sweden, have been investigated. Based on structural geological field work and ongoing petrology, geochemistry and geochronology studies, two distinct compressional deformation events are recognised at 1.88 Ga and approx. 1.80 Ga. The first event (D1) is interpreted as the peak metamorphic event which deformed and locally recrystallised AIO ore bodies. This suggests they formed prior to or during D1 deformation. The second event (D2) can be interpreted as a low-pressure, high-temperature hydrothermal event associated with voluminous intrusions, remobilisation of minerals and IOCG-style alteration and mineralization. Consequently, iron and copper-gold mineralizations in the Gällivare area formed in different tectonic events temporally separated by a clear time gap of approx. 80-100 Ma.

1 Introduction

The Gällivare area in northern Sweden is one of the most active exploration and mining areas in Europe. It includes the Malmberget Fe mine, Sweden’s second largest AIO deposit (after Kiruna), and the Aitik Cu-Au-Ag(-Mo) mine, the country’s largest Cu producer (Fig. 1). Several smaller Cu-Au deposits and prospects with IOCG characteristics also occur, including the Nautanen and Nautanen North deposits (New Boliden 2016). Despite ongoing exploration activities, the relationship between Fe and Cu-Au mineralization in terms of structural setting, timing and genesis was so far poorly understood.

As part of a multi-disciplinary project we aim to unravel the structural setting and evolution of AIO and IOCG-style deposits in the Gällivare area, and ascertain what controls deformation and transposition have had on their formation. Based on extensive field work (with a strong focus on structural geology), geochemistry, high-resolution geochronology and geophysical modelling, this ongoing work preliminarily indicates AIO and IOCG deposits in the area are controlled by two independent tectonic events separated by a clear time gap.

2 Regional geological framework

The geology of the Gällivare area and the entire Norrbotten region is the result of a complex geodynamic evolution including repeated extensional and compressional tectonic events and associated magmatism and metamorphism (Wanhainen et al. 2012; Martinsson et al. 2016). The northern Fennoscandian Shield is dominated by 2.8-2.7 Ga rocks that are part of the Archaean Norrbotten craton (c.f. Nironen 1997; Lahtinen et al. 2005). Karelian continental rifting events at c. 2.1 Ga resulted in the formation of greenstone belts comprising basalts and rift-related sedimentary rocks. Besides an aborted NNE-SSW-trending rift-structure, deep, crustal-scale, rift-parallel fault systems were created (Martinsson 1997). The SW-border of the Archaean craton acted as a passive margin during ocean expansion, but at 1.93 Ga there was a change to destructive margin processes (Weihed et al. 2002). Initial SW-directed subduction resulted in the formation of greenstone belts comprising basalts and rift-related sedimentary rocks. Besides an aborted NNE-SSW-trending rift-structure, deep, crustal-scale, rift-parallel fault systems were created (Martinsson 1997). The SW-border of the Archaean craton acted as a passive margin during ocean expansion, but at 1.93 Ga there was a change to destructive margin processes (Weihed et al. 2002). Initial SW-directed subduction resulted in the formation of greenstone belts comprising basalts and rift-related sedimentary rocks. Besides an aborted NNE-SSW-trending rift-structure, deep, crustal-scale, rift-parallel fault systems were created (Martinsson 1997).

In the northern Norrbotten ore province, Svecofennian arc magmatism at c. 1.9 Ga produced syn-extensional, mafic to intermediate volcanic successions and co-magmatic intrusive suites (Fig. 1; Sarlus 2016), with the former units preferentially hosting AIO and IOCG-style mineralization (e.g. Malmberget, Nautanen). Subsequent uplift and erosion resulted in the formation of sedimentary rocks. By 1.81 Ga, eastward subduction along a N-S-oriented continental margin resulted in widespread S-type magmatism and the extensive I- to A-type felsic batholiths of the Transscandinavian Igneous Belt (1.81-1.65 Ga; Weihed et al. 2002 and references therein).

In the Gällivare area, intrusive rocks formed during two distinct magmatic phases (Sarlus 2016). The first phase
includes the Perthite-Monzonite and Haparanda suites (1.89 – 1.86 Ga), whereas the second phase (1.81 – 1.78 Ga) comprises younger granites and related mafic rocks of the Lina suite (Bergman et al. 2001; Sarlus 2016). Peak metamorphism to upper amphibolite facies and retrogression to upper greenschist conditions also occurred at c. 1.88 Ga and 1.80-1.79 Ga, respectively (Bergman et al. 2001). The most prominent structure in the Gällivare area is the Nautanen deformation zone (NDZ) which hosts the Aitik and Nautanen deposits (Fig. 1; Martinsson and Wanhainen 2004; Lynch et al. 2015). Wanhainen et al. (2012) interpreted Aitik as a ca. 1.9 Ga porphyry Cu deposit that was overprinted by a 1.8 Ga IOCG event.

Figure 1. Inset map: Generalized Fennoscandian Shield geology. Geology drawn after Koistinen et al. (2001). Main map: Structural geological map of the Gällivare area. NDZ: Nautanen deformation zone.

3 Structural evolution

The vast majority of supracrustal rocks and parts of the intrusive rocks in the Gällivare area preserve a penetrative tectonic foliation (S1). The foliation is typically defined by the orientation of amphiboles, micas and quartz. Locally, micro-scale isoclinal folding can be observed within the S1-foliation. Where bedding can be observed it often parallels S1 foliations to form a composite S0/1 fabric. In low strain blocks S0 and S1 can locally occur at an angle to each other.

Subsequently, the S1 foliation (and S0/1 fabric) and related D1 structures were affected by an overprinting deformation event D2 and folded into F2 folds (Fig. 2a and 3). No axial planar parallel cleavage can be observed for the folds. Fold geometries vary depending on the distance to the NDZ. Rocks adjacent to the Malmberget deposit were affected by open, mainly symmetric and upright folding. The footwall and hanging wall rocks of the NDZ show tight to isoclinal and asymmetric fold geometries.
The NDZ is a series of sub-parallel, steeply W-dipping, NNW-striking shear zones with reverse kinematics (Fig. 1 and 2b). The reverse shear zones are connected by sub-vertical, 2nd order shear zones. Within the shear zone the majority of fabrics are transposed into a steep orientation forming a composite fabric.

**Figure 2.** Lower hemisphere, equal area stereographic projections with contoured poles to planes. a S1 foliation from the Malmberget deposit. Black line: best fit plane. b Composite foliation within the Nautanen deformation zone. Black line: mean principal orientation.

4 Hydrothermal alterations and mineralizations related to deformation events

The entire area was affected by several generations of hydrothermal alterations. At least two generations of magnetite, hematite, biotite, quartz and amphibole can be observed. The first generation magnetite, hematite, biotite and amphibole typically occur as fine to medium grained lenses and veins defining the S1 foliation. The AIO ore bodies at Malmberget are parallel with the S1-foliation and folded into a SW-plunging, open synform.

A second generation of magnetite, hematite, biotite, quartz and amphibole commonly developed as coarse-grained patches and veins overgrowing S1-foliation. These second generation of minerals occur together with K-feldspar, epidote, garnet, chalcopyrite and scapolite in the vicinity of 1.81 – 1.78 Ga Lina-type intrusive rocks (Fig. 3). The sulphide ore bodies at Nautanen and Aitik are hosted within the Nautanen deformation zone. In general, the Nautanen deposits occur in close proximity to the interlinking 2nd order structures previously described. Sammelin (2011) showed that Au mineralization in Aitik is also controlled by 2nd order structures.

5 Discussion

Based on the new structural data, combined with ongoing petrology, geochronology and geochemistry studies (Sarlus 2016), we can show that rocks in the Gällivare area have undergone two distinct deformation phases.

**Figure 3.** a Folded S1-foliation. b F2-folded quartz vein overgrown by hydrothermal garnet. c Unfoliated granite with coarse grained alteration minerals cutting foliated volcanic rock.
The first deformation phase (D₁) was responsible for the formation of a penetrative and strong S₁ foliation that affected the AIO ore bodies and their host volcanic rocks. Based on its penetrative character, the alignment of amphiboles and cross-cutting relationships with 1.88 – 1.86 Ga intrusive rocks (Sarlus 2016), the D₁ event is interpreted to coincide with regional peak metamorphism (cf. Bergman et al. 2001). This implies that the AIO ores at Malmberget formed prior to, or at the onset of the D₁ deformation, in any case prior to 1.88 Ga.

All D₁-related structures such as the S₁-foliation were subsequently folded into F₂-folds. Within high strain parts of the NDZ, all previous structures were transposed parallel to the shear fabric. The character and distribution of alteration/metamorphic minerals show that a certain degree of remobilization into D₂ structures occurred. For example, biotite, amphibole, magnetite and hematite occur in two generations with the first generation typically strained and aligned parallel with S₁-foliation. This suggests that the first generation of minerals formed prior to or during the D₁ deformation phase whereas the second generation of minerals are typically coarse grained without any preferred orientation or indications of strain. Furthermore, there often is a spatial relationship of 2nd generation minerals to syn-D₂ granitoids and pegmatites.

Therefore, we suggest that the D₁ compressional event was accompanied by a hydrothermal event that both remobilized existing minerals but also formed new mineral assemblages. This is consistent with the IOCG-type overprint at Aitik around 1.8 Ga (Wanhainen et al. 2012) which caused remobilization of magnetite and sulfides, new amphibole-scapolite and K-feldspar alterations and the potential addition of copper and gold.

Based on cross-cutting relationships and the syntectonic intrusive character of the 1.81 – 1.78 Ga Lina-type intrusions, the D₂ deformation event broadly corresponds to the 1.80 – 1.79 Ga deformation and retrogression event of Bergman et al. (2001). Consequently, there is a clear time gap between the formation of major iron and copper mineralizations in the area.

Based on the lack of an axial planar parallel fabric, the overall character of D₂ structures and PT conditions of 200-500 °C and ~1 kbar reported for the IOCG event at Aitik (Wanhainen et al. 2012) we suggest an upper crustal, shallow setting during D₂ deformation. Hence, the D₂ event can be interpreted as a high-temperature hydrothermal event under low-pressure conditions rather than a metamorphic event.

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Fe oxide-Cu-Au mineralization formed during basin inversion: A special skarn or IOCG deposit clan?

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Abstract. The Phanerozoic IOCG deposits, i.e., those formed in the Mesozoic central Andes or the newly-discovered Paleozoic IOCG-like deposits in the Central Asia Orogenic Belt, usually contain skarn alteration and the controversy on ore genesis between skarn and IOCG mineralization was intensively argued. Many features of these deposits, including the uncertain relationship with intrusions, mineralization hosted in submarine volcanic rocks, separated mineralization stages of magnetite and Cu sulfides with remarkable drop of temperatures (over 200°C), critical contribution of seawater and/or basinal brines for the Cu mineralization, all indicate these Fe-Cu (-Au) deposits are not typical skarn deposits but represent a deposit group formed in continental arc environment during basin inversion.

1 Introduction

Most identified IOCG deposits formed in Precambrian and only some in Phanerozoic, among which the Mesozoic Andean IOCG mineralization is well-known (Williams et al. 2005). Recently, the newly-discovered Paleozoic IOCG-like deposits in the Central Asia Orogenic Belt were reported (Liang et al. 2016; Zhao et al. 2016; Zhang et al. 2017). However, due to many of these Phanerozoic Fe-Cu-Au deposits contain skarn alteration, the controversy on ore genesis between skarn and IOCG mineralization was intensively argued. Some summarization and comparison would be necessary to clarify this.

2 Tectonic environment

In the central Andes, IOCG deposits are linearly distributed along the Mesozoic continental rift basins in the Coastal Cordillera of northern Chile and southern Peru. The Central Andean IOCG deposits are mainly Early Cretaceous (ca. 120–100 Ma) with minor Middle-Late Jurassic (ca. 165–155 Ma) (Chen et al. 2013). The major IOCG deposits all formed between 120 and 100 Ma, including Raúl-Condostable and Mina Justa in southern Peru, and Candelaria and Mantoverde in northern Chile (Sillitoe 2003, Chen et al. 2010). Substantial evidence supports a major extensional to compressive tectonic change during late Early Cretaceous in the Central Andes, such as 1) widespread Early Cretaceous intra-/back-arc basin-related volcanism; 2) pervasive low-grade metamorphism in the Lower Cretaceous strata; 3) the Coastal Range formation and uplifting started with increasing erosion/exhumation rates; 4) mylonitic deformation (ca. 100 Ma) at the western boundary of the Coastal Range, such tectonic transition is timely consistent with the formation of large-scale plume in the Pacific Ocean (Chen et al. 2013).

In the NW China (Xinjiang), many Fe-Cu (-Au) deposits are located in the Paleozoic arcs, such as the Aqishan-Yamansu belt in the Eastern Tianshan and the northern margin of East Junggar Terrane in the Chinese Altay. The Fe-Cu deposits in Eastern Tianshan (e.g., Heijianshan, Duotoushan and Shaquanzi) are mainly hosted by the Carboniferous submarine volcanic and clastic rocks of the Tugutublak formations, whereas the major Fe-Cu deposits in East Junggar (such as Qiaoxiahala and Laoshankou) are mainly hosted in the Middle Devonian Beitashan Formation volcanic and sedimentary rocks. Numerous evidence show that a fore/back-arc basin (Kangguer Ocean) existed during the Carboniferous in the Aqishan-Yamansu belt. The Upper Carboniferous Tugutubulak Formation consists of lava intercalated with red sandstone and tuffaceous sandstone, indicating a marine to terrestrial transition, consistent with the final closure of the Kangguer Ocean (Zhang et al. 2016). In the East Junggar, the transform from coastal- shallow marine (Beitashan Formation) to paralic continental sedimentary may suggest the marine regression and intra-(or back-) arc basin inversion in the Middle Devonian (Liang et al. 2016).

3 Ore deposit geology

Most Fe-Cu (-Au) deposits in both central Andes and NW China are located along the regional fault systems and timely associated with regional intrusive rocks, though the relationships between orebodies and intrusions are sometimes not clear in deposit scale. These deposits more or less contain skarn alteration (such as in Candelaria, Duotoushan, Qiaoxiahala), however, some of them lack such alteration but still show similar mineralization style, such as Mina Justa and Heijianshan. The most distinctive feature of the Phanerozoic IOCG (-like) examples is represented by their complicated paragenesis identified in many deposits. For instance, the paragenetic sequence in the Mina Justa Fe-Cu deposit includes: albite-actinolite
alteration, K-feldspar-magnetite alteration, actinolite-diopside-magnetite alteration, early hematite mineralization, magnetite-pyrite-K-feldspar mineralization (main Fe mineralization stage), copper-sulfide mineralization (main Cu mineralization stage) and late hematite mineralization (Chen et al. 2010). The Mantoverde Fe-Cu deposit contains K-Fe metasomatism (main Fe mineralization stage), chlorite-rich hydrolytic alteration, chalcopyrite-bearing specular hematite-cemented hydrothermal breccias and stockworks (main Cu mineralization stage) and late barren calcite-quartz veining (Benavides et al. 2007). In NW China, the Heijianshan Fe-Cu (-Au) deposit includes chromite stage, epidote alteration, magnetite mineralization, pyrite alteration, Cu (-Au) mineralization and late veins (Zhao et al. 2016). The Duotoushan Fe-Cu deposit contains albite-amphibole alteration, garnet-clinoxyroxene alteration, main magnetite mineralization, late sulphide (pyrite-chalcopyrite) mineralization and late vein alteration (Zhang et al. 2017). The Qiaoxihala Fe-Cu deposit contain early skarn, late skarn, magnetite mineralization, magnetite-pyrite mineralization, chalcopyrite mineralization and late veins (Pei Liang, unpub. data).

In these deposits, magnetite dominates the major Fe mineralization stage and Cu mineralization clearly postdates magnetite stage, though minor Cu sulphides could also coexist within the Fe stage in some cases. Pyrite, as another major sulphides occurring in these deposits, commonly coexist with magnetite or chalcopyrite, but is obviously earlier than major Cu mineralization stage in many deposits.

4 Nature of ore-forming fluids

The nature of ore-forming fluids in IOCG deposits (especially in the Phanerozoic examples), including sources and chemical-physical conditions, has been warmly debated in the past decade (see summary in Chen 2013). Although magmatic-hydrothermal fluid is obviously dominated in the magnetite stage, the contribution of external fluids (including seawater and basin brines) to the ore-forming system (especially the Cu mineralization stage) cannot be despised (Williams et al. 2005; Chen 2013).

At Mina Justa and Mantoverde, Fe mineralization stage formed at high temperatures (500-600°C), whereas temperature could decrease to lower than 200°C during Cu mineralization stage (Benavides et al. 2007; Chen et al. 2011). At the Shaquanzi Fe-Cu deposit, fluid inclusions from the Fe mineralization stage homogenized at 573–348 °C, consistent with the magnetite and quartz oxygen isotope thermometric calculations (570–470 °C). Fluid inclusions from the Cu mineralization stage homogenized mainly peaking at 160 °C (Jiang et al. 2017). At Duotoushan, oxygen isotope geothermometers and mineral paragenesis indicate a temperature range of 400 – 520 °C for magnetite stage, and geothermometer calculated by AlIV contents of chlorite from Cu stage gave a temperature range around 210 °C (Zhang et al. 2017). A remarkable drop of temperatures from higher than 500°C at magnetite stage to lower than 200°C at Cu stage is very common in both central Andean and NW China Fe-Cu (-Au) deposits.

Te and Tm temperatures of fluid inclusions from the Andean IOCG deposits indicate high salinity and Ca-rich fluids for the Cu mineralization stage (Chen et al. 2011). Such featured fluids have been also identified in Cu mineralization stages in many Palaeozoic Fe-Cu (-Au) deposits in NW China, such as in Duotoushan (Zhang et al. 2017) and Shaquanzi (Jiang et al., 2017). Minor contribution of such fluids were also identified in magnetite stage in some deposits, such as Heijianshan and Qiaoxihala Fe-Cu-Au deposits (Liandang Zhao, Pei Liang, unpub. data). Combined with low-temperatures of Cu mineralization stages, a possible fluid source of seawater or basinal brines was proposed in many cases, which is supported by systemic stable isotope studies, such as heavy sulfur isotopic compositions (Benavides et al. 2007; Chen et al. 2011; Zhang et al. 2017; Liandang Zhao, unpub. data).

5 Comparison with skarn

Many magnetite-dominated IOCG deposits, such as Hillside, Ernest Henry, Raul-Condestable, Candelaria and Sin Quye, share some skarn-like alteration features such as widely developed garnet and clinopyroxene, however, they cannot be simply classified as skarn deposits due to many distinct features from skarn-type mineralization. The Phanerozoic IOCG or IOCG-like deposits in both Andes and NW China show uncertain relationships with skarn alteration, as some of them contain typical skarn minerals but some not, indicating skarn alteration is not a pre-requisite for such Fe-Cu (-Au) mineralization.

Most skarn deposits are timely and spatially associated with intrusions, with mineralization hosted dominantly by skarn alteration developed in previous carbonates and minor in endoskarn in intrusive rocks. However, the Phanerozoic IOCG deposits are almost all hosted by submarine volcanic or volcanic-sedimentary units, many of them lack of direct relationship with intrusive rocks but all contain Fe, Cu and sometimes Au mineralization. Although sulfides are commonly later than magnetite mineralization in most skarn systems, only Cu mineralization clearly postdates magnetite in IOCG deposits and pyrite could occur extensively in both magnetite and Cu stages. Temperatures in normal skarn systems could show obvious decreasing from early Fe stage to sulfide stage, but over 200°C remarkable drop of temperature is very rare in skarn deposits but common in IOCG systems, which is hard to be interpreted using single cooling ore-forming process applied to skarn mineralization. Furthermore, the critical contribution of
external fluids, especially seawater and/or basinal brines, in the ore-forming fluid system during Cu mineralization stage and even minor in the magnetite stage in these Fe-Cu (-Au) deposits, is very different from the dominant magmatic-hydrothermal fluids in skarn systems, although minor involvement of external fluids, usually meteoric water, was also identified in some skarn deposits. The last but most important, all these features, especially the nature of fluids in Phanerozoic IOCG deposits, can be well explained by the ore-forming environment, i.e., basin inversion in continental arcs, either in the Mesozoic central Andes or in the Palaeozoic Central Asia Orogenic Belt (including Xinjiang, NW China).

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Post-1590 Ma modification of the supergiant Olympic Dam deposit: links with regional tectono-thermal events

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Abstract. The supergiant Olympic Dam Cu-U-Au-Ag deposit is currently regarded as having formed shortly after the emplacement of the host granite at ca. 1590 Ma. Increasing evidence, however, points to it having been modified multiple times since its initial formation and the mineralisation possibly upgraded. The presence of brecciated sedimentary rocks within the Olympic Dam breccia complex that are younger than ca. 1590 Ma, and which, also contain later secondary minerals, connects Olympic Dam with later basin sediments and infers further tectonic activity 100s of my after its initial formation. The correlation of the post-1590 Ma mineral growth with the ca. 1300-1100 Ma Musgravian Orogeny indicates this event may have contributed to the development of Olympic Dam into the deposit it is today.

1 Introduction

The Olympic Dam (OD) deposit is a flagship deposit of the iron oxide-copper-gold deposit class (Hitzman et al. 1992), though it is distinct from other deposits by virtue of its supergiant size and polymetallic tenor. The deposit is hosted within a large breccia complex (Olympic Dam breccia complex: ODBC) that developed in the ca. 1590 Ma Roxby Downs Granite (RDG) pluton (Reeve et al. 1990). The ODBC consists of a continuum of granite-rich to hematite-rich breccias and includes domains of felsic volcanic breccia and domains of bedded clastic facies. The initial formation of the deposit and host ODBC are regarded to be penecontemporaneous with the emplacement of the RDG (Reeve et al. 1990; Johnson and Cross 1995). There is, however, increasing evidence that points to modification or possible upgrade of hydrothermal minerals within the deposit and ODBC (e.g. Maas et al. 2011; Ciobanu et al. 2013; Kamenetsky et al. 2015; Ehrig 2016). Many of these emerging post-1590 Ma ages correlate with major regional tectono-thermal events either within or proximal to the Gawler Craton (e.g. Musgravian Orogeny; Major and Conor 1993). The effect of these regional tectono-thermal events on the deposit is still poorly understood, especially with regard to metal remobilisation and additional metal inputs.

This study examined brecciated quartz-rich sandstone that occurs within the ODBC and based on petrographic examination and U/Pb geochronology correlated the sandstone with the Pandurra Formation that defines the Cariewerloo Basin. Geochronology of secondary minerals within the brecciated quartz-rich sandstone was used to constrain the timing of diagenesis and a later fluid/thermal event. The correlation of the age of secondary minerals with a regional tectono-thermal event has implications for the mobilisation of metals and the potential for post-1590 Ma upgrade of the OD deposit.

2 Geological setting

The Olympic Dam deposit is situated within the Gawler Craton of South Australia (Fig. 1), which comprises Mesoarchaean to Mesoproterozoic igneous and metasedimentary rocks. The host RDG of the OD deposit is part of a large felsic igneous province incorporating undeformed but locally faulted granitoids (Hiltaba Suite) and comagmatic volcanics (Gawler Range Volcanics). Deformation in the craton post-1590 Ma is restricted to the Kararan and Coorabie Orogenies (between 1570-1540 Ma and 1470-1450 Ma, respectively), both of which were restricted to the north and west of the craton (Hand et al. 2007). Intracratonic basins that formed post-cratonisation include the extensive Cariewerloo Basin in the northeastern portion of the craton. The basin was infilled with fluvial, coarse-grained, quartz-rich sandstone and shale, collectively termed the Pandurra Formation (Cowley 1993). The Pandurra Formation was, in turn, overlain by the Neoproterozoic to Cambrian sediments deposited on the Stuart Shelf along the eastern margin of the craton, which includes the periglacial, aeolian Whyalla Sandstone (Williams 1998). The Musgrave Block formed to the northwest of the craton (over 600 km from OD) during deformation and igneous activity associated with the Musgravian Orogeny which spanned the interval ca. 1300-1075 Ma (Major and Conor 1993).

3 Bedded clastic facies

The bedded clastic facies within the ODBC occur as two large domains (Fig. 2) as well as scattered fragments
These include volcaniclastic facies comprising mudstone, sandstone and conglomerate with a mafic and felsic volcanic provenance. Tuffaceous mudstone is intercalated with intervals of finely laminated hematite-rich mudstone (ironstone) reminiscent of banded iron formation. Other facies include sandstone and mudstone dominated by quartz, feldspars and detrital hematite, which are largely granitoid-derived.

All of the above facies are spatially associated, can be interbedded and are characterised by detrital zircons with a single ca. 1590 Ma population. The bedded clastic facies have been variably altered and mineralised by the OD hydrothermal system, even to the point of textural obliteration (Ehrig et al. 2012). The bedded clastic facies have previously been considered to be indicative of a maar-diатreme architecture (e.g. Reeve et al. 1990) but is more recently interpreted to represent the remnants of a sedimentary basin contemporary with the formation of OD (McPhie et al. 2011).

An additional facies in the form of brecciated quartz-rich sandstone has been encountered in only two closely-spaced drill holes. The intervals of this facies have faulted boundaries and are not interbedded with the other bedded clastic facies. This facies is further distinguished from the other bedded clastic facies by additional populations of older detrital zircons, and abundant metamorphic quartz (McPhie et al. 2016) and is relatively unaltered and lacks sulfide.

4 Provenance of the quartz-rich sandstone

The Pandurra Formation and Whyalla Sandstone are sedimentary successions petrographically similar to the quartz-rich sandstone facies in the ODBC in the vicinity of OD. The detrital zircon age populations of these sedimentary successions were determined along with the quartz-rich sandstone facies at OD to compare maximum depositional age and provenance. U/Pb ages were determined for secondary apatite and xenotime were in the quartz-rich sandstone facies and compared with data from previous studies on the sedimentary successions outside OD. Petrographic observations were supplemented scanning electron microscopy (SEM). U/Pb geochronology of zircon, apatite and xenotime were determined from isotope data using LA-ICPMS with an Agilent 7900 quadrupole ICPMS and 193 nm ArF excimer laser at the University of Tasmania. Zircon and apatite geochronology data presented here are from (Cherry et al., unpublished data). Xenotime geochronology was determined using methods and standards developed in-house at the University of Tasmania.

5 Results

The Pandurra Formation and Whyalla Sandstone are both dominated by quartz-rich sandstones which comprise abundant detrital metamorphic quartz and lesser feldspars, lithic quartz and accessory zircon, rutile, tourmaline and Fe-Ti oxides. The detrital assemblage of both successions is similar to the quartz-rich sandstone in OD. The diagenetic assemblage of the Pandurra Formation comprises pervasive hematite coatings on detrital grains, quartz-overgrowths and cements of illite and/or dickite filling pores. The diagenetic assemblage of the quartz-rich sandstone in OD is similar to that of the Pandurra Formation rather than the Whyalla Sandstone, which has a carbonate-dominated cement.
Detrital zircons in the quartz-rich sandstone in OD, Pandurra Formation, and Whyalla Sandstone all have multiple age populations (Fig. 3). However, the 1200-1100 Ma zircons distinguish the Whyalla Sandstone and convey a younger maximum depositional age.

Figure 3. Probability density distributions of U/Pb age data (<10% discordant) for detrital zircons from the quartz-rich sandstone in the ODBC as well as the Pandurra Formation and Whyalla Sandstone. Data from Cherry et al. (unpublished data).

Clusters or single grains of euhedral apatite occur interstitial to detrital grains in the pore cement of some fragments of the quartz-rich sandstone in the ODBC (Fig. 4a). The majority of analyses form a single population with a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1441 ± 15 Ma (Fig. 4b); the rest are affected by common Pb or very low $^{238}\text{U}/^{206}\text{Pb}$ ratios.

Xenotime overgrowths (Fig. 5a) occur on detrital zircon grains within sandstone fragments in the quartz-rich sandstone. The xenotime overgrowths tend to be anhedral and euhedral quartz projects into xenotime-filled pore-space. Geochronology of the overgrowths returned a U/Pb age of 1081 ± 13 Ma (Fig. 5b).

Figure 4. a Back-scattered electron (BSE) image of euhedral apatite grains amongst platy hematite (white) and illite. b Concordia plot of apatite (1441 ± 15 Ma, MSWD = 3.3, n = 105). Data from Cherry et al. (unpublished data).

Figure 5. a BSE image of xenotime overgrowth on zircon, note euhedral quartz shapes (black). b Concordia plot of xenotime overgrowths (1081 ± 13 Ma, MSWD = 1.7, n = 207).
6 Discussion and implications

The correlation of the detrital and diagenetic mineral assemblages of the quartz-rich sandstone in OD with the Pandurra Formation implies that the Cariewerloo Basin must have one time extended above OD. This interpretation is supported by the diagenetic/minimum depositional age given by the ca. 1440 Ma age of apatite in the quartz-rich sandstone in OD which is consistent with prior whole-rock Rb-Sr (1424 ± 51 Ma; Fanning et al. 1983) and diagenetic illite Ar-Ar (1426 ± 6 and 1458 ± 11 Ma; P. Polito, pers. comm., 2016) geochronology of the Pandurra Formation. The presence of fragments of the Pandurra Formation inside the ODBC indicates faults were active long after the initial formation of the ODBC.

The anhedral shapes and ca. 1080 Ma age of the xenotime overgrowths indicate that this is a late-stage secondary phase. It is currently unknown whether the xenotime formed before or after the Pandurra Formation was entrained into the ODBC (which must have occurred after ca. 1440 Ma). The age of xenotime corresponds with the waning stages of the Musgravian Orogeny and, if related, implies that this event had a very broad thermal footprint on the Gawler Craton. Other recent studies on the Gawler Craton have made similar connections. For example, Reid et al. (2017) recorded Ar/Ar ages of 1300-1100 Ma for adularia veins ~100 km to the NW of OD, Keeling et al. (2016) interpreted widespread crystallisation of illite in the Pandurra Formation with K/Ar ages of 1260-1180 Ma as evidence of warm fluid circulation in the Cariewerloo Basin, and (Ehrig 2016) found a generation of uraninite-pitchblende in the deposit with ages of ca. 1300-1200 Ma (also noted in Johnson 1993). The coincidence of these ages suggests that the thermal pulse of the Musgravian Orogeny, and associated tectonic activity, were factors that influenced fluid circulation within the Cariewerloo Basin on the Gawler Craton at a time when the basin extended across OD. The timing of fluid circulation is reflected in the crystallisation of xenotime in Pandurra Formation at OD and highlights the possibility of basinal fluid interactions with the ODBC that were capable of mobilising U and possibly contributing additional U to the deposit.

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Petrological mapping and chemical discrimination of alteration facies as vectors to IOA, IOCG, and affiliated deposits within Laurentia and beyond

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Abstract. Recent research on iron oxide and alkali-calcic alteration systems of the Great Bear magmatic zone, Romanet Horst, Central Mineral Belt, Bondy Gneiss Complex (Canada) and southeast Missouri (USA) districts highlights the potential for Laurentia to host undiscovered iron oxide-apatite (IOA), iron oxide copper–gold (IOCG), and affiliated deposits. The metasomatic footprints are vertically zoned from deeper Na ( albite), through Ca–Fe ( amphibole-magnetite-apatite), K–Fe ( magnetite-biotite-K-feldspar to shallower hematite-sericite-chlorite-carbonate), and epithermal alteration facies. The facies can be discriminated by Na-Ca-Fe-K-Mg mineral assemblages and cation proportions, and from other ore systems by cation contents and Al-Si proportions. Each facies has distinct paragenetic, chemical, and geophysical characteristics and their metasomatic reaction paths vector to specific deposit types (IOA, IOCG, skarn, albitite-hosted U or Au-Co-U, and polymetallic vein deposits). Exploration in Laurentia can be focused by considering: (1) distribution of IOA, IOCG, and affiliated deposits in mineral belts up to 1500 km long; (2) pan-Laurentia distribution of fertile Paleoproterozoic and Mesoproterozoic terranes; and (3) diagnostic metasomatic signatures that can be used as vectors to ore.

1 Introduction

Exposed prograde, retrograde, telescoped, and cyclical metasomatic reaction paths of mineralized iron oxide and alkali-calcic alteration systems in the Great Bear magmatic zone (Canada)—as well as those from southeast Missouri (USA), Romanet Horst (Canada), and Central Mineral Belt (Canada)—provide evidences of genetic links among iron oxide copper–gold ± Co- and Bi-rich variants (IOCG), iron oxide–apatite ± REE-rich variants (IOA), albitite-hosted U or Au-Co-U, skarn, and polymetallic vein deposits. Recognition of such linkages emphasizes the potential in Laurentia to host additional deposits including high-grade metamorphic terranes (e.g., Kwyjibo, Bondy; Corriveau et al. 2007; Fig. 1). However, most prospective terranes of Laurentia remain under-explored, under-mapped, and under-valued, as are those of many terranes worldwide, (e.g., Bamble and Kangdian districts; Engvik et al. 2017; Zhao et al. 2013; Fig. 1). Herein we highlight the diagnostic geological and chemical attributes of iron oxide and alkali-calcic alteration facies, provide case examples, and describe alteration mapping protocols and chemical discrimination plots useful in exploring these ore systems.

2 Regional geological contexts

The studied ore systems are spatially and temporally associated with, or developed within, mafic to felsic extrusive and intrusive rocks in the southeast Missouri district (~1.49–1.44 Ma), Great Bear magmatic zone (1.87–1.85 Ga), Central Mineral Belt (~1.88–1.85 Ga) and Bondy Gneiss complex (1.4–1.35 Ga). Some of these
terrane sources. In some examples, the regional-scale, iron oxide and alkali-calcic metasomatism was coeval with caldera formation; batholith emplacement followed a few million years later (Day et al. 2016; Montreuil et al. 2016). In another example, alkaline magmas intruded a carbonate-dominant sedimentary basin (Romanet Horst; Corriveau et al. 2014).

Mineral-resource-bearing metasomatic systems linked to voluminous granitic magmatism can extend a thousand km as part of continental magmatic arcs. Many of the associated magmatic systems are compositionally bimodal and many of the mafic end members have tholeiitic affinities. The felsic (and intermediate rocks where exposed or recognised) are dominantly calcalkaline to shoshonitic and A-type compositions (e.g., 1.87 Ga Great Bear magmatic zone; 1.47 Ga Missouri district and Pinwarian arc of Grenville Province; 1.16 Ga intrusive suites hosting Kwyjibo deposit; Corriveau et al. 2007; Montreuil et al. 2016; Day et al. 2017).

3 Alteration attributes and field mapping

A great variety of mineral assemblages and contents, grain sizes, textures, structures, and space-time relationships of metasomatic rocks occurs at the deposit- to regional-scale and poses major challenges to alteration mapping. The morphology (replacements, veins, breccias) and extreme differences in paragenetic sets of altered rocks enable the documentation of a series of distinct alteration facies and their space-time relationships with magmatism and tectonics.

Intervening metasomatites between least- and most-altered sequences are used as proxies for the incremental progress of alteration. Alteration intensity is classified as subtle, weak, moderate, intense, or megascopically complete depending on the degree to which precursor minerals and textures are preserved, grain sizes of metasomatites, and spatial extent of the alteration zone (Fig. 2). Ultimately, paragenetic sets, rock physical properties, and compositions of each alteration facies are diagnostic due to the distinct cations of the dominant mineral phases in the paragenetic sets (Corriveau et al. 2010, 2016; Montreuil et al. 2013; Enkin et al. 2016). The predominant visible grain size of the metasomatites enables the use of a field-based compositional alteration nomenclature (i.e., Na, high temperature (HT) Ca-Fe, HT K-Fe, and low temperature (LT) K-Fe facies; Fig. 2).

Field mapping complexities are largely resolved by (1) focusing description on paragenetic sets and related metasomatic facies, (2) qualifying alteration intensity, reporting mineral assemblages and modes, standardizing terminology for veins, replacements and breccias, mapping crosscutting and overprinting relationships among alteration facies, and documenting alteration facies paragenetic affinities of mineralisation assemblages.

4 Alteration facies as vectors to ore

4.1 Prograde metasomatic paths

The metasomatites and linked deposit types are zoned vertically and laterally, recording a regular sequence of fluid-rock reactions that led to prograde paths with Facies 1 Na (albite) transitioning to high temperature (HT) Na-Ca-Fe (albite, amphibole, magnetite, apatite); Facies 2 HT Ca-Fe (amphibole, magnetite, apatite) and IOA deposits; Facies 3 HT K-Fe (magnetite, biotite, K-feldspar) and magnetite group IOCG deposits; Facies 4 K-felsite (K-feldspar), K-skarn (clinopyroxene, garnet, K-feldspar), and polymetallic Pb-Zn-bearing deposits; Facies 5 low-temperature (LT) K-Fe (hematite, K-feldspar, sericite, chlorite, carbonates), hematite-group IOCG deposits and light REE-rich variants within LT Ca-Fe-Mg (chlorite, carbonates); and Facies 6 epithermal including vein-type mineral deposits. K-feldspar felsite breccias, not large-scale K-feldspar haloes, vector to IOCG mineralisation.
the presence of carbonate alteration zones provide evidence that fluids in these systems can generate their own skarn mineral assemblages without a proximal intrusion. A regular spatial and temporal progression is also observed among brecciation, polymetallic mineralization, and the appearance and increasing intensity of K-Fe alteration facies. Co-crystallisation of iron oxide minerals and K-feldspar is, however, megascopically decoupled. Iron oxide minerals are concentrated within the matrix and K-feldspar replaces host protolith and derived fragments in breccias (Fig. 2d, e). Rocks of the HT Ca-Fe alteration facies commonly undergo ductile deformation during metasomatism; other alteration facies experience brittle to brittle-ductile deformation.

4.2 Telescoped, cyclical, and retrograde paths

Where exposed (e.g., Great Bear), the IOA deposits are deeper expressions of cogenetic IOCG mineralisation, but fluidised-type IOA breccias also point to the ability of magnetite-apatite mush to ascend to higher structural levels. Fluidisation of HT K-Fe metasomatites also occurs. Faulting can telescope albitites into levels where fluids precipitates U (HT and LT K-Fe fields) (Corriveau et al. 2014; Montreuil et al. 2015); younger REE-rich breccias can form through remobilisation of IOA deposits (Harlov et al. 2016). Epithermal veins also form within earlier alteration facies during retrograde alteration. Cyclical development of a fertile alteration facies can increase local metal endowment (e.g., 33 Mt Au-Co-Bi NICO deposit; Fig. 1). Collectively, metal enrichment in these ore systems includes ferrous, base (Fe, Cu, Pb, Zn, Ni), precious (Au, Ag, PGE), specialized (Bi, Co, Mo, V, Nb, Ta, W, HREE, LREE), and actinide (U, Th) metals.

4.3 Exploration and mapping challenges

Metasomatised rocks can resemble common rocks; this can hamper recognition of ore systems. Examples include: (1) albitites for hornfels, K-feldspar- and hematite-altered or silicified zones, anorthosites, rhyolites, and syenites (Fig. 2b, g); (2) Na-Ca-Fe facies for igneous pegmatites (Fig. 2c); (3) un-metamorphosed HT Ca-Fe or LT K-Fe metasomatites for iron formations, metasedimentary rocks, marls, iron oxide lavas, and amphibolites (Fig. 2h); and (4) K-feldspar alteration for rhyolites or albitites, commonly masking the andesite protoliths (Montreuil et al. 2016). Syn-alteration ductile deformation of HT Ca-Fe metasomatites increases their resemblance with metamorphic rocks, and may lead to misinterpretation of syn- or post-metasomatic regional orogenic metamorphism. Selective K-feldspar or magnetite replacement of breccia fragments can mask the timing of brecciation versus alteration and obscure the nature of protoliths (Fig. 2d, e).

Another challenge is the non-recognition of IOA-IOCG systems and metasomatic linkages among deposits, which can result in the deposits being misclassified, such as:

(1) iron formation; (2) VMS; (3) SEDEX; (4) intrusion-related skarns and polymetallic mineralization; (5) diagenetic, metasomatic-metamorphic, sedimentary, magmatic, hydrothermal, shear-hosted, unconformity-type, and stratiform U; (6) polymetallic veins; and (7) syngenetic/diagenetic stratiform Cu, red bed Cu, etc. (e.g., Potter et al. 2013; Slack 2013; Corriveau et al. 2014; Engvik et al. 2017; Sparks 2017 and references therein).

4.4 Chemical mapping

By recognizing metasomatites and recording their mineral assemblages, paragenesis, and spatial distribution, it is possible to map the principal cation mobility across ore environments, from fluid and metal sources to deposits (Corriveau et al. 2016). Geochemical data refine the major-element mobility interpreted megascopically. Efficient whole-rock molar proportions allow mapping alteration footprints from the regional to the drill core scale. Such maps can efficiently guide exploration (Fig. 3).

Figure 3. Chemical alteration map at Terra, northern Great Bear magmatic zone. Chemical data from Corriveau et al. (2015).

5 Chemical discriminants of prograde and telescoped reaction paths

The chemical evolution of these systems can be visualised by plotting the element bar codes on the IOCG geochemical alteration discrimination diagram of Montreuil et al. (2013) (Fig. 4a) and those of Large et al. (2001) and Williams and Davidson (2004). The bar code signatures of megascopically and chemically least-altered igneous and sedimentary rocks (Fig. 4b) can also be discriminated from the mixed signatures induced by superposition of alteration types (Fig. 4c) during prograde, telescoped, and/or retrograde metasomatic paths.

Prograde metasomatism results in a counter-clockwise trend (Fig. 4a). The metasomatites with a single alteration type display bar codes dominated by one or two elements; least-altered bar codes have more even cation proportions. Replacement of early metasomatites by other alteration
facies (e.g., telescoped or retrograde paths) recombines elements and leads to compositions that occupy the least-altered field (Fig. 4c). Bar codes are however distinct from those of the least-altered rocks (Fig. 4b versus c).

Figure 4. Plot of Na-Ca-Fe-K-Mg bar codes on IOCG discriminant diagram of Montreuil et al. (2013) for Great Bear magmatic zone; chemical data from Corriveau et al. (2015). a Prograde path of alteration facies. b Felsic to mafic protoliths. c Replacement of original albitics (light pink) by other alteration facies leading to alteration trends toward least-altered field.

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Constraints on ages of magmatism and iron oxide-apatite (IOA) and iron oxide-copper-gold (IOCG) mineral deposit formation in the Mesoproterozoic St. Francois Mountains Terrane of Southeast Missouri, USA

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Abstract. The Mesoproterozoic St. Francois Mountains terrane of southeast Missouri, USA hosts several iron oxide ± apatite ± REE (IOA) and iron oxide ± copper ± gold (± cobalt) (IOCG) deposits. The timing of magmatic activity and mineralization helps to constrain genetic models for IOA- and IOCG-type deposits. The terrane formed along the southeast margin of the greater than 1.6-old Ga Laurentian craton during two episodes of magmatism: an older period of volcanism and associated plutonism that peaked at ca. 1462 Ma and occurred from 1485 to 1440 Ma, and a younger period of bimodal plutonism that spanned from 1335 to 1275 Ma. The volcanic rocks comprise a rhyolite suite interlayered with lesser Fe-rich rocks of a mafic- to intermediate-composition suite. All known ore deposits are hosted in volcanic, subvolcanic, and associated volcanogenic sedimentary rocks. New SHRIMP U-Pb data greatly increase the areal distribution and density of age information and quantify that emplacement of key members of the mafic- to intermediate-composition rock was coeval with formation of iron oxide ore. These results strengthen the model that the mafic- to intermediate-composition suite provided heat and potentially fluids and metals for ore formation.

1 Regional setting

The Mesoproterozoic St. Francois Mountains terrane of southeast Missouri, USA developed along the southeastern margin of the Laurentia craton (Bickford et al. 2015) in the Shawnee terrane (Lund et al. 2015). Exposures of the Precambrian basement are limited to discontinuous outcrops and drill cores that penetrate the thick (ca. 400m) Palaeozoic and Quaternary cover rocks. Fundamental questions, such as the paleotectonic setting, the nature of the substrate onto which the volcanic rocks erupted, the relative proportion of the various rock types, and source(s) of fluids for ore formation have been difficult to constrain.

The St. Francois Mountains terrane (Fig. 1) experienced two major pulses of igneous activity: (1) an older (ca. 1485 to 1440 Ma) episode of volcanism and associated plutonism that was part of a large silicic magmatic system, and (2) a younger episode (ca. 1335 to 1275 Ma) of bimodal plutonism (Thomas et al. 2012; Bickford et al. 2015; Aleinikoff et al. 2016; Neymark et al. 2016a, b). IOA and IOCG ore deposits formed during the waning stages of ca. 1.46 Ga volcanism. Available geochemistry indicates that the ore-forming fluids were partly or wholly magmatic-hydrothermal in nature (Kisvarsanyi and Kisvarsanyi 1989; Nold et al. 2014; Johnson et al. 2016; Hofstra et al. 2016; Neymark et al. 2016a).

Figure 1. Generalized geologic map of St. Francois Mountains terrane, southeast Missouri with locations of known Mesoproterozoic mineral deposits. Modified after Kisvarsanyi (1981).

The ca. 1.46 Ga volcanic rocks can be divided into two suites: (1) a mafic- to intermediate-composition suite composed of basalt, basaltic andesite, trachyandesite, and andesite, i.e., rocks that contain less than 65 wt % SiO2, and (2) a dacite to rhyolite suite that contains 65–77 wt % SiO2 (Day et al. 2016). The volcanic rocks were invaded by calc-alkaline to alkali-calcic biotite granite plutons and hornblende-biotite granodiorite ring intrusions, and, locally, diorite (Bickford et al. 1981; Cullers et al. 1981; Kisvarsanyi 1981; Sides et al. 1981). Iron, Cu, Au, Co, Mn, and rare earth element (REE) deposits are hosted within the volcanic and contemporaneous volcanoclastic sedimentary rocks (Nold et al. 2014; Day et al. 2016). The ring intrusions locally host...
Ag-Sn-W vein greisen deposits (e.g., Silvermines). Younger ~1.3 Ga bimodal granite and gabbroic intrusions are not known to contain mineral deposits.

Neodymium isotopic data indicate that the ca. 1.46 Ga volcanic and plutonic rocks and associated IOA and IOCG deposits were derived from depleted mantle source(s) (Ayuso et al. 2016). The mafic to intermediate-composition rock suite is relatively enriched in large ion lithophile elements (LILEs) and depleted in Nb and Ta, similar to rocks generated along subduction zones. Rare earth-element (REE) concentrations are consistently enriched in light-REE (LREE) with modest negative Eu anomalies. The rocks have Th-Hf-Ta and Th-Hf-Nb abundances that overlap those of volcanic arc basalts, and Zr/Y vs. Zr patterns like those of continental arc and within-plate basalts (Ayuso et al. 2016). The felsic volcanic rocks have trace element signatures that are like within-plate A-type types granites with lesser quantities that mimic S- and I-type granites generated in arc settings (Day et al. 2016).

2 Geochronology

Uranium-Pb isotopic studies on igneous zircon, titanite, and baddeleyite (Thomas et al. 2012; Bickford et al. 2015; Aleinikoff et al. 2016; Neymark et al. 2016 a, b) provide critical constraints on the timing of magmatism and IOA/IOCG deposit formation. Felsic magmatism started at about 1485 Ma, peaked at 1462 Ma, and continued until approximately 1440 Ma (Fig. 2a). Rhyolite is the oldest rock type observed. Where observed, the granitic plutons intrude the volcanic rocks (Kisvarsanyi 1981). The crustal substrate that underpins the terrane is not exposed, and inherited zircon from pre-existing sialic crust is very rare (Bickford et al. 2015). Neodymium-Sm studies indicate that any significant amounts of pre-existing crust must have been juvenile (less than 50 m.y. old) (Ayuso et al. 2016).

Minerals commonly used for geochronology are rare in the mafic- to intermediate-composition rock suite. However, we have recently recovered igneous zircon from host trachyandesite at the Boss IOCG deposit and zircon and titanite from the trachyandesite subvolcanic intrusion near Pea Ridge IOA deposit (Fig. 2b). The Boss deposit lies within a caldera structure and is hosted in rhyolite, trachyandesite, and diorite (Kisvarsanyi and Kisvarsanyi 1989; Day et al. 2016). Sensitive high-resolution ion microprobe (SHRIMP) U-Pb ages for zircon from trachyandesite and cross-cutting diorite yield ages of 1477 ± 11 Ma and 1471 ± 8 Ma, respectively (Fig. 2b). The Pea Ridge deposit is hosted in rhyolite that is surrounded by a subvolcanic Fe-rich trachyandesite intrusion which forms a prominent “horseshoe-shaped” aeromagnetic high that opens to the north and lies approximately 5 km away from the Pea Ridge deposit (McCafferty et al. 2016). SHRIMP U-Pb ages for zircon from the two samples of trachyandesite are 1463 ± 2 Ma, and 1464 ± 9 Ma, respectively.

The Pea Ridge IOA-REE deposit is a dike-shaped body approximately 2 km long and 750 m wide that is cored by a magnetite zone with a halo of hematite ore and an amphibole-quartz alteration zone that transitions outwardly to a peripheral silica-rich zone within the ca. 1474 Ma host rhyolite. The footwall of the deposit is cut by at least four REE-bearing breccia pipes (Nuelle et al. 1992; Aleinikoff et al. 2016; Day et al. 2016; Harlov et al. 2016; Hofstra et al. 2016; Neymark et al. 2016a). TIMS U-Pb dating of apatite associated with ore-stage magnetite yields ages of 1471 ± 1 and 1468 ± 1 Ma (Neymark et al. 2016a). Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS)
Synthesis of recently published and new preliminary geochronological results suggests that the early Mesoproterozoic pulse of felsic magmatism in the St. Francois Mountains terrane lasted for approximately 45 m.y., during the period 1485-1440 Ma. Rocks of the mafic-to-intermediate-composition suite coevally erupted and intruded felsic suite, overlapping in space and time with products of the more voluminous silicic magmatic system. Limited age data indicate that the IOA deposits formed in felsic volcanic host rock about 10 m.y. after eruption and record a protracted history of hydrothermal activity that terminated at about 1440 Ma. The new data support the model proposed by Ayuso et al. (2016) that the mafic magmatism supplied both heat for partial melting of the crust to form the silicic magmas and provided magmatic-hydrothermal fluids that played a prominent role in IOA and, potentially, IOCG ore genesis.

Acknowledgements

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Stability of Fe(III) chloride complexes and hematite solubility to 300°C: Applications to the origin of IOCG deposits

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Abstract. Experiments are being conducted to determine stepwise formation constants for ferric chloride complexes at temperatures of 150 to 300°C and ΣCl = 0.1 to 3.0 molal. Results show that the tetrahedral FeCl4- species is dominant at T > 200°C and ΣCl > 1 molal. Combined with a parallel set of hematite solubility experiments, a preliminary log K value of +8.2±0.2 has been determined for the following reaction at 25°C: Fe₂O₃ + 6H⁺ + 8Cl⁻ = 2FeCl₄⁻ + 3H₂O. Geochemical reasoning based on these findings indicates that hot brines in equilibrium with hematite-rich sediment (“red-beds”) can transport appreciable iron as Fe(III) chloride or hydroxychloride complexes, provided the rock contains no reductants (such as organic compounds or pyrite), and as long as the brine is at least mildly acidic. Once dissolved, ferric iron can promote dissolution of other redox-sensitive metals through reactions of the following type: X + FeCl₄⁻ = XCl₂⁻ + FeCl₂(aq) (X = Au, Cu, Ag). An acidic, saline fluid enriched in Fe(III) and Fe(II), as well as dissolved Au and Cu, could be a prime candidate for formation of an iron oxide copper gold (IOCG) deposit.

1 Introduction: scope of work

Although the dominant redox state of dissolved iron in most rock-buffered hydrothermal systems is ferrous (Fe²⁺), ferric (Fe³⁺) aqueous complexes may become important in rocks that contain abundant hematite and an absence of reducing phases (e.g., organic matter, pyrite). Hot brines circulating through red-bed sediments may dissolve appreciable quantities of iron and other metals as chloride complexes. If the dissolved iron is in the ferric state, it could act as an aggressive oxidant, helping to dissolve elements such as gold, uranium, and copper that are mobile at relatively high fO₂ conditions. However, our understanding of this potentially important ore-forming process is presently limited by a lack of data on the stability of ferric chloride complexes at elevated temperatures.

The authors are presently conducting hydrothermal experiments to determine hematite solubility and the stability of Fe(III) chloride complexes at temperatures of 150 to 300°C, total chloride concentrations of 0.1 to 3.0 molal, and pressures fixed at the liquid-vapor curve. Additional experiments are being undertaken to measure the solubility of gold at redox states set by coexistence of aqueous Fe(III) and Fe(II) chloride complexes. Although the experiments in progress, we have enough data to shed new insights on the mobility of Fe(III) in hydrothermal brines, and the possible importance of dissolved ferric iron to the formation of iron oxide copper gold (IOCG) deposits.

2 Experimental methods

2.1 Fe(III) chloride complex stoichiometry

The stability of Fe(III) chloride complexes is being measured in sealed silica tubes, following the approach of Gammons and Seward (1996) and Gammons et al. (1996), who derived stability constants for the Mn(II) and Nd(III) chloride complexes, respectively. Briefly, the solubility of AgCl(s) is measured in solutions containing identical HCl concentration but differing amounts of Fe(III) added as FeCl₃(s). As shown by the following reactions, dissolution of FeCl₃(s) may cause an increase or a decrease in the free Cl⁻ concentration, depending on the stoichiometry of the Fe-chloride complex:

\[
\begin{align*}
\text{FeCl}_3(s) &= \text{FeCl}_2^+ + \text{Cl}^- \quad (1) \\
\text{FeCl}_3(s) &= \text{FeCl}_3(aq) \quad (2) \\
\text{FeCl}_3(s) + \text{Cl}^- &= \text{FeCl}_4^- \quad (3)
\end{align*}
\]

Meanwhile, at the conditions of the experiments, the reaction controlling AgCl solubility can be written (e.g., Seward, 1976):

\[
\text{AgCl}(s) + \text{Cl}^- = \text{AgCl}_2^-. \quad (4)
\]

If the dominant Fe(III) species is FeCl₂⁺, the addition of FeCl₃(s) results in an increase in free Cl⁻ concentration (eqn 1), causing AgCl solubility to increase (eqn 4). In contrast, if FeCl₄⁻ is the dominant species, then the concentration of free Cl⁻ will decrease (eqn 3) and the solubility of AgCl will go down.

One advantage of the silica tube method is that experiments can be performed at very low pH, thereby avoiding hydrolysis of the Fe(III) chloride complexes. Further details on how the experiments are set up and interpreted are given in the sources cited above.

2.2 Hematite solubility

A set of 8 short silica tubes was prepared with the same concentration of NaCl/HCl, but with varying amounts of FeCl₃. The tubes were then loaded into a pressure vessel and reacted for several days at the desired temperature. At the end of the experiment the pressure vessel was quenched in cold water and the tubes were examined for hematite.
precipitates. There were some tubes that had no precipitates and some that did, either as a reddish “bathtub ring” or as crystals in the bottom. The equilibrium solubility of hematite was bracketed by the tube with the highest Fe(III) concentration with no hematite and the tube with the lowest Fe(III) concentration that precipitated hematite. After photographing the set of tubes to document the presence or absence of precipitates, the tubes were reloaded into a pressure vessel and re-equilibrated to a new temperature. The precipitates were eventually examined by Raman spectroscopy to confirm that they are hematite.

Enough experiments have been completed at different temperatures to show that hematite found in the tubes after opening the pressure vessel formed at the temperature of the experiment, and not during the quench. Likewise, hematite that formed at high temperature does not redissolve during quench.

3 Results

3.1 Fe(III) chloride complexes

To date, experiments have been completed with 1M HCl and 0.3M HCl + 2.7M NaCl solutions at T = 150 to 300°C. The data show that FeCl₄⁻ is the dominant Fe(III) chloride complex at T > 200°C and ΣCl ≥ 1M. Example solubility data are shown in figure 1. The predominance of FeCl₄⁻ at ΣCl ≥ 1M is in agreement with high temperature Raman study of Murata et al. (1989). Although there is evidence that FeCl₃(aq) and/or FeCl₂⁺ becomes important at lower temperature and lower salinities, we cannot report stepwise formation constants at this time.

3.2 Hematite solubility

One set of hematite solubility experiments using 0.9M NaCl + 0.1M HCl has been completed, with reportable results for 250°C. Based on the presence of hematite in two of the quenched tubes (see figure 2), the solubility of Fe(III) is bracketed between 152 and 201 mmol/kg (8500 to 11250 ppm Fe) for the conditions listed above. Using ion-pair data for NaCl and HCl (Mesmer et al. 1988), the equilibrium pH and aCl⁻ can be computed for 250°C. From this, a log K estimate can be computed for the following reaction:

\[ \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 8\text{Cl}^- = 2\text{FeCl}_4^- + 3\text{H}_2\text{O} \] (5)

Our preliminary log K estimate for reaction 5 at 250°C, taking into account activity coefficients and NaCl and HCl ion pairing, is +8.2±0.2. No literature estimates exist with which to compare this result. However, our findings are in qualitative agreement with the predictions of Liu et al. (2006), based on extrapolation of low-T data, that higher-order Fe(III) chloride complexes (i.e., FeCl₆⁵⁺, FeCl₄⁻) are important in hydrothermal brines above 200°C, and lead to hematite solubilities that are orders of magnitude greater than those calculated (e.g. Tagirov et al. 2000) based on lower order complexes alone (i.e., Fe³⁺, FeCl²⁺, FeCl₃⁻).

![Figure 2. Photo of quenched tubes from hematite solubility experiment at 250°C, 0.9m NaCl + 0.1m HCl. Initial FeCl₃ content increases from left to right. Hematite saturation occurred between tubes 6 and 7 (note solids in bottom of tubes 7,8).](image)

4 Co-transport of iron and gold

Before this study began, we hypothesized that a 300°C brine saturated with hematite and buffered by coexistence of dissolved Fe(III) and dissolved Fe(II) chloride complexes could transport significant amounts of gold as Au(I) chloride complexes. Figure 3 is an fO₂-pH diagram, adapted from Liu et al. (2006), that shows the position of the
dissolved Fe$^{III}$/Fe$^{II}$ boundary (dashed red diagonal line) in relation to the stability fields of hematite and magnetite for a fluid containing 1 molal Cl$^-$ at 300°C. Although the diagram is correct in terms of its topology, it is not accurate in detail, since there is large uncertainty in the position of the aqueous Fe(III)/Fe(II) boundary (indicated by red arrows). Also shown in figure 3 are contour lines of gold solubility at 300°C and 1m ΣCl based on experimental data in Gammons and Williams-Jones (1995). From the diagram, the solubility of gold near the dissolved Fe$^{III}$/Fe$^{II}$ boundary should be in the range of 1 ppb to 1 ppm. This amount of gold in solution could be sufficient to form a gold ore body over a geologically significant length of time.

Figure 3. Log fO$_2$-pH diagram showing stability fields of aqueous and solid Fe compounds at 300°C and the inferred conditions of the gold-solubility experiments. The aqueous Fe$^{III}$/Fe$^{II}$ boundary is dashed because of high uncertainty as to its position. It is drawn here based on a similar diagram in Liu et al. (2006). The shaded region demarks the zone where gold solubility as AuCl$_2^-$ is between 1 ppb and 1 ppm, based on the study of Gammons and Williams-Jones (1995).

To test the ideas put forth in the preceding paragraph, two preliminary hydrothermal experiments were performed in which gold foils were reacted in silica tubes at 250°C for one week with solutions containing 0.9m NaCl + 0.1m HCl + 0.01m total Fe (added as a mix of FeCl$_3$ and FeCl$_2$ salts). The quenched solutions were analyzed for Fe$^{II}$ and Fe$^{III}$ concentrations using the Ferrozine spectroscopic method (Stookey 1970) and the solubility of gold was determined by the change in mass of the gold foil. The results are given in Table 1. Importantly, these results show the expected increase in gold solubility with increase in the dissolved Fe$^{III}$/Fe$^{II}$ ratio. This is an indication that redox equilibrium was attained in the experiments.

Preliminary values of the equilibrium constant (log $K_6^*$) for the following reaction are listed in the last column of the table:

$$\text{Au(s)} + \text{FeCl}_4^- = \text{AuCl}_2^- + \text{FeCl}_2(aq) \quad (6)$$

Although the log $K_6^*$ values show good agreement between the two independent experiments, they are very preliminary. Many more experiments will need to be carried out at different ΣCl and Fe$^{III}$/Fe$^{II}$ conditions to confirm the stoichiometry of reaction (6), and to show that the results are reproducible. Nonetheless, the preliminary data are encouraging because they show that: 1) equilibrium appears to be attainable in this system under the chosen conditions; and 2) the solubility of gold set by the Fe$^{III}$/Fe$^{II}$ redox buffer at 250°C and 1m ΣCl is quite high (0.86 to 4.1 mM, or 169 to 807 ppm). The high gold solubilities obtained in these preliminary experiments indicate that the dissolved Fe$^{III}$/Fe$^{II}$ boundary in figure 3 may need to be shifted to higher values of fO$_2$.

Another complication that needs to be considered is hydrolysis of Fe(III) chloride complexes as pH is raised. In figure 3, it is assumed that FeCl$_4^-$ is the dominant ferric aqueous species to pH 6. It is possible, if not likely, that Fe(III) hydroxy complexes, or mixed hydroxy-chloride complexes, will become important at higher pH. Diakonov et al. (1999) showed that hematite dissolves as the tetrahedral Fe(OH)$_4$ complex in dilute NaCl-NaOH solutions at temperatures up to the 300°C. The pH boundary between chloride-dominant and hydroxy-dominant Fe(III) species is presently not known, nor is the stability of mixed-ligand aqueous species of the type FeCl$_x$(OH)$_{4-x}$.

5 Applications to IOCG deposits

Iron oxide-copper-gold (IOCG) deposits are one of the more enigmatic classes of hydrothermal mineral deposits. Recent reviews of IOCG deposits include Hitzman et al. (1992), Haynes (2000), Williams et al. (2005), and Groves et al. (2010). The deposit type is best represented by the huge Olympic Dam deposit of South Australia, but also includes important deposits in the Cloncurry District of Australia, Scandinavia, Chile/Peru, and the western U.S. and Canada. Defining characteristics of IOCG deposits include: 1) abundant hypogene hematite and/or magnetite; 2) economic to sub-economic concentrations of gold and copper; 3) strong, district-scale sodic alteration of wall rock that is sometimes overprinted by potassic alteration; 4) strong structural control including hydrothermal breccias which lack the usual quartz veining or cement; and 5) no intimate spatial association with igneous intrusions (as in porphyry
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...Fluid inclusion studies (summarized by Williams et al. 2005) show that the ore-forming fluids were high temperature brines with a range in trapping temperature from 200°C to roughly 500°C. However, Groves et al. (2010) suggest that some of the higher temperature deposits included in the discussion of Williams et al. (2005) are not true IOCG deposits, but may instead be variants of skarn or porphyry-related systems.

Between the previous studies, a number of hypotheses have emerged as to the nature of the IOCG ore-forming fluids. These range from heated, sedimentary-basin brines (Haynes 2000) to magmatic fluids (Groves et al. 2010), to mixtures of fluids of shallow and deep crustal origin (Haynes et al. 1995). Most studies agree that the ore fluids were oxidized (hematite stable) with high Cl/S ratio. The present authors are intrigued by the IOCG genetic model of Haynes (2000), who speculated that highly saline brines, heated to temperatures near 300°C and circulated through “red-bed” (hematitic) sediments, could transport significant quantities of Fe, Cu, and Au. In the absence of mineral or organic reductants, a hot brine could dissolve hematite as Fe(III) chloride complexes, which in turn could dissolve gold and copper (as well as uranium, another metal that is highly enriched at Olympic Dam) via reactions such as equation (6). District-scale migration of NaCl-rich brines could explain the widespread sodic alteration that is ubiquitous in deeper levels of IOCG deposits. Deposition of Fe-oxides and gold could occur due to fluid mixing (i.e., dilution), changes in pH, or changes in temperature. Deposition of Cu-Fe sulfides (chalcopyrite, pyrite) could take place where aqueous sulfate is thermochronically reduced to H$_2$S, e.g., by rocks containing ferrous iron.

Using new thermodynamic data generated in the current study (in progress), in combination with published data on the stability of gold and copper chloride complexes (e.g. Gammons and Williams-Jones 1995; Xiao et al. 1998; Stefánsson and Seward 2003), it will soon be possible to run more sophisticated geochemical models to test the ideas expounded by Haynes (2000). Our preliminary results suggest that hot brines in equilibrium with hematite may indeed co-transport Fe(III), Fe(II), gold, and copper, all as chloride complexes. It is not necessary for these brines to be infused with atmospheric oxygen: they just need to have a redox state fixed by the co-existence of hematite, Fe(III) chloride complexes, and Fe(II) chloride complexes.

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References


Abstract. The Pea Ridge deposit is in a 1.48-1.44 Ga volcano-plutonic terrane consisting of rift-related, depleted mantle-derived, tholeiitic, mostly concealed basalt to andesite and voluminous subalkaline ferroan dacite to rhyolite composition igneous rocks. Eruption of the rhyolite host at ~1473 Ma was followed by faulting and formation of the magnetite-apatite deposit (210 Mt, 47-55 % Fe) at ~1471 Ma. Th-rich REE breccia pipes (0.2 Mt, 12% REE oxides) formed at ~1465 Ma. Nd, Pb, and He in IOA and REE mineralization were derived from a mantle source. Ore and gangue minerals precipitated from fluids containing magmatic H, O, C, S, Fe, Cl and Br. The IOA deposit formed at ~1.5 km depth under lithostatic to hydrostatic conditions at ~350-750°C by cooling and decompression of ascending fluids enriched in Fe, Mg, Ca, P and REE that were derived from an intermediate composition intrusion. REE breccia pipes formed under vaporstatic conditions from ~400-200°C hypersaline brine derived from a fractionated alkalic (?) intrusion that dissolved and replaced apatite with monazite, xenotime, and thorite. The results show that IOA deposits and REE breccia pipes can be produced by the discharge of fluids from successive intrusions in an underlying igneous complex.

1 Introduction

The Mesoproterozoic St. Francois Mountains terrane of SE Missouri, USA, is known for its REE-bearing iron oxide-apatite (IOA) deposits, an iron oxide-copper-gold (IOCG) resource, and potential for resources below Paleozoic cover (Starkey and Seeger 2016). Pea Ridge is the largest IOA deposit in the region with 210 Mt of production plus reserve of magnetite iron ore containing 47-55 wt % Fe; a REE resource of 0.2 Mt with an average grade of 12 wt % REE oxides is present in breccia pipes (pre NI 43-101 standard). Apatite recovered during magnetite beneficitation contains ~0.5 wt % REE oxides (Day et al. 2016).

The Pea Ridge IOA-REE deposit was studied to advance understanding of its origin and the relationship between the early magnetite-apatite deposit and later REE-rich breccia pipes (Slack et al. 2016). It also presents an opportunity to determine the genesis of an IOA-REE deposit in a relatively simple magmatic setting.

The Mesoproterozoic St. Francois Mountains terrane is part of the eastern Granite-Rhyolite province on the SE margin of the Laurentian craton. Igneous rocks in this terrane have Sm-Nd model ages (1.66-1.51 Ga) and epsilon Nd compositions (2.35-4.25) that are indicative of a depleted mantle source with little assimilation of older crustal material (Ayuso et al. 2016). Whole-rock geochemical data on the c.a. 1.48-1.44 Ga suite indicate that most mafic to intermediate composition rocks are tholeiitic whereas most felsic rocks are subalkaline and ferroan, which is characteristic of a rift setting (Day et al. 2016, this volume, and du Bray, in prep.). Alkaline andesite and dacite occur locally.

Pea Ridge is hosted in rhyolite underlain by a granite pluton that is ringed by a mafic to intermediate composition intrusion (Fig. 1). Inversion of high-resolution airborne magnetic and gravity gradiometry data yields a mushroom-shaped high density/high magnetic susceptibility body hosted in low density/low magnetic susceptibility rhyolite and/or granite and a magnetite-rich root or mafic to intermediate composition intrusion that extends to a depth of at least 2 km (McCafferty et al. 2016). Inversion of regional data shows that the root extends to a depth of ~ 6 km with additional intermediate to mafic intrusions at depths > 15 km in the middle and lower crust (McCafferty et al., this volume).

2 IOA deposit

The NE-striking, SE-dipping, tabular IOA deposit (Fig. 2) is hosted in steep, NW-dipping, crystal-rich, high-silica
rhyolite tuffs and flows. Zircons yield SHRIMP U-Pb ages of ~1473 Ma (Aleinikoff et al. 2016), Ti-in zircon temperatures of ~770°C, and contain melt inclusions that have alkalic dacite to rhyolite compositions (Watts et al. 2015). Fragments of ~1473 Ma biotite and muscovite in a REE breccia pipe (Aleinikoff et al., 2016) are indicative of an underlying granite pegmatite. Textural and trace element studies show that magnetite and ilmenite phenocrysts in rhyolite tuffs were oxidized to form hematite ± rutile pseudomorphs during eruption and welding (Meighan et al. this volume). Zr-in-rutile hematite ± rutile pseudomorphs during eruption and phenocrysts in rhyolite tuffs and flows. Zircons yield SHRIMP U-Pb ages of ~1473 Ma (Aleinikoff et al. 2016), Ti-in zircon temperatures of ~770°C, and contain melt inclusions that have alkalic dacite to rhyolite compositions (Watts et al. 2015). Fragments of ~1473 Ma biotite and muscovite in a REE breccia pipe (Aleinikoff et al., 2016) are indicative of an underlying granite pegmatite. Textural and trace element studies show that magnetite and ilmenite phenocrysts in rhyolite tuffs were oxidized to form hematite ± rutile pseudomorphs during eruption and welding (Meighan et al. this volume). Zr-in-rutile pseudobreccia and heterolithic breccia, amphibole, silicified and K-feldspar zones, and is mantled on the NW side by a hematite zone (Seeger et al. 2001). Four REE-rich breccia pipes occur near granite dikes on the NW side by a hematite zone (Seeger et al. 2001). Four REE-rich breccia pipes occur near granite dikes on the NW side by a hematite zone (Seeger et al. 2001).

The IOA deposit is ~2 km in length, 500 m in width, and has a vertical extent of more than 600 m. The central magnetite zone is enveloped by magnetite-cemented pseudobreccia and heterolithic breccia, amphibole, silicified and K-feldspar zones, and is mantled on the NW side by a hematite zone (Seeger et al. 2001). Four REE-rich breccia pipes occur near granite dikes on the NW side of the deposit. Mafic dikes are common on the SE side.

The oldest TIMS U-Pb date of ~1471 Ma on primary apatite from the IOA deposit is slightly younger than the rhyolite host (Neymark et al. 2016). In the magnetite zone, relict hematite is mantled by zoned magnetite crystals containing sparse rutile inclusions (e.g. Fig. 3a) that record a core to rim increase in temperature from < 420 to 720°C (Hofstra et al. 2016). The major and trace element compositions of such magnetite are characteristic of hydrothermal magnetite (Mercer et al. 2015) and its δ18O (1.9 to 4.0‰; Johnson et al. 2016) and δ56Fe (0.03 to 0.35‰; Childress et al. 2016) values are indicative of a magmatic source. Actinolite has magmatic δD isotope values (-64 to -53‰); late pyrite has δ34S values (-0.2 to 6.4‰) at the high end of typical magmatic sulfur (Johnson et al. 2016). Fluid inclusion extracts from magnetite, hematite, and pyrite are enriched in Mg, Ca, K and have magmatic Cl/Br ratios (1000-5000; Hofstra et al. 2016).

Figure 2. Cross-section of the Pea Ridge IOA-REE deposit. Granite dike is red and mafic dikes are green. Amp = amphibole, Qtz = silicified, Ps-Bx = pseudobreccia, H-Bx = heterolithic breccia. Dashed lines are mine levels. After Seeger et al. 2001.

The magnetite zone contains about 1-10 wt. % apatite, which is also common in the amphibole, pseudobreccia, heterolithic breccia and hematite zones. Although most apatite is recrystallized, depleted in REE, and contains an abundance of secondary monazite and xenotime inclusions, SEM images and EPMA analyses define relict patches of primary apatite with ~ 2 wt. % REE that lack such inclusions (Fig. 3b); rims on secondary apatite are enriched in Cl (Harlov et al. 2016). Quartz occurs in open fractures and vugs in the magnetite and amphibole zones, as well as heterolithic- and pseudobreccia, and constitutes the silicified zone. Under CL it exhibits dark cores mantled by bright bands that are fractured and rimmed by dark quartz (Hofstra et al. 2016). The Ti-in-quartz (rutile saturation) thermometer records a core to bright band increase in temperature from ~350 to 750°C followed by cooling to temperatures < 315 to 500°C in dark healed fractures and outer rims (Hofstra et al. 2016). At these temperatures, H2O in equilibrium with quartz (δ18O = 12.9 to 16.7‰) has δ18O of ~12‰, which is higher than magmatic water (5.5-9‰). Lower temperatures of 250 to 400°C are required to yield magmatic fluid compositions (Johnson et al. 2016). The dark cores and banded quartz lack primary fluid inclusions. Healed fractures contain vapor-rich inclusions and saline (10-27 wt %) liquid-rich inclusions that record temperatures and pressures of < 350°C and < 150 bars (~1.5 km hydrostatic; Hofstra et al. 2016). The Sm-Nd and Pb-Pb isotope data from altered and mineralized samples lie along 1.45 to 1.48 Ga isochrons and have initial isotope values (143Nd/144Nd=0.51091, εNd=3.54, 206Pb/204Pb=16.5, 207Pb/204Pb=15.4, 208Pb/204Pb=36.2) that are indicative of a depleted mantle source with low Th/U ratios (~2; Ayuso et al. 2016; Neymark et al., 2016). Gas extracted from ore and gangue minerals has 3He/20Ne ratios (~0.0002) that are indicative of a mantle source and 4He/20Ne ratios (~5000) that reflect in-situ U-Th decay over the last ~1.45 Ga (Hofstra et al. 2016).
3 REE breccia pipes

Four small 15 to 60 m thick breccia pipes occur in the hematite zone on the NW margin of the IOA deposit (Fig. 2). They contain fragments derived from adjacent alteration zones that were partially to completely replaced, as follows: magnetite to hematite, actinolite to chlorite, and apatite to fine-grained monazite (CePO₄) and xenotime (YPO₄). K-feldspar was stable or partially altered to sericite (Harlov et al., 2016). Quartz fragments were insoluble and exhibit primary CL zoning (Hofstra et al. 2016). Textures show that apatite was dissolved locally, liberating small grains of monazite and xenotime, whereas in other places it was replaced by fine-grained monazite and xenotime; coarser crystals of apatite, monazite, and xenotime also were deposited in fractures and vugs (Aleinikoff et al. 2016; Ayuso et al. 2016; Harlov et al. 2016; Hofstra et al. 2016). Thorite (ThSiO₄) and cassiterite (SnO₂) are common accessory minerals.

Figure 4. a Chondrite normalized REE patterns for melt inclusions in the host rhyolite (magenta band), K-feldspar zone (white), hematite halo of REE breccia (red), REE-breccia (brown), and molybdenite-bearing breccia (blue). b CaO/Ce vs. Ce plot of apatite and monazite relative to magnetite Fe ore, REE breccia, and other alteration zones. Green lines show wt % apatite in the samples. After Watts et al. 2015; Ayuso et al. 2016; Harlov et al. 2016; Hofstra et al. 2016.

REE mineralization was followed by deposition of barite, pyrite, and calcite in both the IOA deposit and REE breccia pipes. The δ³⁴S values of barite (14.2 to 27.1‰) and pyrite (3.0±3.5‰) record cooling from 450 to 250°C; SO₄/H₂S=1.5 and bulk S=8‰; the δ¹³C of associated calcite (-4.7 to -5.8‰) is magmatic (Johnson et al. 2016). Fluid inclusions in barite and calcite have Na, K, Cl, and Br compositions that are characteristic of evaporated lake (or marine) water (Hofstra et al. 2016). These data may reflect degassing of a concealed intrusion into a caldera lake and reflux of saline evaporated lake water into permeable breccia pipes (Fig. 4; Johnson et al. 2016).

4 Post ore events

A ~1441 Ma SHRIMP U-Pb date on zircon from a medium-grained granite dike that cross-cuts the IOA deposit, together with a ~1441 Ma date on monazite and a ~1440 Ma Re-Os date on molybdenite from one of the REE breccia pipes, indicate that post-ore granite magmatism was accompanied by Mo mineralization (Aleinikoff et al. 2016). Whole-rock geochemical data show that Mo is associated with depletion of HREE’s (Fig. 3a), but does not correlate with other elements.

One of the REE breccia pipes was silicified and
contains hematite, apatite, quartz, allanite, and synchysite in vugs. Dilute fluid inclusions in vug quartz are indicative of boiling (Hofstra et al. 2016). This event redistributed REE, Th, and U and may be responsible for a ~470 Ma Pb-Pb isochron defined by samples from this breccia pipe (Ayuso et al. 2016; Neymark et al. 2016; this study).

5 Model

At ~1473 Ma, rhyolites erupted from silicic magma reservoirs (Fig. 5) that were produced by partial melting of young crust (e.g. an accreted island arc) and fractional crystallization of mafic to intermediate magmas derived from a depleted mantle source. After eruption and tilting of the rhyolite host rocks, the IOA deposit formed along a dilatant, near-vertical fracture zone. Fe-, Mg-, Ca-, P-, REE-, Cl-, and F-bearing fluids discharged from a concealed, plagioclase-bearing, intermediate composition intrusion ascended to the site of ore formation at a depth of ~1.5 km where temperatures progressively increased from < 350 to ~750°C until lithostatic pressure was exceeded and the rocks were fractured and brecciated. Rhyolite was dissolved and actinolite, apatite, magnetite, quartz, and K-feldspar precipitated as hydrothermal fluids cooled, decompressed, and reacted with wallrocks.

The REE breccia pipes and perhaps the hematite zone, formed at ~1465 Ma under vaporstatic conditions from hypersaline brine containing REE, Y, Th, Sn and associated trace elements that were discharged from a highly fractionated alkalic (?) intrusion and, in part, scavenged from the IOA deposit. Discharge of magmatic vapor to the paleosurface facilitated collapse of saline evaporated lake water into the hydrothermal system.


References


New insights on the formation of magnetite-apatite deposits: the Artillero magnetite prospect (Mexico)

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**Abstract.** The Artillero magnetite prospect is a satellite Fe-deposit within the world-class Peña Colorada Iron district. We present a new field observation of the Artillero mineralization styles, Sr-Nd isotopes from Fe-mineralization apatite and U/Pb ages from host sequence and Fe-mineralization. The Artillero Fe-prospect shows features that strongly suggest that it formed by the emplacement of an iron-rich melt in a shallow subaqueous environment and capping a zone of abundant breccias and feeder dykes, dated at ca. 80 Ma. The deposition of magnetite was synchronous with the deposition of welded volcanic rocks, dated at ca. 80 Ma. The welded volcanic rocks are slightly younger than the host sequence (ca. 85 Ma). The likely source of melts was mantle derived material with low crustal contamination. Fluid- and iron-rich melt ascended through strike-slip structures related to the compression/extension caused by the post-Laramide inversion. The shallow emplacement of the magmatic chamber favored the separation of large amounts of low density aqueous fluids, increasing the wetting properties and the explosivity of the ascending iron-rich magma. The Fe-mineralization is syn-eruptive, sourced from an explosive eruption at a subaerial or fluviatil to deltaic environment.

1 Introduction

Iron oxide deposits in Mexico are traditionally separated in two groups associated to Mesozoic and Oligocene magmatic belts (Corona et al. 2007). None of these are directly dated and the proposed ages are indirectly estimated from field relationships with host rock or supposed source rocks and, in few cases, on the dating of the related hydrothermal alteration (Corona and Henriquez 2004; Corona et al. 2009; Camprubi et al. 2017). As most of the magnetite-apatite deposits worldwide, the Mexican iron oxide deposits show complex relationships with the host rocks and are of debatable origin. Their origin is still controversial because they share features with either Kiruna-type, calcic iron skarn or some IOCG deposits, and all these characteristics may occur either in a single deposit or district.

One of the most complex examples is the Peña Colorada deposit at Minatitlán, Colima. Peña Colorada is the largest active iron mine in Mexico, with resources over 300 Mt and average grades between 50 and 60% Fe (Corona-Esquivel and Henríquez 2004). Based on field observation and the age of the potassic alteration, the mineralizing process is interpreted as taking place during almost 15 Ma, from 63 to 48 Ma. Within the Peña Colorada district, the magmatic history is extended from Early Cretaceous to present, with notable changes in composition from basalt to ignimbrite. In the same district there are other iron mines working relative small ore lenses, which have similar characteristics and probably the same origin, such as the case study of the Artillero deposit. The mineralization here has been described as of hydrothermal origin and consisting of a low temperature skarn with a strong telescoping process.

Here we present new geological, petrographic and geochemical data on the Artillero mine; as a whole, they strongly suggest that this deposit was formed in a diatreme-maar complex related to the shallow intrusion and dewatering of an iron-rich melt.

2 Regional tectonic and magmatic setting

The Peña Colorada district is located at the northwest part of the physiographic province of the Sierra Madre del Sur, near Minatitlán, 50 km WNW of the state capital. The oldest rocks known in the area are lower Cretaceous in age (Alberca and Tecalitlán Formations). They consist of Valanginian to Aptian volcanosedimentary successions (~140 to ~125 Ma), consisting of black shale, fine-grained sandstones and andesitic tuffs, which evolve, during the Barremian and Aptian to rhyolitic pyroclastic flows, sandstones and conglomerates (see age range in Fig. 1). Next, the Tepalcatepec Formation, Albian to Cenomanian in age (~130 to ~113 Ma), is characteristic of an extensional arc-back environment and hosts the iron mineralization. It is made up of thick limestone layers interbedded with scarce andesitic lava flows, and some horizons of volcanlastic and calcareous rhythmic deposits, tuffs and rhyolites, conglomerates and sandstones, red siltstones, and some evaporites (Grajales-Nishimura and López-Infanzón 1984).
The fossil association suggests an Albian to late Cenomanian age (~113 to ~100 Ma). The Tepalcatepec Formation is covered by the Cerro de la Vieja Formation (Parga 1977). It constitutes a conglomeratic unit composed of limestone fragments, which was folded together with the underlying Cenomanian limestone. Conglomerates contain sandstone and silt layers with sedimentary structures and textures that suggest a fluvial depositional environment.

This Mesozoic sequence was deformed during the Laramide orogeny and later intruded by the Manzanillo Batholith (U-Pb on zircon, from 74 to 62 Ma; Panseri 2007; K-Ar and Ar-Ar from 68 to 55 Ma; Moran-Zenteno et al. 2007) of granodioritic composition, and small bodies of plagiogranites and gabbros. Finally, in the area of Peña Colorada, the whole column is cut by dykes of possible Tertiary andesite.

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**Figure 1.** Stratigraphic column showing the main lithologies in the study area and the nearby region (modified from Villanueva-Lascurain et al. 2016).

### 3 El Artillero magnetite deposit

The Artillero iron deposit is located 5 km northeast of Minatitlán (Colima) and has been mined in several small open pits. It has an average grade of 64.9% Fe with 1.44% SiO₂, 0.88% Al₂O₃, 0.22% CaO, 0.27% MgO, 0.077% P, and 0.015% S (after ABNNewswire comm. 2007). The ore body is hosted by a subaerial andesite flow belonging to the Upper Tepalcatepec Formation (Cenomanian; Zücher, et al. 2001). The mineralization is complex and includes several stratiform lenses of magnetite capping a, sometimes jigsaw, breccia with fragments of andesite supported by magnetite and several subvertical veins of magnetite; these late ones are up to 5 meters thick and 30 m long and crosscut the bedding. The stratiform mineralization is subhorizontal, tabular, massive, with an average thickness of about 20 meters and unknown lateral continuity but extends east-west over more than 540 m according the magnetometer surveys and drilling information (London Mining 2007, pers. comm.). Mineralogically, it is mainly composed by magnetite, rare hematite (martitization is uncommon), and minor quantities of apatite. This stratiform mineralization is dominant and consists of alternating layers of magnetite and fragments of volcanic rocks. The bedding is parallel to the local stratigraphy and show unequivocal structures of sedimentary deposition, dewatering and compaction. There are abundant subaqueous sedimentary structures, including laminar and graded bedding. The amount of magnetite in these sedimentary layers usually exceeds 98%, but in some beds rich in volcanic fragments, magnetite may be below 50%. Some levels show large, sometimes flattened, clasts of highly altered andesite? in a fine-grained groundmass of magnetite with chaotic (Fig. 2) or well-laminated structures. Volcanic clasts present a pervasive alteration with rare remnants of plagioclase and clinopyroxene phenocrysts, and with primary biotite almost entirely transformed to microcline and vermiculite. There is abundant evidence of widespread devitrification such as spherulites. The former glass and most of the phenocrysts are replaced by K feldspar, reflecting a pervasive potassic alteration. Euhedral crystals of fluorapatite occur as clusters in some dusty aggregates of pure magnetite. It is noteworthy that quartz and all the other silica polymorphs are absent. The dominance of the former juvenile pyroclasts and the internal organization of the volcanic fragments and magnetite grains in the welded volcanoclastic sediments strongly suggest that the mineralization is syn-eruptive, sourced from an explosive eruption at a subaerial or shallow subaqueous environment. The internal textures shown by the magnetite and the volcanic fragments are mostly secondary and were formed synchronously with the devitrification and the hydrothermal alteration. We have not found magnetite spherules similar to those found by Nyström et al. (2016) at El Laco magnetite deposit.

**Figure 2.** Layered magnetite ore showing gradded bedding and fragments of devitrified and altered andesite, Artillero deposit. Black fine laminae are composed by fine-grained magnetite.
4 Geochronology

In order to have a better control of the age of the host rock and the magnetite mineralization and the stratigraphic position, we performed U-Pb dating of zircon grains from the hosting andesite and the stratiform mineralization as well as U-Pb dating of apatite from the massive magnetite mineralization.

4.1 U-Pb dating of the host sequence

Seventeen analyses were performed on zircon crystals separated from the hosting andesite, yielding $^{206}\text{Pb}/^{238}\text{U}$ ages in the range between 84.1±1.8 Ma to 93.0±3.6 Ma. Three analyses were discarded due to the high sigma errors. From the remaining fourteen concordant ages, nine analyses form a tight cluster (Ludwig 2008) that gives a weighted mean crystallization age for the volcanic host rock of 85±1 Ma (Fig. 1).

4.2 U-Pb dating of the mineralization

Sixteen analyses performed on zircon grains separated from the stratiform magnetite ore yielded $^{206}\text{Pb}/^{238}\text{U}$ ages in the range between 78.4±2.2 Ma to 97.3±2.9 Ma. The weighted mean crystallization age (Ludwig 2008) is 83±2 Ma (Fig. 1). Nevertheless, the two youngest ages are more representative as minimum effusive emplacement age (Ludwig 2008) at 78.6±2 Ma ($n=2$; MSWD of 0.1; Fig. 1).

Twenty-six analyses on apatite crystals separated from a subvertical magnetite dyke yielded $^{206}\text{Pb}/^{238}\text{U}$ ages in the range between 80±24 Ma to 485±26 Ma. Five analyses were discarded due to high sigma errors. From the remaining twenty-one age data, twenty results form a tight cluster. In the Concordia diagram, the results obtained draw a well defined line, with and intercept age of 90±11 Ma. Nevertheless, in the $^{238}\text{U}/^{206}\text{Pb}$ ages distribution diagram (Ludwig 2008), the youngest age seems representative of the effusive emplacement age at 80.7±24 Ma (Fig. 1).

5 Apatite source

The geochemistry of apatite (REE contents and Sr/Nd isotope geochemistry) can help constrain the source and origin of the related magnetite ore. The apatite shows a significant chemical variation in a chondrite-normalized REE diagram. In general, the REE pattern shows a systematic enrichment in LREE with a high (La/Yb)$_n$ ratio accompanied by a strong negative Eu/Eu*$_n$ anomaly.

Strontium and neodymium isotope ratios were determined for two apatite samples separated from the massive stratiform orebody. Corrected $^{87}\text{Sr}^{86}\text{Sr}$ ratios are between 0.70650 and 0.70733 and the initial $^{143}\text{Nd}^{144}\text{Nd}$ value is around 0.5130; these values plot in the quadrant I of the Sr-Nd isotopic correlation diagram (Fig. 3), being more enriched in $^{87}\text{Sr}$ than the associated volcanic rocks that belong to an island arc sequence of the Guerrero Terrane.

![Figure 3. Sr-Nd isotopic correlation diagram for Cretaceous to Cenozoic rocks in the Guerrero terrane and the Artillero apatite data. LC and CM are data from La Perla and Cerro del Mercado iron oxide deposits. The Japan field is an average of the Japanese island arc. NVZ and SVZ are the northern and southern volcanic zone of the Andes, respectively (all data from Winter (2001)).](image)

6 Discussion and conclusions

The magnetite orebody of the Artillero deposit shows features that strongly suggest that it formed by the emplacement of an iron-rich melt in a shallow subaqueous environment and capping a zone of abundant breccias and feeder dykes. The deposition of magnetite was synchronous with the deposition of welded volcanic rocks. The most likely interpretation is that the deposit formed in a subaerial maar-diatreme complex related to the violent degassing that accompanied the emplacement of a water-rich iron-rich melt accompanied by an immiscible silicate melt. Similar complexes have been described in other magnetite-apatite deposits such as Olympic Dam, among other (see Williams et al. 2005; Tornos et al. this volume). The volcanic host rock has a Santonian age (~85 Ma) which is significantly younger than the Tepalcatepec and Cerro de la Vieja Formations (Albian to Cenomanian; ~113 to ~94 Ma) to which it was previously associated. The Artillero andesitic flow could be defined as the first expression of post Laramide extension. The U-Pb zircon and apatite ages of the discordant and stratiform mineralization range between ~78 to ~80 Ma. These ages are in good agreement with field evidence that strongly suggests the contemporaneous eruption of two immiscible melts (Fig. 2). Mineralization ages are slightly younger than the andesite host rock, but significantly older than the published cooling ages for the Peña Colorada deposit (~63 to 48 Ma; Tritlla et al. 2003).

The Sr-Nd isotopic data obtained from apatite from the Fe-mineralization suggest that no Triassic material (Arteaga complex) or old Grenvillian crust was involved in the formation of the iron-rich melts. The likely source of melts was mantle derived material with low crustal contamination. Subaqueous sedimentary structures, including laminar and graded bedding suggest an explosive eruption at a subaerial or shallow subaqueous environment, as also suggest for contemporary Cerro de la Vieja fluvial to deltaic depositional environment (Parga 1977). The apatite
Sr anomaly and Nd isotopic signature point out the participation of high Sr radiogenic river or deltaic waters enriched in Sr during continental material weathering.

The existence at the Artillero deposit of diatreme and stratiform magnetite assemblages could be explained by a model invoking the ascent and emplacement of a fluid- and iron-rich melt as Tornos et al. (2016) has recently proposed for El Laco magnetite deposit. In this case, the iron-rich melt likely separated from the parental andesitic magma at depth, both ascended in a same time through strike-slip structures related to the compression/extension caused by the post-Laramide inversion. The shallow emplacement of the magmatic chamber facilitated the separation of large amounts of low density aqueous fluids, increasing the wetting properties and the explosive nature of the ascending iron-rich magma. The Fe-mineralization is syn-eruptive, sourced from an explosive eruption at a subaerial or fluvial to deltaic environment.

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Crustal architecture beneath the southeast Missouri (USA) Mesoproterozoic Iron-Oxide province from geophysical models

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Abstract. Results from three-dimensional (3-D) density and magnetic susceptibility models provide tectonic-scale geophysical constraints on crustal architecture underlying the Mesoproterozoic iron province in southeast Missouri, USA. The iron province contains one iron oxide-copper-gold (IOCG) and several iron oxide-apatite (IOA) ± rare earth element (IOA±REE) deposits within 1.48 to 1.44 Ga rhyolites and intermediate to mafic composition igneous rocks of the mostly concealed St. Francois Mountains terrane. The geophysical models cover over a 900 x 900 km area; susceptibility distributions are calculated within a volume defined by the Cambrian erosion surface and the Moho. Density distributions are constrained by these surfaces, but extend from sea level to 50 km depth. The models show that the iron deposits occur along the edges or in the center of caldera structures underlain by partly coincident dense and magnetic domains interpreted as intermediate to mafic composition intrusions in the middle and lower crust. Several such calderas are associated with known iron deposits, whereas others highlight the potential for new areas of IOCG and IOA±REE mineralization. A major crustal boundary, demarcated by Nd isotopic data, coincides with abrupt density and susceptibility boundaries that extend to the mantle.

1 Introduction

The iron metallogenic province in southeast Missouri (Fig. 1; Day et al. 2016) has been the subject of an ongoing research project within the U.S. Geological Survey (USGS) Mineral Resources Program (Slack et al. 2016). Goals of the project are to use a wide variety of geoscience approaches to characterize known IOA±REE and IOCG deposits, and ultimately, their genesis. Recent geophysical efforts have focused on deposit-scale modeling of high-resolution airborne magnetic and gravity gradiometry data acquired over several of the known deposits (McCafferty et al. 2016). Results of the deposit-scale research show most of the known iron deposits have underlying magnetic and dense sources that extended to depths of at least 2 km beneath the deposits. This study evaluates the iron province at deeper depths by placing the individual deposits within a broad regional geophysical and geological framework to map the underlying crustal architecture that may help explain the locations of the deposits and deep controls on mineralization.

Over the last several decades, the Mineral Resources Program of the USGS has developed large-scale geophysical databases including those for magnetic and gravity data at continental scales. We use these data in this study to define individual and multi-parameter physical property models for delineating major crustal boundaries and conduits that may have acted as controls on the emplacement of the iron deposits in southeast Missouri. A goal of our study is to improve the understanding of how heat, magma, and fluids interact at crustal scales to generate large mineralized systems.

Figure 1. Geophysical 3-D model area centered on southeast Missouri iron metallogenic province. Iron deposits that form the province (red dots) are hosted in exposed and buried igneous rocks of the St. Francois Mountains terrane (blue). Mesoproterozoic granite-rhyolite provinces (Van Schmus et al. 1987) and inferred Precambrian structures, most interpreted from regional magnetic anomaly data (Sims 1990) are overlain on Precambrian topography (Marshak et al., 2016). Locations of two cross sections (Figs. 2, 3) extracted from their respective 3-D models are shown along lines A-A' and B-B’. Dashed “Nd-line” marks the Nd-isotope boundary between rocks of older (>1.6 Ga) continental crustal origin to the northwest and younger rocks (ca 1.5 Ga) with a juvenile origin to the southeast (Bickford et al. 2015).
2 Approach

Two-kilometer grids were extracted from the gravity and magnetic compilations of the United States (https://mrdata.usgs.gov) for a 1024 x 1024 km area surrounding the iron province (Fig. 1). The magnetic data were reduced to the magnetic north pole and used to calculate magnetic susceptibility models. The Bouguer gravity grid was used to calculate the density model.

Inversion software used here to derive both physical property models implements the modeling methodology of Pilkington (1997, 2009), Caratori Tontini et al. (2009), Phillips (2014), and Phillips and Simpson (2015). The software uses a 3-D fast Fourier transform algorithm to rapidly invert a potential field on a surface to a physical property distribution in the underlying volume. Crustal thickness data, derived from Earthscope regional seismic measurements (Shen and Ritzwoller 2016), were used to define the base of the susceptibility model and an important interface in the density model, equivalent to the Moho. Crustal thickness within the model area (Fig. 1) ranges from 30 to 49 km and averages 45 km beneath the iron province. The top surface of the models was delineated by topography on the Precambrian basement (Marshak et al., 2016).

The final models each contain individual voxel elements (cubes) that have a horizontal dimension of 2 x 2 km and a vertical dimension of 500 m and display a 3-D physical property volume of either density or magnetic susceptibility.

3 Results

Two west-to-east profiles; A-A’ and B-B’ (Fig. 1) were extracted from the 3-D models and show the physical property distributions from the top of the Precambrian to the mantle. The northern profile (Fig. 2) intersects the concealed deposits that are covered by 200 to 400 m or more of lower Paleozoic sedimentary rock at Bourbon (B; IOCG?), Kratz Spring (KS; IOA) and Pea Ridge (PR; IOA+REE). The southern profile (Fig. 3) crosses the concealed Boss (IOCG) deposit, which is at a depth of approximately 200 m. The profile also crosses an area of exposed Mesoproterozoic rocks, which occur in the St. Francois Mountains. Volcanic units within the St. Francois Mountains host the shallow or exposed iron oxide deposits at Cedar Hill (CH; IOA), Shepard Mountain (SM; IOA), and Pilot Knob (PK; IOA) (Fig. 3).

Figure 2. West to east sections extracted along A-A’ (Fig. 1). Upper section a 3-D susceptibility model; Lower section b 3-D density model. The shaded-relief images emphasize major physical property boundaries. Nd-line marks isotopic boundary that separates ~1.6 Ga Nd model ages for basement to the west from younger model ages to the east (Bickford et al. 2015). Iron deposits: B: Bourbon; KS: Kratz Spring; PR: Pea Ridge.
The susceptibility model for the Pea Ridge, Bourbon, and Kratz Spring deposits (Fig. 2a), delineates a mostly vertical, 40 km-wide monolithic column of increased values. The column originates at the mantle and develops extensions or “branches” at mid-crustal levels that extend to the Precambrian basement surface. High densities underlie the deposits (Fig. 2b), but are restricted to the upper 5 km of crust (Fig. 2b). Coincident dense and high susceptibility areas are interpreted as potential intermediate to mafic rocks. Predominant magnetite alteration of low density volcanic and granitic rock is expected in areas where low density and high magnetizations are present. Previous geochronology studies (Aleinikoff et al., 2016) and geophysical modeling (McCafferty et al., 2016), provide support for the interpretation that the likely source of lower susceptibility and density surrounding Pea Ridge is an early Mesoproterozoic granite pluton overlain by rhyolite. Physical property similarities between PR, KS, B, and the area east of Pea Ridge suggest additional iron mineralization there.

Along the southern section (Fig. 3), it is interesting to note that Boss, the only known Cu-bearing iron deposit in the province, occurs at the top of a branch projecting from a broad (75 km-wide) main chamber of high magnetic susceptibilities and high densities that underlies the three more shallow deposits (Fig. 3a). We interpret the mostly coincident dense and magnetic mass under the shallow deposits to be related to a high volume of intermediate to mafic rock at depth. These dense and magnetic domains are interrupted at the Precambrian surface by ovoid shaped lows that continue to depths of 4 to 6 km in the density model (Fig. 3b) and 12 to 15 km in the susceptibility model (Fig. 3a). The lows correspond to surface structures related to the Taum Sauk and Butler Hill calderas. Until now, the geophysical signatures associated with the calderas had not been recognized. There are several areas that share this caldera signature (i.e. east of the Boss deposit). Hence, it is likely that several more unmapped calderas underlie the province and occur throughout the extensive Eastern Granite Rhyolite Province.

The southern section also intersects the Missouri Gravity Low (MGL), a long recognized northwest-trending ~700 km-long x ~160 km-wide gravity low that has been interpreted either as a 1.3 Ga batholith (Hildenbrand and Hendricks, 1995) or related to a Precambrian rift (Guinness et al., 1982). Model results over the MGL show a shallow dense and vertically extensive magnetic source just east of
the Nd-line suggesting a potential iron mineralization system based on its similarity with the known areas.

Both profiles cross the “Nd-line”, a major crustal boundary, marked by Nd isotope compositions, which separates ~1600 Ma old basement to the west from younger basement to east. Whether the boundary is diffuse or abrupt has not been resolved isotopically. However, the geophysical models suggest this boundary is abrupt as mapped in steep physical property boundaries present in the models. Continental crustal features such as those mapped in our geophysical models and those that are supported by isotopic data, conceivably could have enhanced and focused heat in the lithosphere. These boundaries could provide avenues for fluid circulation and melt transfer, and for metal flux from the mantle into the shallow crust.

4 Conclusions

The 3-D inversion models of gravity and magnetics over the iron province in southeast Missouri map notable features that are tectonic in scale and provide several insights into crustal characteristics underlying the iron mineralization. The magmas forming the iron deposits originated from the mantle in several places over the province. The magma’s ascension from the mantle and through the crust is marked by steeply-sided columns of increased susceptibility and variable densities. The only known Cu-bearing deposit (Boss) lies along the margin of the same system that hosts the shallow deposits in the St. Francois Mountains. The likely age of the sources are early Mesoproterozoic as supported by numerous geochronological dates of host rocks and ore deposits (Alienikoff et al. 2016). Caldera structures, recognized, geophysically, for the first time, act as important controls on iron mineralization. The nature of the crustal boundary defined in the Nd isotopic data coincides with steep, through-going physical property boundaries. All iron mineralization is located east of this boundary.

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Chaos and control: the interplay between discordant IOCG-related breccias and their bounding fault and shear arrays, Cloncurry District, northern Australia

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Abstract. In the Cloncurry District, several ~1530 Ma iron oxide-copper-gold (IOCG) deposits such as Ernest Henry, and the Merlin Mo-Re deposit, are hosted by polymictic hydrothermal breccias with textures implying fluidization. Similarly textured breccias, highly discordant yet barren, are found along fault arrays and junctions in specific corridors through the Cloncurry district. We generated geomechanical models of the stress and fluid pressure requirements for failure along the fault arrays thought to be active at the time of IOCG and Mo-Re mineralization. The richest mineralized breccias occur within corridors in areas of overlap of predicted highest rock failure potential for the two main structural events. Most barren breccias and some IOCGs without fluidized breccia occur in low to moderate failure potential sites of only one of the deformation events. We infer the mineralizing, high energy packages were structurally connected to mid-crustal metal + fluid sources (e.g. from intrusions) along deeper-penetrating and longer-lived master structures. Barren, very high energy breccias, were connected, probably more transiently, to metal-poor fluid sources due to time/space differences in fluid release, or because more extreme overpressures failed to precipitate metals.

1 Introduction

Discordant, fluidized breccias are usually considered to have a complex, disruptive or chaotic relationship with the surrounding structural framework of faults or shears, because these breccias are rapidly, forcibly emplaced upwards, driven primarily by extreme magmatic- and/or hydrothermal overpressure. Kimberlites are an example; explanations for their localisation usually consider deep and broad tectonic controls, as well as reactivation of older structures (e.g. White et al. 1995). Many papers dealing with kimberlites and/or other diatremes also note the capacity of such breccias to deviate significantly from controlling structures (e.g. Vearncombe and Vearncombe 2002).

Many IOCG deposits show a strong structural control (Williams et al. 2005), and geophysical targeting has proven able to recognise these structural controls as well as the magnetic and electrical signatures of the oxide-sulphide complexity surrounding mineral deposits. Holistic approaches to IOCG exploration have used multi-layer prospectivity analysis (including interpreted structures from geophysics); in the Cloncurry District (McLellan et al. 2010) this approach confirmed the predominance of structural controls over other spatial indicators.

The apparent balance between chaotic breccias hosting some mineralization, and systematic structural controls relating to fault- and shear architecture, is the topic of this paper. We aim to explain how chaotic mineralized breccias relate to their hosting structures, and to provide some speculation on the reasons for differences between mineralized breccias, barren breccias, and non-breccia occurrences of IOCG-style mineralization along faults.

2 Geomechanical prediction of Cu and Mo

We used UDEC software (described in McLellan and Oliver 2008), a 2-dimensional distinct element code, which enables numerical simulation of mechanical responses of faults, contacts and rocks to an imposed stress. The geology is used for deformation scenarios (two were used here, D3 and D4), bounding stresses are imposed and the model block is deformed until the system reaches numerical equilibrium, with local tension or shear failure. Failure potential (Fig. 1) was calculated by assessing the proximity of each block to the Mohr failure envelope.
Figure 1. Structural map, breccia corridors and summary results of geomechanical models of fault and rock body arrays in the Mount Isa Inlier around Cloncurry, adapted from McLellan et al. (2016); inset shows position of Cloncurry District within the Eastern Fold Belt (EFB). Pre- to syn-mineralization intrusions of the Williams-Naraku Batholiths are shown (orange crosses), the remainder (white, with thin grey foliation traces) are complex clastic and chemical metasedimentary and metavolcanic rocks regionally metamorphosed prior to most intrusions, with widespread pre- and syn-intrusive poly-phase albite-actinolite alteration. Green shades represent areas of failure potential for the NW-SE directed shortening event “D4” of the late stages of the 1600 to 1500 Ma Isan Orogeny; red areas represent areas of failure potential for the WSW-ENE-directed “D3”. Failure potential, moderate and strong, represent combined conditions of pore fluid pressure, minimum compressive stress and differential stress which place the rocks close to, or on the Mohr failure envelope (respectively) for the combination of rock, contact and fault properties in the model. The best mineralized IOCG- and Mo-rich fluidized breccias lie mostly at overlaps between the two sets of failure potential; barren breccias lie within the corridors but usually not in overlap zones; copper deposits without strong IOCG or fluidized breccia associations lie on faults but not in the main predicted failure corridors – some of these also are older style (basinal) copper systems.
Although there are many caveats to the use and interpretation of the results, we successfully predicted most major deposit locations generated by multi-layer prospectivity models (McLellan et al. 2010). Notably, several deposits were formed before the late, brittle-dominant deformation episodes modelled here, although these deformations produced complex overprinting in some deposits (Eloise, Osborne, Starra). Secondly, we consider some favourable zones, particularly along the Cloncurry Fault Corridor (Fig. 1) to have been too proximal to source intrusions to have developed IOCGs, even though they display excellent examples of discordant breccias emanating from intrusion carapace zones (Oliver et al. 2006).

2 Discussion and conclusions

The Ernest Henry and Rocklands corridors (Fig. 1) show a central core with the main mineralized breccia bodies lying on or near overlap of the predicted failure zones for the two modelled deformation scenarios. Adjacent lie barren breccias and/or IOCGs with weaker breccia affiliations; some barren breccias overprint mineralization in the corridor cores. The Selwyn corridor has several deposits and breccia types tightly focussed into a narrow zone little broader than 200m wide, coincident with overlapping zones of strong rock failure potential for both D3 and D4 structural scenarios. It includes the relatively recently discovered Merlin deposit (Babo et al. 2017), the world’s highest grade Mo deposit, in which molybdenite forms the hydrothermal precipitate in the cement of a polymictic fluidized breccia body (Fig. 2). Further away around the Selwyn corridor zones of predicted rock failure in either scenario contain sporadically distributed copper prospects with only local, fault-related hydrothermal breccia, one of the largest being Wewak where there is some overlap of predicted failure potential for D3 and D4.

The Cloncurry Fault corridor appears to be central to the other branching corridors, and near intrusions displays many examples of fluidized but barren breccia pipes and dykes emanating from the carapace zone of a mingled mafic-felsic complex (Oliver et al. 2006). Many of them lie away from the major structural core, emanating laterally and vertically from intrusive carapace zones along faults and fault junctions, having reamed out the adjacent rocks by forceful upwards explosion (and possible surface venting) rather than “stalling” in complex dilatant bends (Ernest Henry) or major shear zones (Mt Dore, Mt Elliot, Merlin). The main corridor appears to have been favourable for failure mostly during D3 (Fig. 1).

The tops and bottoms of this system are incompletely exposed via differential exhumation (Fig. 3). However, we have demonstrated that some barren breccias represent extremely high energy escape paths for mixed CO2–H2O fluids released from the top of mingled mafic-felsic intrusions emplaced at ≥ 10 km depth (Oliver et al. 2006). The energy was so high that these breccias probably vented at surface. If they carried Cu, Au or Mo, they may have been lost to the surface; alternately the high energy may also have been associated with a different fluid composition that carried few metals of interest. This high energy also resulted in a variable relationship between predicted dilatant zones and these breccias. Some Mo (Merlin) and smaller IOCGs may have formed in more distinct structurally controlled environments at this time, Merlin possibly in response to fluid release from more evolved (felsic) magmas than the IOCGs, and some of the copper probably derived by more local circulation of metamorphic/basinal brines (Fig. 3).

The main IOCGs hosted by fluidized breccias (Ernest Henry, Rocklands, Mt Elliot) show a moderately protracted paragenetic history and a connection to long-lived and deep seated shear or fault zones. The simplest explanation relative to the barren breccias is that the upward flow of metal-laden fluid and fragments was capped, and energy expelled, by interaction with the most dilatant structural sites within the D4 mechanical framework. This velocity and fluid pressure drop may have been the fundamental cause of ore genesis (Rusk et al. 2010), in conjunction with the interaction of magmatic-hydrothermal fluids with upper crustal fluids already focussed into these same zones via the protracted deformation. More complex scenarios, speculatively presented on figure 3, relate to the evolution of different packets of fluid from the Williams-Naraku Batholith at different times. In such scenarios, the variation in breccia type and metal association would have at least partly related to primary variations in the composition and volatility of fluids evolving from these intrusions in the 1540 to 1500 Ma period when the D3 and D4 deformations were also active.

Exploration for new mineral deposits in this belt, although challenging, will increasingly depend on adding significant knowledge layers to the interpretation of structural geometry from geophysics, such as the predictive modelling presented here.

Figure 2. Much of the Merlin Mo-Re deposit is defined by a spectacular molybdenite-cemented polymictic hydrothermal breccia (Babo et al. 2017).
Figure 3. Two time slices along a schematic south-to-north (left-to-right) section showing the evolution from a) magmatism and deformation before and during the NE-SW directed shortening event (D3), to b) magmatism and deformation during the ESE-WNW directed shortening event (D4). Pink/purple rocks are felsic to mafic intrusions of the 1540–1500 Ma Williams-Naraku Batholith, blue and brown rock packages are pre- and post 1700 Ma metasediments respectively. Breccia and deposit symbols same as for Fig. 1. Grey = barren breccias (both D3 and D4) caused by extremely high energy volatile release (large stippled yellow arrows) from intrusions. Green shading and smaller yellow areas = fluids moving into D3 high failure potential sites with different chemistry or energy than the barren breccias, initiating IOCGs and Mo mineralization, with more restricted structurally-driven fluid flow (thin brown arrows) generating some Cu. Red shading, stipple and arrows = second generation, metal rich breccia emplacement into D4, high failure potential sites with ore deposition triggered by breccia ‘stalling’ and/or interaction with earlier fluids in these sites. Intrusion colours relate to speculation about different magma batches generating fluids with different metal and volatile content.

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References


Abstract. The Proterozoic East Arm Basin of Great Slave Lake, Canada, hosts iron oxide-apatite (IOA), five-element and Cu ± Au vein-type deposits associated with a string of ca. 1.87 Ga sills termed the Compton intrusions. Updates to our understanding of the regional geology of the East Arm Basin and iron oxide-copper-gold (IOCG) and affiliated deposits within broader iron oxide-alkali-calcic alteration systems highlight geochemical and temporal similarities between the Compton intrusions and co-magmatic volcanic rocks with the ca. 1.87 Ga intrusive and volcanic rocks of the Great Bear magmatic zone that are associated with known IOA and IOCG systems. Geochemistry of the host rocks and mineral occurrences of the East Arm Basin are also identical to those of the IOA-IOCG systems of the Great Bear magmatic zone, reaffirming that both regions have similar geologic origins and experienced similar magmatic-hydrothermal events. As such, we propose that the resource potential of the East Arm Basin includes all sub-types of the IOA-IOCG spectrum, such as hematite- and magnetite-group IOCG±U deposits and affiliated deposit types (e.g., iron oxide-U and albite-hosted U). Similarities between these two settings and mineralization in the Central Mineral Belt in Labrador warrant re-examination of Geon 18 terranes in Canada and abroad.

1 Introduction

The “East Arm Basin” refers to a ca. 100 by 300 km area on the eastern extension of Great Slave Lake in the Northwest Territories of Canada (Fig. 1) comprised of Paleoproterozoic sedimentary and volcanic rocks plus unconformably overlying sedimentary and volcanic rocks. The area has been withdrawn from exploration since 1970 for a proposed national park (Wright 2013). As such, our understanding of the metallogeny of the region has not kept pace with modern advances in ore deposit studies, in particular recognition of the iron oxide-copper-gold (IOCG) deposit model (e.g., Hitzman et al. 1992). The volcanic-sedimentary sequences are situated along the boundary between the Archean Slave Structural Province to the north (Hoffman 1973); to the south the basin is truncated by the Great Slave Lake shear zone, a crustal-scale continental transform structure that penetrates to depths of 180–210 km and offsets the Moho (Snyder and Kjarsgaard 2013). This crustal architecture bears attributes above which iron oxide-copper-gold (IOCG) deposits occur (c.f., Drummond et al. 2006; Corriveau and Mumin 2010).

Figure 1. Location of the East Arm Basin. Monzonitic intrusions of the Great Bear magmatic zone are shown in red while metasedimentary and volcanic rocks are shown in green. HT=Hottah Terrane, TMTZ=Taltson magmatic-tectonic zone, GLSZ=Great Slave Lake shear zone, TTZ=Taltson-Thelon orogenic belt, CMB=Central Mineral Belt. After Potter et al. (2013) and references therein.

2 Geology of the East Arm Basin

The supracrustal rocks in the East Arm Basin are divided into four unconformity-bound sequences termed (from oldest to youngest): 1) Union Island Group; 2) Wilson Island Group; 3) Great Slave Supergroup, and; 4) Et-Then Group. Mapped exposures of the Wilson Island and Union Island groups consist of metasedimentary and metavolcanic rocks whereas the Great Slave Supergroup is composed of alternating fluviatile and marine sedimentary rocks with evidence of former evaporites, intercalated with volcanic sequences (Hoffman 1968; Kjarsgaard et al. 2013; Kjarsgaard in prep.).

In terms of IOCG potential of the East Arm Basin, key geological features are the belt of 1.87–1.86 Ga calc-alkaline Compton intrusions (Bowring et al. 1984 and references therein) and potentially co-magmatic Pearson Formation volcanic rocks (Kjarsgaard et al. 2013). The intrusions exhibit locally significant metasomatic enrichment in sodium and depletion in potassium. The tops
of the intrusions (and host country rocks) are pervasively altered to a carbonate-sericite-chlorite-hematite assemblage while the intrusive contacts consist of zones of igneous and sedimentary rock fragments set in a red felsite matrix comprised of antiperthitic albite and quartz (Badham 1978). At some locations, the intrusions are thought to have intruded along solution collapse megabreccia units filled with water and possibly brines, resulting in sills with explosion breccias up to 30 m in thickness, and pervasive alteration of the country rocks and hydrothermal breccias and veins comprised of actinolite, apatite, magnetite and uranium (Badham 1981; Fig. 2). The Pearson Formation basaltic flows occur in the upper part of the Christie Bay Group, in a belt that is parallel to and north of the Murky Channel fault and Compton intrusions (Kjarsgaard et al. 2013). These subaerial flows range in thickness from 1–20 m, have variable hematite staining and are interbedded with thin mudstone (Hoffman et al. 1977; Goff 1984).

Historically, tectonic models of the Great Bear magmatic zone involve continental arc magmatism generated by eastward-dipping subduction during collision of the Hottah terrane with the Slave craton (Calderian orogeny of Hildebrand et al. 1987, 2010). However, the linear nature of the Compton intrusions and Pearson Formation volcanic rocks perpendicular to the eastward dipping Great Bear magmatic zone subduction zone are difficult to reconcile with this model (Kjarsgaard et al. 2013). As proposed by van Breemen et al. (2013), the Hottah-Slave collision that initiated the Wopmay orogen (Hoffman et al. 2011) may have also caused reversal of the paleocurrent indicators in the Great Slave Supergroup. As such, the authors propose that the base of the 1898–1864 Ma Great Slave Supergroup is likely correlative with the uppermost Coronation Supergroup units; the entire Coronation Supergroup was deposited from 1844–1882 Ma (Bowring and Grozinger 1992; Davis and Bleeker 2007; Hoffman et al. 2011). Conversely, the presence of duplexed crust or crust imbricated with upper lithospheric mantle observed across the Slave-Talson-Churchill teleseismic transect (Snyder and Kjarsgaard 2013) may explain the subduction-related geochemical signature observed in the co-magmatic Compton intrusive and Pearson Formation volcanic rocks (Fig. 3).

A new model by Ootes et al. (2015) proposes rifting and translation of the Hottah terrane from the southern margin of the Slave craton northwards along the proto-Wopmay fault to its present position west of the Slave craton, where collision with the Slave continued through to the end of Great Bear magmatism ca. 1855 Ma. This model is supported by detrital zircon data of Davis et al. (2015), which suggest the Hottah terrane was located on the margin of the Talson magmatic zone, and was dextrally transported by transtensional shear movement during basin opening as recorded by the Bell Island Bay Group (Ootes et al. 2015). If correct, the Wilson Island in the East Arm basin (Bowring et al. 1984; Johnson 1990) may represent the northeastern continental margin of the rifted basin and be correlative with the Bell Island Bay Group. As shown in Figure 3, felsic and mafic rocks of the Wilson Island Group do exhibit similar trace element patterns to those from the Zebulon Formation of the Bell Island Group in the Hottah terrane – a pattern that is also similar to the Compton intrusions and Pearson Formation – plus volcanic rocks of Faber and Sloan groups of the Great Bear magmatic zone. As such it is likely that magmatism in the East Arm and Great Bear magmatic zone were generated by similar processes beginning at ca. 1900 Ma and continued until at

3 Origin of the East Arm Basin and linkages with the Great Bear magmatic zone

The presence of subsidence and nappé tectonics plus the calc-alkaline Compton intrusions led Hoffman (1987) to propose that basin formation may have been related to subduction of a re-entrant oceanic lithosphere south of the Slave province, equivalent to the slab above which the Great Bear magmatic zone was generated. Gandhi and Prasad (1982) proposed that compositional data, differentiation along the trend of the Compton intrusions and the presence of mafic cognate inclusions indicate that they represent products of differentiation from mafic magmas at depth. Alternatively they could record injection and mixing of mafic magmas within intermediate to felsic magma chambers. The depositional environment of underlying Union Island (margin of a rift) and Wilson Island groups (thick platformal sequence deposited on thinned sialic crust) suggest the presence of weakened lithosphere. Therefore, the underlying geology and tectonic history support that this linear corridor was a preferential conduit for magmas generated at depth to intrude the Paleoproterozoic sedimentary rocks.
least ca. 1857 Ma when Great Slave Supergroup magmatism appears to have ceased in the East Arm, and magmatism in the Great Bear magmatic zone ended at ca. 1855 Ma.

**Figure 3.** Trace element spider diagrams of: *a* Great Bear (Sloan Gp) and Hottah (Zebulon Fm) basaltic rocks, *b* East Arm (Reinhardt and Pearson Fms) basaltic rocks, *c* Hottah terrane (Zebulon Fm) and Great Bear (Faber Gp) rhyolitic rocks, and *d* Compton intrusions, Pearson Formation and Faber group intermediate volcanic rocks. Data from Ootes et al. (2015), Kjarsgaard et al. (2013) and Azar (2007), normalized to primitive mantle of McDonough and Sun (1995).

4 IOCG potential of the East Arm Basin

The East Arm Basin shares certain key geological features with the Great Bear magmatic zone that are relevant to the development of IOA-IOCG systems. In particular, the Compton intrusions plus co-magmatic Pearson Formation volcanic rocks are coeval with, and similar in character, composition and mineralization to the 1872–1867 Ma intermediate plutons and volcanic rocks of the Great Bear magmatic zone (Fig. 1; Hoffman et al. 1977; Bowring et al. 1984 and references therein). In the Great Bear magmatic zone, these intrusions exhibit spatial and temporal relationships with several IOA-IOCG systems, regional iron oxide-alkali-calcic alteration and affiliated occurrences (e.g., NICO and Fab in the south, and Camsell River plus Balachev pluton, and Port Radium–Echo Bay districts in the north; Corriveau et al. 2016; Montreuil et al. 2016a, b). While the Great Bear magmatic zone experienced more voluminous magmatism, the majority of this post-dated IOA-IOCG mineralization (i.e., 1867–1855 Ma; Ootes et al. 2015 and references therein), as formation of the IOA-IOCG deposits has been constrained to 1875–1865 Ma during eruption of the 1.87 Ga magmas under largely sub-aerial conditions while cogenetic sub-volcanic intrusions were emplaced at the base of the volcanic piles (Hildebrand 1986; Hildebrand et al. 2010; Davis et al. 2011; Montreuil et al. 2016a).

As illustrated by case examples from the Great Bear magmatic zone and Chilean Cordillera, Corriveau et al. (2010, 2016), Mumin et al. (2010), Potter et al. (2013) and Barton et al. (2013) were able to provide examples of the continuum between IOA and IOCG deposit types within regional iron oxide-alkali-calcic footprints. The various affiliated deposits that can form during evolution of these systems have important ramifications for regional exploration and mineral assessment in underexplored regions such as the East Arm Basin where mineral occurrences were often categorized based on morphology (e.g., veins) and metal contents (see also Corriveau et al. 2017). There is thus a need of reassessing the metallogenic framework and mineral potential of areas hosting a great variety of U, Au, Ag, Cu, Co, REE, Cu, etc. showings and prospects in close proximity as well as areas with known regional iron-alkali-calcic enrichments such as IOA occurrences. The same is true for settings that host U deposits along strongly albitized zones.

The Central Mineral Belt of Labrador is one of these districts (Fig. 1) with well-known and widespread U ± Fe, Cu and Au occurrences with potential IOCG linkages (Corriveau et al. 2010b). Recent research and exploration along regional- to deposit-scale Na, Ca, K and Fe hydrothermal alteration, breccia zones and mineral occurrences has reinforced the temporal association of U mineralization and iron oxide-alkali metasomatism along the belt from 1.88–1.66 Ga (Sparkes 2017). Hence the seemingly disparate U-Fe, REE, Mo, Cu, Ag, U or Au-U occurrences in the Central Mineral Belt may be united, explained, predicted and explored for under the iron oxide-alkali-calcic alteration system model as done for the historic prospects in the East Arm Basin and the Great Bear magmatic zone.

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Evidence for a cryptic paleo-suture zone: implications for IOCG mineralisation in the Gawler Craton

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Abstract. The recognition of a paleo-suture zone in the eastern Gawler Craton is based upon differences in Archean basement ages, Paleoproterozoic magmatism and orogenesis, the geochemical and isotopic composition of A-type Mesoproterozoic granites, along with major contrasts in geophysical response, particularly magnetotelluric. Mafic rocks in the eastern Gawler Craton contain geochemical signatures of an enriched mantle, likely modified by subduction. Differing electrical conductivity at mantle-depths beneath the eastern and western Gawler Craton potentially records metasomatism linked to an early phase of subduction-accretion. While there is no evidence for a direct subduction link in the c. 1590 Ma iron oxide-copper-gold (IOCG) mineralisation of the eastern Gawler Craton, the presence of a fertile mantle formed by a prior subduction episode may have influenced the formation of IOCG mineralisation.

1 Introduction

Iron oxide-copper-gold (IOCG) mineralisation is developed in the eastern Gawler Craton within the Olympic Cu-Au Province (Fig. 1; Skirrow et al. 2007). Mineralisation is associated with early Mesoproterozoic A-type, intracontinental magmas that lack any direct association with subduction (e.g. Creaser 1996), potentially formed as a result of a mantle plume (e.g. Flint et al. 1993). In contrast, IOCG systems such as the Mesozoic Andean continental arc (Sillitoe 2003), and – based on recent recognition of shoshonitic and other subduction-related magmatism synchronous with mineralisation – Paleoproterozoic IOCG systems within the Great Bear Magmatic Zone (Snyder et al. 2014; Ootes et al. 2017) are related to contemporaneous subduction zone processes. The question arises as to what effect subduction has on the mineral systems and indeed if subduction is a necessary pre-requisite for IOCG mineralisation?

The Gawler Craton has generally been viewed as a single cratonic block developed over the interval c. 3150 – 1500 Ma (Daly et al. 1998; Hand and Reid 2012); however, it has been suggested that the eastern Gawler Craton could be a distinct piece of lithosphere from that of the western Gawler Craton (Hand et al. 2007; Hronsky et al. 2012), and therefore that the Gawler Craton may be a composite terrane containing a paleo-suture internal to the present boundaries of the craton. However, the location of such a suture, the timing of its formation has yet to be fully evaluated.

2 Geological Context

Rock forming events within the Gawler Craton can be summarised as: (i) c. 3150 Ma granitic basement reworked from an earlier but not exposed c. 3.4 Ga tonalite-trondhjemite-granodiorite source; (ii) c. 2550 – 2420 Ma Neoarchean – earliest Paleoproterozoic volcano-sedimentary complexes deformed during a c. 2470 – 2420 Ma tectono-metamorphic event; (iii) overlain and intruded by c. 2020 – 1720 Ma volcano-plutonic events and associated sedimentary successions, with major igneous events at c. 2000 Ma, c. 1920 Ma, c. 1850 Ma and c. 1730 – 1670 Ma; and, (iv) relatively minor c. 1650 – 1590 Ma sedimentation broadly associated with voluminous c.1620 – 1605 Ma and c. 1590 – 1570 Ma magmatic events.

The region underwent three major deformation and metamorphic events that variably reworked these lithostratigraphic units; the c. 2465 – 2420 Ma Sleaford–Kimba Orogeny, c. 1730 – 1690 Ma Ramberg–Kimba Orogeny; and the c. 1590 – 1550 Ma Kararan Orogeny (Hand et al. 2007). A fourth deformation and magmatic event, referred to as the Cornian Orogeny, occurred at c. 1850 Ma and is of more local extent, being restricted to the eastern Gawler Craton.

3 Evidence for a lithospheric-scale discontinuity in the eastern Gawler Craton

The region of the Gawler Craton that shows greatest geological variability corresponds to a roughly north-south trending region between what we here term the ‘eastern Gawler Craton’ and the ‘western Gawler Craton’ (Fig. 1).
Differences between the eastern and western Gawler Craton can be summarised as follows: (1) Archean basement ages; (2) location of the 1850 Ma magmatism; (3) location and eastern orogenic front associated with the c. 1730 – 1690 Ma Kimban Orogeny (Reid and Fabris 2015); (4) geochemistry and isotopic composition of c. 1590 Ma igneous rocks (Hiltaba Suite and Gawler Range Volcanics; e.g. Budd et al. 2001); (5) the widespread presence of mafic rocks with geochemical signatures consistent with derivation from subduction-modified mantle in the eastern Gawler Craton (e.g. Huang et al. 2016); (6) gradient in deep crustal electrical resistivity derived from 3D magnetotelluric models (Fig. 2); and, (7) variations in modern heat flow. Differences are also manifest in the style of c. 1590 Ma mineralisation across the Gawler Craton, with Cu-rich mineralisation being dominantly hosted in the eastern Gawler Craton, while to the west similar aged mineralisation is either Au-dominant or polymetallic but typically Cu-poor.

Magnetotelluric imaging of the mantle lithosphere beneath the Gawler Craton identifies a highly electrically resistive ‘core’ zone that corresponds broadly to the western Gawler Craton (Heinson et al. 2006; Thiel and Heinson 2013). Crust of the eastern Gawler Craton in contrast sits above generally more conductive mantle lithosphere, with some zones of enhanced electrical conductivity reaching into the upper crust in the Olympic Cu-Au Province (Thiel and Heinson 2013). The broad lithospheric architecture thus supports the notion that these two domains within the Gawler Craton are associated with significantly different lithospheric columns.

The co-location of different lithospheric columns between the eastern and western Gawler Craton can be explained if there was an early accretion event that brought these two pieces of crust and mantle lithosphere together. Potentially, the lithospheric boundary in the Gawler Craton could represent a paleo-suture zone. If this is the case, we suggest that the suturing event must have occurred prior to c. 1750 Ma, since volcano-sedimentary successions of similar style and provenance occur on both sides of the apparent suture zone. The c. 1850 Ma magmatism of the Donington Suite could represent a magmatic arc, however, mafic rocks of this age also contain evidence for a pre-existing modified lithospheric source (Mortimer et al. 1988). An alternative timing of suturing earliest Paleoproterozoic associated with the c. 2465 – 2420 Ma Sleafordian Orogeny, potentially making this suture zone a very old feature of the lithosphere of southern Australia.

4 Influence of a paleo-suture zone on Mesoproterozoic IOCG mineralisation

Lithospheric discontinuities provide pathways via which mantle-derived magma, fluids and heat can ascend into the crust (e.g. Griffin et al. 2013). The mixing of such material and thermal inputs from the mantle with the crust and crustal fluids provides conditions for the formation of ore deposits, including those of the IOCG class (e.g. Groves et al. 2010). Lithospheric discontinuities at a variety of scales have acted to channel magmas and associated fluids into depositional sites for copper-gold mineralisation (e.g. Sillitoe 2003; Corriveau 2007).

The spatial correspondence between highly conductive mantle lithosphere beneath the eastern Gawler Craton could be a signature of metasomatism of the mantle during an early subduction-accretion event. Subduction prior to suturing results in metasomatism of otherwise refractory peridotite via introduction of volatiles such as H2O, CO2, H2, F, C, along with magmatophile elements such as Fe, Cu and Au (e.g. Beyer et al. 2006; Zhang et al. 2009). Mantle metasomatism also leads to increased fertility for partial melting during subsequent tectonothermal events (e.g Turner et al. 1996). Melting of metasomatized and heterogeneous mantle during the Mesoproterozoic likely caused A-type magmatism across the Gawler Craton. Variation in the composition of the mafic magmas, and the crustal column that underwent associated melting and assimilation resulted in relatively oxidised magmas primed for Cu-Au mineralisation across the eastern Gawler Craton (Budd et al. 2001). Interaction of these magmatic-derived fluids with upper crustal/meteoric fluids within regional, hypersaline hydrothermal systems (e.g. Williams et al. 2005; Barton and Johnson 1996) and focused by contemporaneous mid- and upper-crustal deformation led to the formation of the Olympic Dam IOCG deposit and related mineralisation within the Olympic Cu-Au Province.

Whilst in IOCG terranes, such as the Andes or Great Bear Magmatic Zone, subduction is directly associated with mineralisation, in the Gawler Craton subduction may have occurred up to c. 0.9 Ga prior to A-type magmatism and associated mineralisation. In this respect, the metallogenic evolution of the Olympic Cu-Au Province is more akin to mineralisation formed above paleo-suture zones; one notable example of which is the Voisey’s Bay Ni-Cu-Co deposit formed above the boundary between the Churchill and Nain Provinces (e.g. Ryan 2000). It therefore appears that a compositionally heterogeneous mantle remains fertile for the production of metalliferous magmas either during a subduction event, or potentially many millions of years after the metasomatic event.


The point of intersection between the porphyry and IOCG spectra of ore deposits

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Abstract. The porphyry and IOCG spectra of ore deposits intersect in intrusion-related hydrothermal systems formed in arc and back-arc tectonic settings, where S-rich magmas and hydrothermal fluids form pyrite-dominated porphyry deposits, or S-poor magmas and fluids form magnetite-hematite-dominated IOCG deposits. Alkaline-type porphyry deposits show the closest similarity between these two groups.

1 The porphyry and IOCG spectra

The “porphyry” and “IOCG” (iron oxide-copper-gold) deposit classifications both encompass a wide range of sub-types. The porphyry spectrum is united by derivation from magmatic-hydrothermal fluids exsolved from crystallizing magmas in the upper crust, but these magmas can range from oxidized dioritic–granodioritic I-type to reduced granitic S-type. Resultant ore deposits can be Au-, Cu-, or Mo-rich (or any combination), or Sn-W-rich, but share many vein and alteration characteristics, such that they are all generally recognizable as porphyry-type deposits (Lowell and Guilbert 1970; Gustafson and Hunt 1975; Carten et al. 1993; Sillitoe 2010).

On the other hand, IOCG deposits, in their broader classification, do not have an agreed common origin, and magmatic, basinal, and metamorphic fluid sources have all been proposed (depending on the deposit sub-type; Barton and Johnson 1996, 2004; Haynes 2000; Hitzman 2000; Pollard 2000, 2006; Sillitoe 2003; Mark et al. 2004; Williams et al. 2005; Williams 2010; Marschik and Kendrick 2015). Where they are associated with igneous rocks, these tend to be I-or A-type granitoids, locally with coeval mafic (bimodal) magmatism (Williams et al. 2005; Groves et al. 2010). The metal inventory of IOCG deposits is also not restricted to Fe-Cu-Au, but commonly includes enrichments in lithophile elements (e.g., U, REE, Co, Bi, Ag, P; Barton 2014), while some classifications include deposits with no Au, or even no Cu and Au, such as sediment-hosted Cu deposits, and iron oxide-apatite deposits (Williams et al. 2005; Hunt et al. 2007; Corriveau and Mumin 2010; Reich et al. 2016).

Porphyry Cu-Mo-Au deposits are classically associated with I-type arc magmas in subduction zone settings, but this is now recognized to extend to distal or post-subduction (e.g., collisional) settings (Hou et al. 2009; Shafiei et al. 2009; Richards 2009), where more alkaline (commonly shoshonitic) compositions occur. Molybdenum and Sn-W porphyry deposits associated with felsic I- and S-type magmas occur in continental interior settings, and predominantly involve continental crustal melts, possibly with contributions from more mafic mantle-derived melts. In contrast, while the tectonic setting of IOCG deposits is less clear, they seem to be more typically found in extensional or transtensional tectonic settings, in back-arc or continental interiors (Hitzman et al. 1992; Oyarzun et al. 1999; Groves et al. 2010).

2 A point of intersection?

The closest point of intersection between these broad deposit categories is Cu-Au deposits formed in association with calc-alkaline to mildly alkaline I-type magmas in orogenic (subduction, distal subduction, or collision-related) to post-orogenic (post-collisional extension) tectonic settings (Groves et al. 2010; Tornos et al. 2010).

In these deposits, mineralization occurs as chalcopyrite and bornite (with associated Au) accompanied by variable amounts of pyrite, and magnetite (at depth) or hematite (at shallower levels). A simple distinction between porphyry and IOCG deposits is that the former are dominated by pyrite (Fe-sulfide), and the latter by magnetite/hematite (Fe-oxide). Alteration styles in both deposit types include potassic, sodic, and sodic-calcic, but more acidic alteration styles such as phyllic and argillic alteration are typically less well developed in IOCG deposits (Hitzman et al. 1992; Williams et al. 2005; Pollard 2006; Mumin et al. 2010; Corriveau et al. 2016). Relatively oxidized, high-temperature, saline hydrothermal fluids are involved in both deposit types (Burnham 1979; Candela 1989; Pollard 2006; Wilson et al. 2003; Rusk et al. 2004; Williams et al. 2005; Klemm et al. 2007; Groves et al. 2010).

The closest similarity between these broad deposit groups occurs in alkaline porphyry Cu-Au deposits, which are characterized by potassic, sodic, sodic-calcic, and calc-potassic alteration styles with abundant hydrothermal magnetite and hematite (Lang et al., 1995; Cooke et al., 2007; Jago et al., 2014; Micko et al., 2014). These deposits typically form in distal subduction (back-arc) tectonic settings.

A study of igneous rocks associated with porphyry and IOCG deposits in the Cretaceous Coastal Cordillera of northern Chile suggests that the only significant compositional difference relates to the sulfur content of the magmas, which are otherwise almost indistinguishable in terms of major and trace element and isotopic composition (Richards et al. 2017). There is also a small but important change in tectonic setting, despite the
almost complete spatial overlap: during the mid-Cretaceous, this area of the Coastal Cordillera experienced localized back-arc rifting, and it was this extensional or transtensional phase, or its termination (Chen et al. 2013) that was associated with S-poor IOCG deposit formation. Earlier and later regular arc magmatism was associated with S-rich porphyry Cu±Mo±Au mineralization. Richards et al. (2017) proposed that the lower S-content of the IOCG-related magmas reflected the back-arc tectonic setting, distal from the flux of volatiles including S below the main arc axis (which would have lain to the west at that time). It is possible that the IOCG-related magmas were derived by remobilization of previously subduction-modified lithosphere during back-arc or intra-plate rifting and invasion of asthenospheric melts (Groves et al., 2010; Richards and Mumin 2013), which would have occurred under lower $/S_2$ conditions due to the lack of a flux of fresh sulfur from active subduction. A hint of this is seen in the rare occurrence of slightly more alkaline and isotopically primitive magmas in the mid-Cretaceous suite.

3 Conclusion

Porphyry Cu±Mo±Au and Cu-Au-rich IOCG deposits share an origin in saline, oxidized hydrothermal fluids, but may be differentiated by the amount of sulfur in those fluids and source magmas. Sulfur-rich magmas and exsolved fluids form pyrite-rich porphyry-type mineralization, whereas S-poor magmas and fluids form magnetite-hematite-rich IOCG deposits. Whereas porphyry Cu±Mo±Au deposits are unified by formation from oxidized, saline hydrothermal fluids exsolved from magmas crystallizing in the upper crust, broadly similar fluids can also form in other environments such as sedimentary basins, resulting in a wide range of deposit types collectively referred to as IOCG-type. The porphyry and IOCG spectra most closely overlap in arc environments (broadly including back-arc settings) which give rise to magmatic-hydrothermal systems with variable S contents. IOCG deposits in these settings might be described as S-poor porphyry deposits.

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Apatite textures and REE chemistry in the iron oxide-apatite (IOA) deposits of the eastern Adirondack Highlands, New York, USA

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Abstract. The iron oxide-apatite (IOA) deposits of the eastern Adirondack Highlands have recently attracted renewed attention due to their potential for REE resources. Apatite is the main REE-host and is found in variable quantities within the magnetite deposits. Neither the textures nor the chemistry of the apatite crystals are consistent between all iron ore seams, and even seams that are only a few meters apart show variation. Some deposits contain unaltered apatite crystals, whereas other deposits have portions of crystals that have been altered and leached of chemical impurities. The leached areas have higher concentrations of Ca and P and lower concentrations of impurities such as REE, Y, Th, and Si. Within these leached areas, the REE were remobilized and concentrated to form inclusions of monazite, xenotime, and allanite. Reconciling the chemistry of the fluids necessary for ore deposit formation is problematic; a Na-rich fluid is required for the albite alteration that is associated with magnetite-apatite crystallization but a Na-poor fluid is necessary to leach and remobilize the REE from the apatite. Therefore, the formation of the IOA deposits of the Adirondacks required multiple events.

1 Introduction

The iron oxide-apatite (IOA) deposits of the north-eastern Adirondack Highlands of New York have been known since the mid-1700s for their rich magnetite ore (Lupulescu 2008). Recent interest has focused on the potential rare earth element (REE) resource associated with accessory apatite and discrete REE-bearing phases such as monazite, xenotime, stillwellite, and allanite (Lupulescu et al. 2012; Singer and Lupulescu 2016). Apatite is the main host for REEs, Y, Th, and U (McKeown and Klemic 1956). Waste rock piles are associated with all of the mines, and large tailings piles with abundant apatite can be found in the Mineville area; however, these are currently used only for industrial purposes such as for road gravel and construction. Radiometric airborne surveys show large positive eTh and eU anomalies corresponding to tailings piles and roads (Shah et al. 2016; Shah 2016).

The genetic origin of these deposits remains controversial. Various hypotheses suggest the deposits are formed by orthomagmatic, metamorphic, hydrothermal, or brine-related processes (e.g., Valley et al. 2011). Determining the relationship between various iron ore and accessory minerals and mechanisms for REE enrichment will aid in our understanding of these historically significant deposits. Additionally, developing a better understanding of the REE distribution within apatite and remobilization into discrete REE-bearing phases will benefit our understanding of the potential REE resource in the readily available waste piles as well as ore that remains in the ground.

2 Geology

The Adirondack Highlands of the Proterozoic Grenville Province record multiple high-grade intrusive and deformation events between roughly 1.3 to 1.0 Ga; however, the exact timing of these events is controversial due to recently reinterpreted zircon ages (Aleinikoff and Walsh 2015). These Kiruna-type IOA deposits are predominantly hosted within the K- and Na-altered Lyon Mountain Granite Gneiss (LMG); few deposits are hosted in paragneiss or other Mesoproterozoic rocks (Fig. 1). Ore-related zircon crystals have yielded ages 40-90 million years younger than the hosting LMG which is interpreted to have been emplaced ~1140-1110 Ma (Aleinikoff and Walsh 2016; Walsh et al. 2016), or alternatively interpreted as being emplaced ~1060-1050 Ma (Valley et al. 2011).

Electron microprobe U-Th-Pb data suggest that monazite formed even later at around 980 Ma (S. Regan, unpublished data). Magnetite-rich pegmatites (~1045-1016 Ma; Valley et al. 2011) are also recognized.

The ore bodies typically have sharp contacts with host rock, or are less commonly gradational. In addition to magnetite and apatite, the ore may contain pyroxene, quartz, feldspars, zircon, sphene, monazite, and/or allanite. The mineralogy of individual deposits and between ore seams within a deposit is variable. Paragneiss-hosted deposits (e.g., Vineyard mine) tend to be more sulfide-rich, with the pyrite content making them less suitable for iron mining (Newland 1908).

3 Methods

In situ work on polished thin sections of ore was conducted for 20 deposits. Each sample was examined with a petrographic microscope to identify and locate apatite crystals and to document ore textures. Multiple apatite crystals from each sample were then imaged with high-contrast back-scattered electron (BSE) imaging using a JEOL 5800LV scanning electron microscope to determine
whether the crystals were altered, unaltered, and/or zoned. Qualitative energy dispersive spectroscopy (EDS) chemical maps were produced using a JEOL 5800LV SEM over a scan time of approximately two hours each. The major and trace element chemistry of these apatite crystals was then determined using a JEOL 8900 Electron Microprobe with five wavelength dispersive analyzers. Elements analyzed include, Al, Si, P, Ca, Pb, Th, U, Sc, As, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, F, and Cl. All lab work was completed at the U.S. Geological Survey Microbeam Laboratory, Denver, Colorado.

Figure 1. Generalized geologic map of the Adirondack Highlands, New York, with locations of select mines and districts sampled in this study (after McLelland et al. 2013).

4 Results

Apatite samples from the ore seams were characterized, imaged, and analyzed for major and minor element geochemistry. Apatite crystals are found adjacent to all of the major ore and gangue minerals and appear to have crystallized prior to magnetite. Using high-contrast BSE imaging, a variety of textures are distinguishable (Fig. 2). Some apatite crystals are unaltered, whereas others are altered and contain brighter primary zones and darker altered zones. Other crystals contain what appears to be subtle but primary growth zoning. Some of the altered crystals have depleted edges and parallel stripes of bright primary areas and dark depleted areas. In the stripped apatite, REE-bearing phases occur in fractures, on the edges of the apatite, and as inclusions within the BSE-dark stripes. Monazite inclusions and rims are spatially associated with the darker altered domains in the altered apatite crystals. Unaltered crystals do not contain monazite inclusions, but may have monazite rimming portions of the crystals. Less commonly, apatite crystals contain rounded apatite with internal growth zoning and a bright apatite overgrowth. The BSE-brighter areas have more impurities whereas the darker areas contain more Ca and P, but less impurities.

Figure 2. High-contrast BSE images showing the various textures of the apatite crystals. The brightest crystals are monazite. a Unaltered apatite from the Cheever mine. b Zoned apatite crystals amalgamated together with a BSE-bright overgrowth from the Hammond Pit, Hammondville. c Altered apatite with bright monazite inclusions within altered regions from Dog Alley, Hammondville. d Close up of bright monazite inclusions along a leached fluid flow path in apatite from Long Pond, Skiff Mtn. ap=apatite; mt=magnetite, mz=monazite.

Nearly 250 EPMA data points indicate that the apatite crystals are classified as fluorapatite, with F content ranging from 3.5 to 6.6 wt%; Cl content ranges from 0.04 to 0.89 wt%. Apatite crystals exhibit consistent REE patterns within each ore seam, but not between seams or deposits (Fig. 3); the REE profile can even be different for apatite crystals from adjacent ore seams only a few meters apart. In deposits that have altered apatite, the altered areas are consistently more depleted in REEs than the unaltered areas (Fig. 3). Unaltered apatite has total REE oxide (TREO) contents ranging from 0.04-7.15%, bright domains in altered apatite range from 0.63-12.71%, and dark domains of altered apatite range from 0.30-7.45%. Generally, the apatite with the highest As content has lower TREO contents. Chemical impurities such as REE, Th, U, and Si are positively correlated and are all negatively correlated with Ca and P.

All of the apatite is slightly more enriched in LREE than HREE, but are still relatively enriched in both. There is no Ce or Eu anomaly that distinguishes each type of apatite, but nearly all of them have positive Ce and negative Eu anomalies. Only one analysis contained Pb concentrations above the detection limit of ~600 ppm; Sc and Tb were also rarely observed in concentrations above their detection limits of ~200 and 950 ppm, respectively. Thorium concentrations rarely exceed 0.5 wt%, but thorite crystals are noted in the ore samples.
5 Discussion

The fluorapatite crystals contained within these IOA deposits are a repository for REE. Ore-related apatite crystallized prior to magnetite but has been subsequently altered. The primary apatite consists of chemically homogenous crystals and small, round, concentrically zoned crystals that have been amalgamated together.

A later metasomatic event altered and recrystallized portions of the apatite crystals. The original, unaltered apatite crystals contain various concentrations of impurities such as REE, Th, and Si; altered portions of apatite that appear darker in BSE images contain lower concentrations of REE, Th, and Si, but higher concentrations of Ca and P (Fig. 4). All inclusions of monazite, xenotime, and thorite within the apatite crystals are only found within these metasomatized regions. There is no preferential depletion of either LREE or HREE compared to the other.

Monazite inclusions within apatite can be produced through metasomatic reactions (Harlov and Forster 2003). Monazite, xenotime, and thorite inclusions formed via fluid-mediated dissolution-reprecipitation of apatite and remobilized various impurities that compose the REE inclusions. This metasomatic event is likely what was dated around 980 Ma (S. Regan, unpublished data), which is younger than the host rock and younger than the oldest ~1.1-1.0 Ga ore-related zircon crystals (Valley et al. 2009; Aleinikoff and Walsh 2016).

Extensive albite and microcline alteration of the host LMG requires fluids rich in Na and K, respectively. The growth of magnetite-apatite ore is associated with Na-rich fluid alteration (McLelland et al. 2001; Valley et al. 2011). However, the existence of monazite inclusions within leached apatite suggests that the late altering fluids were Na- and Ca-poor since these would stabilize the apatite and...
5 Conclusions

Apatite crystals within the IOA deposits of the Adirondacks contain significant quantities of REE. However, the chemistry and textures exhibited by the apatite varies between ore seams and deposits. Apatite that has been altered contains BSE bright and darker regions, with higher and lower concentrations of REE, respectively. Monazite and lesser xenotime and thorite inclusions are spatially associated with the BSE-dark regions in the apatite crystals. Nucleation of monazite within altered apatite crystals is fluid-induced and associated with remobilization of REE from the primary apatite.

The ore is largely associated with Na-altered host leucograniates and it is suggested that the growth of magnetite-apatite ore is due to Na-rich fluids (Valley et al. 2011). However, the alteration of the apatite and remobilization of REE forming secondary inclusions of monazite requires a Na-poor fluid. Coupling this discrepancy in fluid chemistry with various ages of minerals from the ore seams indicates that multiple events are responsible for the mineralogy of the deposits.

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References


Metallogenic significance of altered volcanic rocks near the Prominent Hill IOCG deposit, South Australia

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Abstract. The blind Prominent Hill hematitic IOCG deposit occurs in a steeply-dipping overturned rock sequence with no surface exposures. Ore is localized within an interpreted Paleoproterozoic marine carbonate and siliciclastic unit whereas younger subaerial mafic-intermediate volcanic rocks and red beds physically underly the deposit. Geochemical data and previously-presented detrital zircon ages suggest that the younger rocks are equivalent to the ca 1.59 Ga Gawler Range Volcanics (GRV) in other parts of the Gawler Craton. However, in common with examples from near Olympic Dam, some of the volcanic rocks near Prominent Hill are strongly enriched in incompatible elements compared to GRV from type sections with no known IOCG association. Volcanic rocks at Prominent Hill are extensively altered and clearly predate the ore-forming hydrothermal system. In the more distal footwall they range from essentially unaltered to pervasively albitized. Albite was sequentially overprinted by chlorite, sericite (Mg-Fe illite) hematite and sulphides + carbonates and the development of the latter minerals increases towards the interpreted ca 1.6 Ga unconformity/disconformity and the orebody. These observations indicate that fluid flow associated with ore formation at Prominent Hill was focussed close to a major regional stratigraphic discontinuity at the base of the GRV-equivalent sequence.

1 Introduction

Prominent Hill (discovered in 2001) is one of the principal hematitic Cu-Au deposits in the archetypical IOCG district of the eastern Gawler Craton in South Australia which is associated with a 1.56-1.60 Ga large igneous province (e.g. Haywood and Skirrow 2010). In common with other large deposits such as Carrapateena and the giant Olympic Dam deposit, Prominent Hill is characterized by abundant breccias, large volumes of hematite-white mica-carbonate altered rock, variation of the dominant Cu mineral species (native copper/chalcocite/bornite/chalcopyrite), and a significant enrichment of F, Ba, LREE and U (Belperio et al. 2007). The mineralized Proterozoic basement near Prominent Hill is concealed by approximately 100m of Palaeozoic and Mesozoic sedimentary cover and the recent exploration at in the surrounding area has revealed a previously-unknown but extensive package of volcanic rocks and red beds (“Neptune Volcanics” of Freeman and Tomkinson 2010) which includes the rocks in the immediate structural footwall of the Prominent Hill deposit. Detrital zircon U-Pb geochronology indicates that the red beds are no older than ca 1.59 Ga whereas the youngest zircons in the shallow marine sedimentary sequence that hosts the ore deposit have ages around 1.75 Ga (Bull et al. 2015; Allen et al. 2016). Separately, new work at Olympic Dam has shown that there are relics of sedimentary rocks that also contain ca 1.59 Ga zircons in the upper parts of the mineralized breccia complex there (McPhie et al. 2016). Furthermore, altered mafic-ultramafic volcanic rocks interpreted to belong to the regional 1.60-1.59 Ga Gawler Range Volcanics (GRV) Suite are now known to locally directly overly the Olympic Dam breccia complex (Huang et al. 2016). These observations suggest it is possible that the large hematitic IOCG deposits of the Gawler Craton are somehow related to the basal contacts of the GRV basin or its equivalent subbasins. This paper examines this issue further by describing the geochemical affinity and alteration history of the volcanic rocks at Prominent Hill.

2 Geology of the Prominent Hill deposit

Prominent Hill is ca 650 km NNW of Adelaide and ca 200 km NW of Olympic Dam in the northeastern part of Gawler Craton of South Australia. Extended descriptions of the geology and geological setting of the ore deposit are available in Belperio et al. (2007), Freeman and Tomkinson (2010), Schelgel and Heinrich (2015) and Williams et al. (in press).

The deposit is located in the proximal footwall of a major N-dipping regional fault system along which metamorphic domains of the northern Gawler craton are thrust over a foreland composed mainly of Archean rocks (Mulgathing Complex; Harris et al. 2013). Prominent Hill, discontinuous bodies of barely metamorphosed shallow marine mixed carbonate-siliciclastic rocks are preserved immediately below the
thrust. One of these bodies hosts the Prominent Hill orebodies and based on their lithological character and detrital zircon evidence (Bull et al., 2015) these rocks are considered probable equivalents of the ca 1.75 Ga Wallaroo Group which is extensively developed in the eastern Gawler Craton IOCG province (cf. Skirrow and Haywood, 2010). At Prominent Hill, the sequence dips steeply N and is overthrust such that the orebodies are structurally underlain by the younger association of subaerial volcanic and red bed sedimentary rocks (Freeman and Tomkinson, 2010). Seismic reflection data indicate that the volcanosedimentary sequence has a maximum thickness of ca 4.5 km near Prominent Hill and persists in subcrop for around 7 km southwards where it overlies Archean basement along a contact with much shallower northerly dip than characterizes the sequence at the mine (Harris et al., 2013).

Production at Prominent Hill commenced in 2009 with resources identified to May 2010 of 278.8 Mt @ 0.98% Cu, 0.75 g/t Au (Freeman and Tomkinson, 2010). The majority of this was in the Malu resource in the eastern part of the mine area with additional production from the much smaller Ankata resource 2 km to the west. A predominantly volcanic sequence occupies a consistent structural position in the Malu footwall area and its contact with the Palaeoproterozoic host rocks there is interpreted to be an overturned unconformity or disconformity.

3 Petrochemical characteristics and regional affinity of the volcanic rocks

Many volcanic intersections in OZ Minerals exploration drill core from near Prominent Hill were assayed at 1 or 2m intervals using lithium borate fusion followed by multi-element analysis by ICP-MS (including all silicate major components and a range of useful petrogenetic indicator elements such as Zr, REE and Th). As a consequence there is a very large high quality geochemical dataset for these volcanic rocks. Intersections considered to be representative of the overall variation in the regional sequence were selected from ten drill holes extending from the Umbriel Prospect (ca 20 km west of Prominent Hill) to the Halifax Hill prospect (ca 30 km east of Prominent Hill). The data include three holes from a strike interval of ca 2 km in the Malu area at Prominent Hill (drill holes PH11D576, PH11D561 and PH10D527W1). The data were manually-filtered with reference to down-hole geochemical variation in order to remove anomalous samples from lithologically mixed assay intervals. Additionally, all samples with >15 wt % Fe were removed in order to reduce mass dilution effects in the data due to the density increase associated with locally intense hematitization. The residual regional dataset after the application of these filters contains 2773 samples (Fig. 1).

A plot of Zr/TiO₂ against SiO₂ (normalized to volatile-free totals of 100 wt%) reveals aspects of the overall compositional variation of the volcanic rocks in the Prominent Hill area (Fig. 1). The ratio Zr/TiO₂ is used in the manner of Winchester and Floyd (1977) to provide an independent differentiation index that is unlikely to be significantly-affected by alteration. The data display the expected positive correlation though with considerable scatter along horizontal (i.e. constant Zr/TiO₂) trends. This is probably due mainly to phenocryst-sorting associated with dynamic emplacement (consistent with variably-crowded porphyritic textures exhibited by the rocks). There will also be a contribution from hydrothermal quartz infill and dilution associated with hematization that are observed features in these rocks. Despite these complications, the primary magmatic variation can be reasonably deduced from the overall distribution of data in the large dataset. There is a broadly trimodal distribution including a dominant continuous basalt-dacite series with internal modes close to 53 and 63 wt % SiO₂, separated by a compositional gap from more fractionated rocks with SiO₂ mainly between 72 and 78 wt %

![Figure 1: Zr/TiO₂ - SiO₂ plot for volcanic rocks in the Prominent Hill region. (SiO₂* is SiO₂ normalized to a major component total of 100 wt% in order to remove the effects of variable hydration and carbonation in altered samples).](image)

![Figure 2: Primitive mantle normalized trace element patterns of representative mafic rocks from the Prominent Hill area (coloured symbols) with examples of GRV basalts from other locations in the Gawler Craton (black).](image)
volcanic rocks from the Prominent Hill area have characteristic similarities with GRV from other parts of the Gawler Craton (Fig. 2). These include marked enrichment of the most incompatible elements along with negative Nb-Ta, Zr-Hf and Ti anomalies. Prominent Hill area basalts also exhibit strong similarities with a marginal facies of the large White Hill Gabbro body that intrudes metamorphic rocks in the upper plate of the regional thrust system ca 5 km NW of the mine (Freeman and Tomkinson, 2010) and has given a U-Pb zircon age of 1562±14 Ma (Allen et al., 2016). Despite these regional similarities, there is also significant variation in the degree of incompatible element enrichment displayed by the ca 1.59 Ga volcanic associations in different parts of the craton. Extreme enrichment (e.g. 30-50 ppm Th in basalt) characterizes some rocks near Prominent Hill and has also been reported in olivine basalts from the Wirrda Well IOCG prospect near Olympic Dam (Huang et al., 2016; Fig. 2).

![Figure 3. Down hole variation of K/Al and Zr/TiO₂ (cf. Fig. 1) in drill hole PHD527W1. The variation in K/Al ratio is related to alteration. Range A broadly corresponds to albitionized rocks. Range B includes weakly altered ‘rocks, albitionized rocks overprinted by white mica alteration, and the K feldspar altered core of the Gairdner-type dyke. Range C corresponds to strong white mica alteration and range D to strong K feldspar alteration which is restricted to rocks near the contacts of the Gairdner-type dyke.](image)

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4 Alteration in the Prominent Hill footwall volcanic sequence

The alteration paragenesis in the footwall volcanic sequence has been investigated in drill hole PHD527W1 (Fig. 3) which was drilled near the eastern edge of the Malu resource. This hole was drilled from south to north (oblique to bedding) producing an unusually long (ca 1000m) intersection of the volcanic sequence with exceptional resolution of the lithological and chemical variation near the contact with the Paleoproterozoic host rocks which are present below a down hole depth of ca 1100m (Fig. 3). The volcanic rocks are mainly basaltic andesite and andesite and a distinct chem stratigraphy is revealed by the Zr/TiO₂ variation in the assay data (Fig. 3). A very distinctive pepperitic crowded plagioclase porphyry stratigraphically over lain by a thin shale occurs near 500m depth and is a useful stratigraphic and chemical marker that can be traced westwards in other drill holes along strike in the Malu resource area.

![Figure 4. Scanned thin section (a) and backscattered electron image (b) of an altered basaltic andesite from 349m depth in drill hole PH10D527W1. Albitionized plagioclase phenocrysts have been largely replaced by illite. Microscopic hematite is localized by the primary porosity (interconnected vesicles) and has directly replaced the silicate matrix. Ab - albite; Brt - barite; Chl - chlorite; Hem - hematite; Ill - illite.](image)

Figure 4. Scanned thin section (a) and backscattered electron image (b) of an altered basaltic andesite from 349m depth in drill hole PH10D527W1. Albitionized plagioclase phenocrysts have been largely replaced by illite. Microscopic hematite is localized by the primary porosity (interconnected vesicles) and has directly replaced the silicate matrix. Ab - albite; Brt - barite; Chl - chlorite; Hem - hematite; Ill - illite.

The youngest part of the volcanic intersection (ca 200-350m down hole) is weakly altered though variably affected by cryptic albitionization that occurred by pseudomorphic replacement of the primary calcic plagioclase (Fig. 4). The intensity of albitionization increases down hole and it is chemically most evident between ca 375 - 525 m. At greater depths, albite is itself increasingly replaced by white mica resulting in increased K/Al. The deepest part of the volcanic intersection is characterized by intense pervasive white mica alteration (+ hematization) though there is a complication near 1000m down hole.
where the sequence is intruded by a postmineralization dolerite dyke which is thought to belong to the ca 820 Ma Gairdner Dyke suite (cf. Freeman and Tomkinson, 2010).

Albite was sequentially overprinted by chlorite, Fe-Mg-bearing illite, hematite and sulphides+carbonates. White mica-hematite alteration intensity increases unevenly towards the orebody with a variety of controlling features including primary porosity, stratigraphic contacts and fractures (e.g. Fig. 4a). Much of the hematite formed by direct microspecularite replacement of the major rock-forming silicates (i.e. no precursor magnetite; Fig. 4b). Hematite is commonly associated with minor minerals including apatite, barite and REE minerals (mainly Ca-REE fluorcarbonates rocks as opposed to the monazite, florencite and REE-only fluorcarbonate phases that occur in the orebody). The principal sulphides in the volcanic rocks are pyrite and chalcopyrite as opposed to rare pyrite, chalcopyrite, bornite and chalcocite in the orebody. The altered structural footwall is also characterized by Mn-enrichment related to carbonate veins. The Gairdner-type dyke and adjacent volcanic rocks are overprinted by a separate younger alteration sequence that includes a second phase of albitization succeeded by K-feldspar alteration which is most intense where it affects previously sericitized volcanic rocks at the dyke contacts (Fig. 3).

5 Discussion and conclusions

Recent exploration near Prominent Hill has delineated an extensive concealed belt of GRV-equivalent volcano-sedimentary rocks including some of the most extensively-preserved mafic-intermediate volcanic rocks of this age in the Gawler Craton. Basaltic andesite and andesite dominate the immediate structural footwall sequence near the main Prominent Hill resource and are interpreted to be separated from older rocks that host the orebodies by an overturned unconformity or disconformity. Volcanic rocks near Prominent Hill are generally, if inconsistently-enriched in incompatible elements compared to exposed GRV in their type areas 200-300 km to the south where there are no known IOCG deposits. Despite the hydrothermal disturbance it can reasonably assumed that the magmas were additionally enriched in incompatible ore-related elements Ba, LREE and U and it is therefore possible that there is a genetic association between the enriched igneous rocks and IOCG deposits.

Prominent Hill volcanic rocks were albited before ore-formation and younger ore related hematite-white mica alteration becomes more intense and pervasive towards the contact with the orebody host rocks. The possibility that some component of the metal in the ore deposit was hydrothermally leached from the GRV needs to be considered (cf. Barton and Johnson, 1996). The distribution of ore and ore-related alteration at Prominent Hill suggests that fluid flow during mineralization was strongly influenced by the major discontinuity at the stratigraphic base of the volcanic sequence.

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Geology and metallogeny of Neoarchean and Paleoproterozoic copper systems of the Carajás Domain, Amazonian Craton, Brazil

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Abstract. The copper deposits of the Carajás Domain in the southeastern Amazonian Craton (Brazil) are grouped into iron oxide-copper-gold (IOCG) and Cu-polymetallic systems. These systems represent multiple ore-forming hydrothermal events that took place in the Neoarchean (2.70 Ga and 2.56 Ga) and Paleo-proterozoic (1.88 Ga) during the reactivation of regional-scale shear zones. The world-class Neoarchean (2.70 Ga and 2.56 Ga) IOCG systems were emplaced at deeper crustal levels compared to the Paleo-proterozoic analogues. The Neoarchean and Paleo-proterozoic Cu-polymetallic deposits are typically shallow hydrothermal systems and as a contrast to the IOCGs result in lower sulfidation state and more reduced ore assemblages. Mixing of high temperature hypersaline metalliferous fluids with other fluid types is a marking feature in both copper system groups and a trigger to ore precipitation. While a magmatic fluid source still remains unclear, non-magmatic brines (e.g. bittern fluids) seem to be an important component in the Neoarchean IOCG systems. A-type magmatism, on the other hand, could have acted as source of fluids or heat to move non-magmatic brines to form the Paleo-proterozoic copper systems.

1 Introduction

The copper reserves in Brazil are in the order of 11 Mt (1.5% of the world), ca. 85% of which concentrated in the Carajás Province, an Archean crustal segment in the southeastern Amazonian Craton, northern Brazil. This province is divided into two tectonic domains: the Rio Maria Domain in the south and the Carajás Domain (CD) in the north.

The CD consists of Mesoarchean (3.0 – 2.83 Ga) basement rocks, with TTG-like gneisses-migmatites, orthogranulites and calc-alkaline granitoids, overlain by Neoarchean metavolcano-sedimentary sequences of the Itacaiunas Supergroup and Rio Novo Group (ca. 2.76 to 2.73 Ga) and metamasiclastic rock units of the Águas Claras Formation (ca. 2.65 Ga - 2.70 Ga as minimum ages of sedimentation). Magmatic events are represented by ca. 2.75 Ga mafic-ultramafic intrusions, 2.75 - 2.70 Ga and locally ca. 2.56 alkaline granites, and ca.1.88 Ga A2-type granites (Xavier et al. 2012).

A variety of copper deposits is concentrated in the CD and may be broadly divided into two systems, namely iron oxide-copper-gold (IOCG) and copper – polymetallic. Collectively these systems yield resources of more than 8 billion tonnes of Cu-Au ore at 0.9 wt% Cu and 0.2 g/t Au to the CD.

This work summarizes the main geologic characteristics of these two copper systems of the CD, placing emphasis on their hydrothermal alteration types, mineralization styles and ages, fluid regimes and isotopic signatures. Critical issues are also raised that currently hamper the development of a unifying genetic model for these systems in the CD.

2 Copper systems of the Carajás Domain

2.1 Iron oxide – copper – gold (IOCG) deposits

This group includes the most economically important deposits of the CD (100 – 990 Mt @ 0.77 – 1.4 % Cu and 0.28 – 0.86g/t Au). These are structurally controlled by regional-scale WNW-ESE–striking brittle-ductile shear zones in the northern and southern sectors of the CD, close to the contact between the basement and supracrustal units. Mesoarchean basement gneisses/granitoids, remains of greenstone belt rocks, as well as Neoarchean metavolcano-sedimentary units of the Itacaiunas Super group, gabбро/diorite, quartz-feldspar porphyry and A2-type anorogenic granite may be hosts to the IOCG systems (Xavier et al. 2012). Geochronological data reveal that the Carajás IOCG systems were emplaced during multiple hydrothermal episodes during the Neoarchean and Paleo-proterozoic with the ore-forming events marked at: (i) 2.72 – 2.68 Ga, represented by the Sequeirinho - Pista deposit at the Sossego mine (245 Mt @ 1.1 wt. % Cu, 0.28 g/t Au), Cristalino deposit (500 Mt @ 1.0 wt.% Cu; 0.3 g/t Au) and satellite deposits, including Bacuri, Bacaba, Castanha, Visconde and Pedra Branca, all in the southern sector; (ii) 2.56 Ga recorded at the Salobo mine (1.11 Gt at 0.69 % Cu and 0.43 g/t Au) and Igaraçu Bahia/Alemão deposit (219 Mt @ 1.4 wt.% Cu, 0.86 g/t Au) in the northern sector (Moreto et al. 2015a,b). The Paleo-proterozoic IOCG events have been constrained at 1.90 Ga and 1.88 Ga, having as examples the Sossegó-
Curral deposit (Sossego mine) and Alvo 118 (ca. 170 Mt @ 1.0% Cu and 0.3 g/t Au) deposit, also in the southern sector of the CD (Grainger et al. 2008; Moreto et al. 2015a).

The Neoarchean 2.72 – 2.68 Ga IOCG systems are generally emplaced at deep crustal levels. In the southern sector of the CD the IOCG deposits commonly show distal sodic - calcic alteration, with albite - scapolite – hastingsite - actinolite – epidote, followed by variable combinations of more proximal calcic - ferric (actinolite - magnetite - apatite) and/or potassic - ferric (K-feldspar and biotite - magnetite) alteration types that commonly envelop chalcopyrite - pyrite - sigenite - magnetite - actinolite - chlorite - apatite - allanite breccias (e.g., Sequeirinho – Pista, Cristalino, Visconde and Pedra Branca deposits; Fig. 1A; Xavier et al. 2012). The copper ore zones at the Bacaiba, Castanha, and Bacuri deposits are associated with chlorite-epidote alteration with distal potassic-ferric alteration envelopes (Moreto et al. 2015b).

In Neoarchean 2.56 Ga IOCG systems from the northern sector of the CD, sodic – calcic (hastingsite-actinolite) alteration followed by silicification, iron-enrichment with almandine - grunerite – tourmaline - magnetite, and potassic - ferric alteration (biotite – magnetite) are common at the Salobo, Grota Funda, Furnas and GT46 deposits (Melo et al. 2016). These alteration types envelop massive magnetite lenses containing disseminated bornite–chalocite (e.g., Salobo; Fig. 1B), magnetite – chalcopyrite - actinolite breccias (e.g., Grota Funda), chalcopyrite - bornite - magnetite veins, stockworks and breccias (e.g., Furnas) or contain chalcopyrite disseminations along the mylonic foliation (e.g., GT46). Dissimilar from the above IOCG examples of the northern sector, sodic-calcic (actinolite + albite + scapolite + epidote) and potassic (biotite) alteration at the Igarapê Bahia/Alemão deposit are replaced by chlorite – carbonate (calcite + siderite) - apatite - tourmaline associations in strongly foliated zones which wrap around massive magnetite + chalcopyrite ± bornite + pyrite breccias within the Itacaiúnas Supergroup (Xavier et al. 2012).

Comparedly with the Neoarchean examples, the Paleoproterozoic IOCG systems represent hydrothermal systems developed at shallower crustal levels and controlled predominantly by brittle structures. These systems are generally characterized by poorly developed or absence of sodic-calcic or calcic-ferric alteration, but commonly display strong and pervasive potassic - ferric (K-feldspar and biotite with magnetite) alteration. This alteration stage is commonly overprinted by extensive zones dominated by chlorite - epidote - calcite or sericite that host the copper-gold ore. The ore forms breccia (Sossego-Curral; Fig. 1C) and vein systems (Alvo 118) containing quartz, calcite, actinolite, magnetite/hematite, apatite and sulfides (chalcopyrite – pyrite - sigenite). In both Neoarchean IOCG systems, the Fe-Cu-Au association is generally accompanied by variable concentrations of P-LREE-U-Ni-Co-Pd.

### 2.2 Copper - polymetallic deposits

These deposits contain reserves of < 50 Mt @ < 2% Cu and include as main examples the Breves (50 Mt – 1.22% Cu, 0.75g/t Au, 1200g/t W, 70g/t Sn, 175g/t Mo, 75g/t Bi), Estrela (Cu-Au-Li-Be-Sn-W-Mo), Águas Claras (Cu-Au-W), Gameleira (Cu-Au-Co-F-U-Mo-REE), Santa Lucía (Cu-Au-Bi-Sn-W-Mo), and Tarzan (Cu-Co) deposits.

![Figure 1. Mineralization styles of Neoarchean and Paleoproterozoic Cu systems in the Carajás Domain.](image)

**Figure 1.** Mineralization styles of Neoarchean and Paleoproterozoic Cu systems in the Carajás Domain. a 2.70 Ga Sequeirinho IOCG ore breccia (Sossego mine) with clasts of actinolite-magnetite in a chalcopyrite-rich matrix. b Massive magnetite with chalcosite-bornite seams at the 2.56 Ga Salobo IOCG deposit. c Calcite-quartz-apatite-actinolite-magnetite ore breccia of the 1.90 Ga Sossego deposit (Sossego mine) containing angular clasts of strongly chloritized granophyric granite. d Quartz-apatite-chalcopyrite-pyrite-pyrrhotite-phalalerite vein breccia of the 2.70 Ga Santa Lucía Cu-polymetallic deposit. e 1.88 Ga (?) sediment-hosted Tarzan Cu-Co deposit. Chalcopyrite-pyrite-quartz-chlorite ore zone. f Chalcopyrite nodule within a pellet rip-up clast in a greywacke sequence of the Igarapê Bahia/Alemão IOCG deposit.

General characteristics of these deposits include: (i) structurally controlled by brittle structures; (ii) styles of mineralization dominated by vein systems, stockworks and breccias with abundant quartz; (iii) very low contents (e.g., Águas Claras, Estrela) or lack of iron oxides (magnetite/hematite) related to copper mineralization; (iv) important potassic alteration with biotite (e.g., Estrela and Gameleira) or hydrolytic alteration dominated by chlorite-sericite (e.g., Águas Claras, Tarzan) or of greisen-type with phengitic muscovite (e.g., Breves and Santa Lucía; Figs. 1D-E); (v) lower sulfidation and more reduced ore assemblages consisting of variable combinations of...
chalcopyrite - pyrite - arsenopyrite - pyrrhotite – sphalerite - galena; (vi) geochemical signature similar to the IOCG systems, but with more elevated values of granitophile elements such as W, Sn and Bi.

The age of the ore-forming events for the Cu – polymetallic systems has been constrained at ca. 1.88 Ga, on the basis of SHRIMP II 207Pb/206Pb ages in monazite and xenotime (e.g., Breves) and bulk ore Sm-Nd isochron (e.g., Estrela), which is broadly coeval with the widespread

However, recent SHRIMP II 207Pb/206Pb analyses performed on ore breccia-related monazite grains have yielded a mean age of 2,688 ± 27 Ma for the Santa Lucia Cu-polymetallic deposit revealing that ore-forming conditions for these copper systems may have also prevailed coevally with the Neoarchean IOCG systems.

3 Multiple Neoarchean and Paleoproterozoic hydrothermal events

Overprinting of temporally distinct hydrothermal events, some of which associated with copper ore formation, has been suggested at the scale of individual Carajás IOCG deposits (Moreto et al. 2015a,b, 2015c). 2.76 Ga (molybdenite Re-Os) recorded in early chalcopyrite-calcite veins and 2.70 Ga (monazite U-Pb) for the ore stage at the Bacuri deposit; ages of 2.68 Ga and 2.06 Ga acquired in both cores and rims of different ore-related monazite grains at the Bacaba deposit.

Different styles of copper mineralization are commonly registered at individual deposits, such as magnetite – chalcopyrite – actinolite breccias and chalcopyrite – pyrite quartz veins with or without magnetite, such as at the Neoarchean Cristalino and Grotta Funda deposits. Despite the lack of the geochronological data, these features have been accounted as indirect evidence of possible overprinting of Neoarchean and Paleoproterozoic mineralizing events. In addition, finely-laminated sedimentary units at the Neoarchean (ca. 2.56 Ga) Igarapé Bahia/Alemão IOCG and Paleoproterozoic (?) Tarzan Cupalumetalic deposits commonly display rounded chalcopyrite nodules (Fig. 1F). Although undated, these nodules may represent the earliest hydrothermal precipitation of copper in the province (> 2.76 Ga?; diagenetic origin?).

4 Fluid regimes and isotopic signatures

Fluid inclusion data for both Neoarchean and Paleoproterozoic IOCG systems point to similar trends in fluid evolution. These trends consistently involve highly saline (35–70 wt % NaCl, eq.) and hot (>500°C) metalliferous brines, and lower temperature (generally <250°C) aqueous fluids of low to intermediate salinity, with or without the participation of CO₂ + CH₄-rich fluids (Xavier et al. 2012). LA-ICP-MS fluid inclusion analyses show that IOCG hypersaline brines are Na-Ca-Fe-dominated (> 1%) and strongly enriched (> 0.1% up to 1%) in K, Sr, Ba, Mn, Zn, and Pb. Copper concentrations in these IOCG brines are mostly in the range of a few hundred parts per million or less.

Fluid inclusion studies reveal that fluid regimes for the Carajás Cu – polymetallic systems also had the participation of highly saline (> 30 wt% NaCl eq.) Na-Ca-rich aqueous fluids and low-salinity aqueous-carbonic fluids (> 350°C) that progressively mixed with aqueous fluids of lower to moderate (0.2 – 26.2 wt% NaCl eq.) salinity and lower temperature (130 °C – 230°C) (e.g., Breves and Estrela). CO₂-rich fluids are lacking in some deposits and fluid evolution takes place essentially with aqueous fluids of variable salinities (0.3 – 45 wt% NaCl eq.) and temperatures (360 - 160°C) (e.g., Águas Claras and Gameleira).

The calculated δ¹⁸O and δD isotopic compositions of the ore-forming fluids range from 4.8‰ to 10‰ and from -74‰ to -39‰, respectively, for the Neoarchean (e.g., 2.70 Ga Sequeirinho-Pista, Castanha and Bacaba) and Paleoproterozoic (e.g., 1.88 Ga Sossego-Curral) IOCG systems in the southern sector of the CD. These values suggest that magmatic fluids might be associated with early hydrothermal alteration stages in these deposits. However, fluid evolution in these cases is accompanied by the introduction of δ¹⁸O-depleted and more δD-enriched fluids, isotopically similar to seawater values (e.g., Sequeirinho-Pista and Bacaba; Xavier et al. 2012). In addition, variable light and heavy δ¹¹B values in tourmaline (~8‰ to 11‰ at the Sequeirinho-Pista deposit) and fluid inclusion Cl/Br-Na/Cl systematics further support mixed sources for the ore-bearing fluids, including magmatic and modified seawater (e.g., bittern brines generated by seawater evaporation; Xavier et al. 2012).

The Neoarchean (ca. 2.56 Ga) Igarapé Bahia/Alemão and Salobo IOCG deposits in the northern sector of the CD show calculated δ¹⁸O-H₂O values in the 5‰ - 16.5‰ and in the 6.6‰ - 12.1‰ ranges, respectively, compatible with magmatic fluids, but that have undergone strong crustal rock interactions. Nevertheless, heavy δ¹¹B values of 14‰ to 26.5‰ in tourmaline from these deposits, in combination with calculated δD-H₂O in the range of -30‰ to -10‰ (at 400°C) and Cl/Br-Na/Cl systematics for the Igarapé Bahia/Alemão deposit point to an important involvement of non-magmatic fluids (seawater-derived fluids; Xavier et al. 2013).

The fluid evolution trend in Paleoproterozoic IOCG systems is broadly similar to the Neoarchean analogs, with the influence of δ¹⁸O-depleted hydrothermal fluids (~1.8 ± 3.4‰ at 300°C) suggestive of influx of surficially derived waters of meteoric or basinal origins (Sossegos-Curral and Alvo 118 deposits).

Fluids in equilibrium with the hydrothermal assemblages at the Cu – polymetallic Breves and Estrela deposits have calculated δ¹⁸O and δD values of -1.2‰ to 10.2‰ and -47‰ to -78‰, respectively. These data, together with fluid inclusion halogen data, are also compatible with magmatic fluids, but also point to mixing of external fluids, either meteoric or modified seawater during the ore-forming events. δ¹¹B values of ore-related
vein tourmaline from the Breves deposit range from -3.6‰ to 1.8‰ and corresponding δD values vary from -116 to -99‰, compatible with magmatic signatures (Xavier et al. 2013).

In situ sulfur isotope analysis of sulfide minerals by SIMS defines three distinct δ34S ranges: (i) -3.3‰ to +3.0‰ for the Neoarchean IOCG deposits; (ii) +2.5‰ to +4.7‰ for the Paleoproterozoic IOCG deposits; and (iii) -0.4‰ to +0.9‰ for the Cu-polymetallic systems (Santiago 2016). These sulfur isotope compositional ranges support contributions of magmatic sulfur, as well as and input of heavy sulfur from surficial reservoirs (e.g., sulfate from evaporated seawater or meteoric fluids) for both Carajás IOCG and Cu – polymetallic systems.

5 Discussion and concluding remarks

Copper metallogeny in the CD may have initiated as early as 2.76 Ga with the formation of diagenetic chalcopyrite (e.g., Igarapé Bahia/Alemão and Tarzan deposits) during the deposition of the rift-related Itacaiúnas Supergroup shallow marine volcano-sedimentary sequences. The Neoarchean and Paleoproterozoic Carajás Cu systems (IOCG and Cu – polymetallic deposits) are broadly controlled by regional WNW- ESE -striking transpressive shear zones that likely mark limits of tectonic blocks in the Carajás Mineral Province. Field relationships and geochronological data have indicated that nucleation and/or reactivation of these regional-scale structures may have taken place during the closure of the Itacaiúnas Supergroup rift system at ca. 2.68 Ga – 2.63 Ga (Tavares 2015). Reactivation of regional structures in the northern CD (e.g., Cinzento lineament) occurred at a later and still poorly constrained episode ca. 2.61 Ga – 2.52 Ga (Tavares 2015). These tectonic events have probably acted as first order controls for deep-seated fluid circulation and emplacement of Neoarchean and Paleoproterozoic Cu systems in the CD.

It is noteworthy that the Neoarchean Cu systems postdate the 2.76-2.74 Ga ultramafic-mafic and anorogenic granitic intrusions. In addition, A-type felsic magmatism was also poorly developed or recognized during the 2.70 Ga and 2.57 Ga (e.g., Old Salobo granite) tectonic events. As a consequence, the genetic link between ore-forming fluids of magmatic origin and copper mineralization, as suggested by stable isotope data, remains difficult to be clearly defined. This genetic link is more straightforward for the Paleoproterozoic IOCG and Cu-polymetallic systems, as they broadly overlap with the widespread ca. 1.88 Ga A2-type granites recognized in the Amazonian craton.

The current knowledge on the Carajás Domain copper metallogeny allows to conclude that: (i) IOCG and Cu-polymetallic systems are the result of multiple structurally-controlled ore-forming hydrothermal episodes emplaced at different crustal levels during the Neoarchean and the Paleoproterozoic; (ii) fluid regimes seem broadly similar for both copper system types and point to mixing of high temperature hypersaline metalliferous fluids with other fluid types as an important trigger to copper mineralisation; (iii) the origin of these fluids is still controversial, but non-magmatic brines (e.g. bittern fluids) seem to be an important component in the Neoarchean IOCG systems; (iv) felsic magmatism could have acted as source of fluids and/or heat to move non-magmatic brines to form the Paleoproterozoic copper systems; (v) the formation of different but coeval copper systems are likely dependent upon a combination of deposit-scale factors, such as, sulfur availability, sulfidation state and redox conditions during fluid evolution.

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The tectonic overprint on the Per Geijer apatite iron ores in Kiruna, northern Sweden

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Abstract. This ongoing project focusses on the structural evolution of the Per Geijer apatite iron ores in Kiruna, northern Sweden. The Per Geijer iron ores are situated in a NNE-SSW trending shear zone. This study indicate that the shear zone was active during D2 E-W compression giving rise to dip-slip and oblique slip components. The ductile fabric is overprinted by brittle structures carrying Cu, possibly representing traces of a separate Iron Oxide Copper Gold event in northern Norrbotten.

1 Background

The Kiruna area is a well-studied Archean/Paleoproterozoic terrain overlain by Caledonian rocks to the west. The area hosts numerous metal deposits whereof the Kiirunavaara apatite iron oxide (AIO)-ore constitute the most famous example. The Paleoproterozoic supracrustal units host the metal deposits in the area. In central Kiruna, the Kiirunavaara Group (KG) hosts the AIO-mineralization (Fig. 1). This rock unit is a mafic-felsic volcanic succession with minor meta-sedimentary rocks. The KG is subdivided into three units (Fig. 1): 1) the Hopukka Formation (HF), 2) the Loussavaara Formation (LF) and the 3) Matojärvi Formation (MF) that contains a mixture of volcanic and sedimentary rocks (Martinsson 2004). The overlying Hauki Quartzite (HQ) represents a quartz-arenitic unit with conglomeratic horizons at its basal and middle parts (Martinsson 2004).

It has been suggested that the Kiruna area situates the eastern limb of a large amplitude antiform (Wright 1988). Previous and ongoing regional research of Svecokarelian (1.96-1.78 Ga) deformation in the area indicates an early developed cleavage designated as S1. The shortening direction producing the S1 fabric is obscured by later folding and shearing. The shear zones are steep and strike approximately NNE-SSW in the central Kiruna area and Bergman et al. (2001) indicate that the shearing in central Kiruna represents a splay from a regional shear zone northeast of Kiruna.

The Per Geijer iron ores are mixed magnetite-hematite bodies containing 40-50% Fe and 3-5% P hosted by hydrothermally altered felsic porphyries (Martinsson 2015). The main horizon of the Per Geijer iron ore field forms a ca 5km continuous belt of apatite and/or iron oxide mineralization at the footwall contact of the Matojärvi formation (Geijer and Ödman 1974). Along the contact three bodies have been mined, Nukutus, Henry and Rektorn. Also subscribed to the Per Geijer iron ores are the previously mined Hauki hematite deposit, situated near the hanging wall contact of the Matojärvi formation.

Figure 1. Geological map of the central Kiruna area, modified after Martinsson et al. (2013). Red mark indicate the position of the Per Geijer AIO-field. Younging to the east.
of volatile rich melts giving rise to both magmatic and hydrothermal features. Recently, this view has gained support by workers focusing on the Los Colorados and El Laco AIO deposits (Knipping et al. 2015, Valesco et al. 2016) indicating very high temperatures of the fluids involved (Tornos et al. 2016). Furthermore, Reich et al. (2016) demonstrate the potential of the magmatic-hydrothermal fluids to carry metals after AIO deposition, thus indicating a possible link between AIO- and Iron-Oxide Copper Gold (IOCG) formation.

The age of the Per Geijer iron ores was recently constrained in the Nukutus ore to 1877.1 ± 3.5 Ma (Westheus et al. 2016) and the same study indicate that the whole ore-host rock sequence, including the stratigraphically lower Kiirunavaara deposit, formed in a short time interval of approx. 15 m.y. These results are in line with earlier studies indicating AIO emplacement in Kiruna at approx. 1888 Ma (Cliff et al. 1990, Romer et al. 1994) that also indicates the minimum age of the early tectonic overprint (D1) of the area (Cliff et al. 1990).

Structurally, the ore bodies have been suggested to be boudinaged along an extensional axis plunging 60° SSE (Vollmer et al. 1984). Nevertheless, only one detailed description of the tectonic overprint of an AIO body in Kiruna have been published (Wright 1988) and that particular description is from the stratigraphically lower Loussavaara deposit at the HF-LF contact (Fig. 1).

In this study, we focus on the structural characteristics of the Per Geijer AIO field in order to put better constraints on the structural evolution of the Kiruna area and its relation to ore formation and ore body transposition.

2 Results

The host rocks and especially the hanging wall rocks (MF) of the Nukutus, Henry and Rektorn deposits are strongly sheared. This also counts for the stratigraphically higher Hauki deposit. Based on regional observations we interpret this fabric as S2. Strain partitioning often concentrates deformation into narrow zones leaving low strain rock in between (Fig. 2A). In certain cases a compositional banding, parallel with the mylonitic fabric, forming a spaced cleavage may be interpreted as a preserved primary volcanic bedding (S0) but could as well be interpreted as a secondary fabric (Fig. 2B). Other secondary ductile features include pinch-and-swell structures (Fig. 2C) and small-scale drag folds of apatite, carbonate, and quartz veins (Fig. 2D). The ore did not take up much strain but a weak foliation may be present, however, it is not obvious that the foliation is secondary.

Parts of the Matojärvi rocks are classified as proto-ultra mylonites and petrographic analysis reveal muscovite-sericite as the dominant phyllo-silicate forming the shear zone fabric (Fig. 3A) but calcite and chlorite are also common. Rotation of asymmetric feldspar and iron ore clasts is frequently occurring (Fig. 3B).

The foliation of the foot wall rocks is in general N-S to NNE-SSW striking but in e. g. the Henry deposit the foliation of the hanging wall rocks are distinctly deviating in strike relative the foot wall foliation (compare Fig. 4 A, B).

The stretching lineation is in places strongly developed. The plunge changes from steep in the north to moderate steep in the south (Fig. 4C).

A brittle overprint (D3) is evident by fracturing and developed slickensides on both foliation and fracture planes. The orientation of slickenlines is similar to the orientation of stretching lineation (Fig. 4C). Hydrobreccias are common and form narrow vein systems (Fig. 2F) or larger apatite-carbonate-quartz veins carrying xenoliths (Fig. 2F). Secondary Cu-minerals, seen as Cu-carbonates in pressure shadows of slickensides and in open fissures are common (Fig. 2G). Pyrite and chalcopyrite also shows a spatial relation to brittle structures or brittle reactivation of ductile structures (Fig. 2H).

3 Discussion

This study shows that the footwall and hanging wall contacts of the Matojärvi formation (MF) are tectonic. This is evident from the plastically deformed character of the hanging wall rocks to the Nukutus, Henry and Rektorn...
deposits at the LF-MF contact and the Hauki deposit situated at the stratigraphically higher MF-HQ contact. The Matojärvi formation took up the strain in central Kiruna, together with the meta-conglomeratic and phyllitic horizons in the area. We suggest that, due to strong strain partitioning, first order structures developed at the lithological/rheological contacts to the Matojärvi formation. Second order structures then developed within the Matojärvi formation linking up the first order structures at its contacts. These second order structures are reflected by the deviation in strike of the foliation in the hanging wall rocks of the Henry deposit (compare Fig. 4A and 4B). The AIO-deposits are found at the first order structures at or near the Matojärvi contacts. We do not exclude that the structural pattern indicated by this study also counts for other parts of the central Kiruna area. We hereby call this shear zone in Kiruna the Per Geijer Deformation Zone (PGDZ).

The plunge of the stretching lineation changes from steep in the north to moderate steep in the south (Fig. 4C). This kinematic change from dip-slip to oblique-slip happens somewhere, or continuously, between the Rektorn and Henry deposits (Fig. 1). This area is not well exposed and the cause of this kinematic change of the shear zone requires further studies to understand.

The magnetite/hematite ore bodies appear relatively undeformed. This is a common feature of Swedish AIO-bodies in deformed settings where the Grängesberg-(Högdahl et al. 2016) and the boudinaged Malmberget (Bauer et al. unpublished data) deposits constitute recently studied examples. We stress the importance of considering competence contrasts during geological modelling of deformed AIO-deposits.

Based on on-going regional research in the Kiruna area we interpret the mylonitic fabric of the PGDZ as S2. We base this on field observations in the region where an early formed cleavage (S1) is folded and transposed into later shear zones. The orientation of the PGDZ together with the orientation of stretching lineation indicate E-W shortening which is in line with earlier studies (e.g. Wright 1988). The timing of the E-W compression in northern Norrbotten has been subscribed to 1886-1750 Ma (Bergman et al. 2001), thus late-orogenic and distinctly post AIO emplacement (Cliff et al. 1990, Romer et al. 1994, Westheus et al. 2016). However, it is important to point out that the structural characteristics described in this study only record the latest activity of the shear zone and that the structure probably was active already prior to D2. Reactivation of former normal faults associated with the emplacement of greenstones in northern Fennoscandia has been suggested east of Kiruna and extensional tectonics.
potentially producing normal faults, at approx. 1.9 Ga is evident by the alkaline character of the Porphyry group (Bergman et al. 2001, Martinsson 2004). Furthermore, the geological setting producing the Kurravaara Conglomerate has been interpreted as a possible fan delta environment (Kumpulainen 2000) and the Hauki formation to have formed in tectonically active grabens (Witchard 1984), thus further strengthening the case for an extensional pre-history of the D2 compressional structures. Based on this background and the steep dip of the PGDZ we tentatively suggest that the shear zone indeed may have originated as a syn-extensional normal fault.

The late Svecofennian D2 event is suggested to mark the timing for IOCG emplacement during ductile-brittle conditions in the Aitik/Nautanen area, southeast of Kiruna (Wanhainen et al. 2012, Lynch et al. 2015, Martinsson et al. 2016). An IOCG overprint on the Per Geijer AIO field with a similar timing is supported in this study due to the late, brittle characteristics of Cu-minerals. This brittle event is designated D3 in this study. The orientation of slickenlines in relation to stretching lineation within the PGDZ (Fig. 4C) indicate a similar shortening direction during D2 and D3. This observation leads us to propose that a weak IOCG overprint took place during the final and brittle stage of the PGDZ activity, hence, much later than the AIO emplacement. An alternative interpretation, is that the observed Cu-minerals represent remobilized Cu from the iron ore itself. Anyhow, due to the scarcity of matrix-hosted Cu-sulphide in the ore this alternative is less likely.

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Recognizing IOCG alteration facies at granulite facies in the Bondy Gneiss Complex of the Grenville Province

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Abstract. The Bondy gneiss complex in the southwestern Grenville Province of Canada, hosts a series of granulite facies 1.4–1.35 Ga mafic to felsic volcanic rocks. Metamorphosed hydrothermal alteration zones constitute large sectors of the complex and have mineral occurrences. Mineral assemblages and lithogeochemical analysis of meta-hydrothermal zones have attributes of Na, Ca-Fe, K-Fe, K, Mg, argillic, phyllic and advanced argillic altered volcanic rocks. In alteration discrimination diagrams, the hydrothermal system shares attributes of IOA-IOCG systems that evolve toward epithermal caps (e.g., Great Bear magmatic zone, Canada; Central Andes, Chile). The Bondy footprint is significantly distinct from VMS deposits and other deposit types. We thus interpret the Bondy hydrothermal system as prospective for the variety of mineralisation types typical of Proterozoic IOA-IOCG-epithermal systems.

1 Introduction

The discovery of SEDEX, VHMS, epithermal, porphyry, IOCG, and IOA deposits metamorphosed at upper amphibolite to granulite facies (Corriveau and Spry 2014) calls for a re-evaluation of historically under-explored mineral occurrences in high-grade metamorphic terranes. In known deposits, the meta-alteration zones preserved the imprint of the chemical changes undergone by the protoliths during pre-metamorphic hydrothermal alteration. Consequently, petrological and lithogeochemical tools to identify and quantify hydrothermal alteration associated with ore deposits can be applied to environments metamorphosed to high grades. In this contribution, we compare the composition of metamorphosed hydrothermal alteration zones in the Bondy Gneiss Complex of the southwestern Grenville Province to a variety of deposit types and illustrate that they are significantly similar to those of IOCG deposits that evolve to epithermal caps.

2 The Bondy Gneiss Complex

The Bondy Gneiss Complex represents a 1.4–1.35 Ga volcano-plutonic edifice metamorphosed to granulite facies between 1.2 and 1.18 Ga (Corriveau and van Breemen 2000; Blein et al. 2003; Wodicka et al. 2004; Corriveau 2013). Its outcrop forms a structural window of Laurentian basement within the northern half of the Central Metasedimentary Belt in Québec (Fig. 1).

In the complex, granitic to tonalitic orthogneiss dominate. Units of amphibolite, mafic granulite and quartzofeldspatic gneiss locally preserve primary layering and fragmental textures. The northern half of the complex consists of a hydrothermal system at granulite facies with, from north to south: (1) tourmalinites among phlogopite-sillimanite gneisses; (2) plagioclase-cordierite-orthopyroxene white gneisses; (3) gneisses rich in biotite, cordierite, garnet, K-feldspar, orthopyroxene and/or sillimanite; (4) laminated quartzofeldspatic gneisses; (5) a series of magnetite and garnet-rich gneisses, garnetites, biotite-orthopyroxene gneisses and locally magnetite-rich amphibolites; (6) a hyperaluminous sillimanite-quartz gneiss unit with pyrothite; (7) biotite-rich garnetites and garnet-rich gneisses; and (8) a diverse array of layered, garnet amphibolites (Corriveau 2013).
systems of the Great Bear magmatic zone (Corriveau et al. 2016, 2017; Trapy et al. 2015) allow the following field interpretation. The garnetites and tourmalinites among sillimanite ± garnet ± orthopyroxene ± cordierite gneisses, and felsic and mafic layered gneisses show very poor layering in contrast to what would be expected of exhalites. They grade into a variety of tourmaline, kornurupine and garnet gneisses that remain atypical of metamorphosed sedimentary rocks. The tourmaline-rich unit hosted by phlogopite-sillimanite-bearing gneisses is a good candidate for a metamorphosed tourmaline alteration zone among argillic or sericitic altered units; the poorly layered cordierite-orthopyroxene-bearing but plagioclase-dominant white gneiss resembles chloritised albite units; the biotite, cordierite, garnet, K-feldspar, orthopyroxene and/or sillimanite gneisses are good candidates for high-to low-temperature (HT, LT) K-Fe, argillic, and sericitic altered volcaniclastic rocks; the magnetite-rich gneisses and the garnetites are candidates for iron oxide-altered, magnetite dominant and magnetite-phyllosilicate dominant HT Ca-Fe or HT K-Fe alteration types; the sillimanite-quartz-pyrrhotite rocks are typical of advanced argillic or phyllic alteration zones, and the biotite garnetites could either be K-altered amphibolites or HT or LT K-Fe metasomatites.

3 Geochemical signatures

3.1 Lithogeochemistry

The isochemical nature of high-grade metamorphism allows for chemical discrimination of metamorphosed hydrothermal ore deposits based on alteration indices and discriminant diagrams. The alteration index (AI) (Ishikawa et al. 1976) calibrates the intensity of sericitic and chloritic alteration of volcanic rocks, the chlorite–carbonate–pyrite index (CCPI) index (Large et al. 2001) plots carbonate and pyrite alteration proximal to VMS mineralisation, the Benavides et al. (2008) index helps to detect IOCG footprints, and the Montreuil et al. (2013) discriminant plot distinguishes the key alteration facies in IOCG systems.

In the Montreuil et al. (2013) discriminant plot, the vertical axis discriminates between sodic and potassic alteration facies, while the horizontal axis discriminates alkali alteration from Ca-Fe, K-Fe, and Fe alteration facies. In Figure 2, whole-rock geochemical data of Corriveau (2013) from the Bondy Gneiss Complex are plotted on the Montreuil et al. (2013) plot. The addition of molar proportions of Na (pink), Ca (dark green), Fe (black), K (red), Mg (light green), and Si/8 (yellow) further discriminates the main alteration facies as these cations are excellent proxies for their dominant mineral phases (Corriveau et al. 2016, 2017; Montreuil et al. 2013). Corriveau et al. (2017) further refine the understanding of IOCG footprints by discriminating prograde metasomatic paths of iron oxide and related alkali-calcic alteration from the imprint of retrograde alteration.

3.2 Discriminant diagram

In the IOCG discrimination diagram, Bondy metasomatites plot in the Na, HT Na-Ca-Fe, HT Ca-K-Fe, HT-LT K-Fe and K alteration fields; one or two cations dominate molar Na- Ca-Fe-K-Mg proportions (Fig. 2). Plagioclase-dominant gneisses with cordierite-orthopyroxene layers fall within the field of Na alteration with some Mg addition attributed to chloritization of original amphibole-bearing HT Na-Ca-Fe layers (Fig. 2A). Orthopyroxene-rich aluminous gneisses and amphibolites fall within HT Ca-Fe alteration. Magnetite-orthopyroxene gneisses outline Fe-rich alteration zones with the development of massive to well-layered magnetite-rich gneisses. Magnetite-rich, garnet-bearing gneisses and biotite garnetites fall within the K-Fe alteration field. Locally, K-feldspar prevails in laminated quartzofeldspathic gneisses that plot within the K alteration facies. These rocks fall on the prograde path of IOA-IOCG systems, though an Mg component typical of LT Ca-Mg K-Fe occurs throughout (Fig. 2A, B).

Some amphibolites and aluminous gneisses exhibit transitional alteration types dominated by two or three elements. These rocks record K alteration of HT Ca-Fe or HT Na-Ca-Fe metasomatites; retrograde overprints skew the signatures towards the field of least-altered rocks (Fig. 2A, B). In Figure 2A and 2B, some altered rocks
display bar codes dominated by Mg and/or Si. These reflect intense chloritisation and silicification of earlier Na, Ca-Fe, Ca-K-Fe, K-Fe and K metasomatites.

The Bondy hydrothermal footprint is distinct from the ones of typical VMS deposits (Fig. 3A, B) in that intense carbonatation, chloritization and silicification are not observed whereas Fe-dominant alteration is abundant. Moreover, extensive albitites are not developed in VMS deposits though albitisation is common. Most of the Bondy hydrothermal footprint is distinct from the ones of typical epithermal deposits (Fig. 4A, B) in that intense K and silicification is only restricted to part of the system. Comparison of Bondy data with the magnetite-dominant IOA-IOCG footprint of the Great Bear magmatic zone (Fig. 5A, B; Corriveau et al. 2017) illustrates that data from Bondy fall within most alteration facies but are slightly off from the prograde metasomatic path of the Great Bear systems, and at current levels of exposure, lacks an IOA component (shown by lower Fe-enrichments). It does display a pervasive and intense Mg footprint which is very typical of low temperature alteration facies, such as chloritization and silicification, over Na, Ca-Fe and/or K-Fe metasomatites. The latter is common in hematite-dominated IOCG deposits such as in the Mantoverde district (Fig. 6) and was not common in the magnetite-dominant IOCG settings of the Great Bear. At Mantoverde, Si and Mg enrichments are superimposed over K-Fe and K alteration facies.

Figure 3. IOCG discriminant diagram of Montreuil et al. (2013) applied to VMS deposit chemical footprints, using data compiled by van Ruitenbeek et al. (2012). Same symbols as Figure 2.

Figure 4. Plot of epithermal deposits (Warren et al. 2007) on IOCG discriminant diagram of Montreuil et al. (2013). Same symbols as Figure 2.

Figure 5. Plot of Great Bear magmatic zone IOA-IOCG-epithermal footprints. Only samples with a single alteration types were chosen from Corriveau et al. (2015) dataset. Same symbols as Figure 2.
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4 Summary and conclusions

The metamorphosed hydrothermal footprint of the Bondy gneiss complex comprises (i) Na, (ii) HT Ca-Fe, (iii) HT K-Fe, (iv) LT K-Fe, chlorite and epithermal type alteration facies. The chemical changes recorded by these facies have similarities to hematite-group IOCG deposits evolving towards epithermal caps. The study illustrates that IOCG systems can be preserved in the high-grade metamorphic Proterozoic terranes of the Grenville Province. Being within a structural window in the Central Metasedimentary Belt, it is possible that other systems remain to be found in other 1.4 Ga components of the Grenville Province, providing new targets for mineral exploration.

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Figure 6. IOCG discriminant diagram of Montreuil et al. (2013) for the Mantoverde district, Chile using data from Benavides et al. (2008). Same symbols as Figure 2.
Resolving the magmatic-hydrothermal signal using Fe and O stable isotope pairs at the world class Mantoverde iron oxide – copper – gold deposit

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Abstract. Iron oxide – copper – gold (IOCG) deposits are a globally important source of Fe, Cu, Au, Ag, U, REE, Ba and F. Several genetic models for the formation of IOCG deposits have been proposed, including formation by magmatic-hydrothermal fluids, non-magmatic hydrothermal fluids such as basinal brines, a combination of magmatic-hydrothermal fluids and basinal brines, metamorphic fluids, and immiscible iron-rich magmatic melts. This study focuses on the world class Mantoverde IOCG system located within the Chilean Iron Belt. Here, we report the first $\delta^{56}$Fe and $\delta^{18}$O stable isotope pairs for ore-stage magnetite and late-stage hematite in the Mantoverde system. Magnetite $\delta^{56}$Fe values range from 0.46 ± 0.04‰ to 0.58 ± 0.02‰ and average 0.51 ± 0.16‰ (n=10; 2σ). Three hematite $\delta^{56}$Fe values were measured to be 0.34 ± 0.10‰, 0.42 ± 0.09‰, and 0.46 ± 0.06‰. Magnetite $\delta^{18}$O values range from 0.69 ± 0.04‰ to 4.61 ± 0.05‰ and average 2.99 ± 2.70‰ (n=9; 2σ). Hematite $\delta^{18}$O values range from -1.36 ± 0.05‰ to 5.57 ± 0.05‰ and average 0.10 ± 5.38‰ (n=6; 2σ). The combined $\delta^{56}$Fe and $\delta^{18}$O data fingerprint a magmatic source for Fe and O and, importantly, eliminate a non-magmatic ore fluid.

1 Introduction

Iron oxide – copper – gold deposits contain anomalous concentrations of magnetite and or hematite and Cu- and Au-bearing sulfides. Since the discovery of the giant Precambrian Olympic Dam deposit in Australia in the 1970s, i.e., the largest known deposit of this type, IOCG deposits have been the focus of investigations to determine the source reservoir(s) of the ore-forming fluids and metals responsible for mineralization. Iron oxide – copper – gold deposits occur globally, commonly in subduction zone environments, ranging in time from the Archean to the Cenozoic. The deposits typically exhibit variable quantities of their namesake metals, containing up to thousands of millions of tonnes of mineable Fe ore and hundreds of millions tonnes of mineable Cu ore, and some deposits contain variably elevated, and sometimes mineable, grades of light rare earth elements (LREE), P, U, Ag, Co, Ba and F. A comprehensive genetic model for the formation of IOCG deposits remains elusive. Disagreement on a genetic model stems from a lack of correlation between IOCG deposits and specific tectonic or magmatic settings and a lack of geochemical constraints on the source of the ore fluids required for efficient metal transport and mineralization. Working hypotheses proposed to explain the origin of the ore-forming fluids include: 1) a magmatic-hydrothermal fluid evolved from a silicate magma; 2) non-magmatic hydrothermal fluids such as meteoric fluids or basinal brines driven by heat from either a magma body or the crustal geotherm; 3) metamorphic hydrothermal fluids derived from metamorphic devolatilization and water-rock interaction; and 4) a magmatic-hydrothermal fluid evolved from a volatile-bearing iron oxide melt, which itself evolved via liquid immiscibility from a silicate magma (Barton, 2014). Currently, no single genetic model explains the formation of all IOCG deposits, and it has been proposed that the smaller and rarer Phanerozoic IOCG deposits formed in tectonic settings where conditions were similar to those in the Precambrian. In this study, we primarily examine iron and oxygen isotopes in magnetite and hematite from Mantoverde, Chile (Fig. 1) to further constrain potential genetic modes for these deposits.
Figure 1. Map of Mantoverde. Green star shows location of sampled drill hole. Modified from Rieger et al. (2012).

2 Samples

Magnetite and hematite (var. specularite) were sampled from an approximately 200m long section along a single drill core from ~10m intervals within the Mantoverde mining district just northeast of Mantoverde Norte near the Mantoverde fault.

3 Methodology

Magnetite and hematite samples were separated by using a hand magnet and tweezers to pick grains from broken rock. We used a field emission scanning electron microscope (FE-SEM) and electron probe microanalyzer (EPMA) to assess compositional zoning and quantify the minor and trace element compositions of magnetite and hematite. Solution MC-ICP-MS following the double-spike method of Millet et al. (2012) was used to measure Fe isotopes in magnetite and hematite. Laser fluorination gas isotope ratio mass spectrometry in dual inlet mode was used to measure O isotopes in magnetite and hematite.

4 Chemistry of magnetite and hematite

4.1 Magnetite minor and trace elements

The concentrations of [Al+Mn] vs [Ti+V] for magnetite from Mantoverde are plotted in figure 2 along with magnetite from the Los Colorados iron oxide – apatite deposit. These data have been plotted without Ca due to potential for Ca micro- and nano-inclusions (Nadoll et al. 2014) and for comparison with data from the higher temperature Los Colorados iron oxide – apatite deposit of similar age and similar geologic setting (Knipping et al. 2015). The average [Ti+V] and [Al+Mn] values for all magnetite analyses (n = 323) plot in the IOCG field. However, the trace element concentrations within individual magnetite grains vary widely. There is no apparent correlation between trace element concentrations and the depth of samples within the deposit. The positive correlation between [Al+Mn] and [Ti+V] values are consistent with a general trend for magnetite mineralized from a single cooling fluid. Temperatures of the ore fluid responsible for main-stage magnetite mineralization at Mantoverde range from 278 – 530 °C (fluid inclusions in quartz, Rieger et al. 2012) and >800 °C (melt inclusions in magnetite, Knipping et al. 2015) for Los Colorados. Aluminum and Ca concentrations vary significantly in magnetite and hematite from Mantoverde, likely reflecting pervasive potassic alteration, silicification, and hydrolytic alteration of the host rocks, and multiple stages of post-mineralization hydrothermal alteration (Rieger et al. 2010). Similarly, variability of [Ti+V] concentrations likely reflect secondary alteration. Late stage hematite displays a similar spread of values for [Al+Mn], possibly due to the remobilization and oxidation of magnetite. However, [Ti+V] concentrations of hematite from Mantoverde are significantly elevated relative to magnetite from deeper levels of the same drill core. Overall, the trace element concentrations in magnetite record a cooling fluid, and in magnetite and hematite record hydrothermal alteration.

4.2 Iron and Oxygen stable isotopes

Magnetite and hematite samples analysed in this study have δ56Fe (56Fe/54Fe relative to IRMM-14) values that range from 0.46 to 0.58 ‰ and from 0.34 to 0.46 and are presented with oxygen isotopes (δ18O; 18O/16O relative to VSMOW) in figure 3. These magnetite values are
comparable to published values for magmatic and magmatic-hydrothermal magnetite that range in $\delta^{56}$Fe values from $-0.0$ to $0.86$ ‰. The $\delta^{56}$Fe isotope data clearly discriminate between magnetite grown from a melt or magmatic-hydrothermal fluid, and magnetite that grew in equilibrium with meteoric water or a basinal brine (values commonly $< -0.0$ ‰). Iron isotope abundances in magnetite and hematite appear to be relatively insensitive to low to moderate degrees of hydrothermal alteration.

**Figure 3.** Iron and oxygen isotope paired values for magnetite and hematite from Mantoverde. Pink box represents range of natural ortho-magmatic magnetite. Error bars are $2\sigma$. Hypothetical fluid values calculated using fractionation factors from Zheng (1991) and Cole et al. (2014).

Globally, $\delta^{18}$O values for magnetite in the range of 0.9 to 5.0 ‰ fingerprint an ortho-magmatic origin for magnetite (Taylor, 19687). Magnetite $\delta^{18}$O values that are $<1$ ‰ or $>5$ ‰ (i.e., outside the ortho-magmatic range) are interpreted as having undergone secondary alteration by a lower temperature fluid. All except one $\delta^{18}$O value for magnetite samples from Mantoverde are consistent with the global database for magnetite crystallized from silicate magmas and magmatic-hydrothermal fluids. Using fraction factors between hematite and water developed by Zheng (1991) low $\delta^{18}$O values in hematite are consistent with hematite that grew in equilibrium with an ore fluid at a temperature of $\sim250$ °C. Notably, magnetite and hematite at Mantoverde yield $\delta^{18}$O values that are strikingly similar to the Cloncurry District and neighboring IOCG districts within the Proterozoic eastern Mt. Isa Block, Australia (Marshall and Oliver, 2006), where $\delta^{18}$O values for magnetite range from 0.7 to 10.0 ‰ (average 4.78 ‰, n = 10) and $\delta^{18}$O values for hematite range from -5.3 to 1.1 ‰ (average -0.9 ‰, n = 5). Marshall and Oliver (2006) conclude that the $\delta^{18}$O values from the Cloncurry and Mt. Isa Block IOCG districts reflect magmatically sourced mineralizing fluids that underwent cooling and variable re-equilibration with igneous host rocks.

**Conclusions**

New Fe and O stable isotope data reported here for magnetite and hematite from the Mantoverde IOCG district support the hypothesis that mineralization in the Mantoverde district is primarily the result of magmatic-hydrothermal fluids. Oxygen isotope values vary among individual magnetite and hematite samples likely due to variable degrees of hydrothermal alteration or re-equilibration with subsequent fluids, supported by widely varying Al, Ca, Mn, Ti, and V concentrations in magnetite and hematite. Oxygen isotope values of late stage hematite are consistent with a predominantly magmatic-hydrothermal fluid as the main source of Fe even during the latest stages of Mantoverde mineralization. Iron isotopes are minimally affected by hydrothermal alteration and, when coupled with O isotopes, are a robust tool to differentiate between magmatic and meteoric fluid sources.

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Structural and geological controls on the Iron Oxide Copper Gold mineralization in the Candelaria–Punta del Cobre district, Atacama region, Chile

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Abstract. The Candelaria–Punta del Cobre Iron-Oxide Copper-Gold (IOCG) district covers a significant area (~18 x 12 km) and hosts eight active mines and numerous prospects. Major centers of IOCG mineralization are mainly located in volcanic units that occur at the base of the Chañarcillo extensional basin. The basin was inverted during the Late Cretaceous. Previous research has focused on the character of the mineralization and alteration in individual deposits, particularly Candelaria. In this study we evaluate the regional volcanic and structural architecture placing the geology and mineralization in this framework. Variation in the volcanic stratigraphy, the character and thickness of individual units, a marked break between the Lower and Upper Andesites, and proximity to the Copiapó batholith all appear to influence alteration and mineralization. The geometry of the basin, primary extensional structures, and inversion of some structures are locally important. Mineralizing events demonstrate a complex temporal history with respect to the Copiapó batholith.

1 Regional setting

The Coastal Cordillera in northern Chile hosts a major Jurassic-Cretaceous Iron-Oxide Copper-Gold (IOCG) belt, the world’s youngest significant IOCG deposits. The Candelaria–Punta del Cobre district, with an aerial extent of ~ 18 X 12 Km, is the most important IOCG district in Chile and hosts the largest deposits currently known, Candelaria (Fig. 1) with a current resource of 431 Mt @ 0.5 % Cu and 0.1 g/t Au. In addition to Candelaria, there are seven more IOCG deposit being actively mined (Santos, Alcaparrosa, Carola, Punta del Cobre, Atacama Kozan, Mantos de Cobre and Granate) and tens of prospects.

The regional geology in the area is characterized by the volcanic-dominant Punta del Cobre Formation (Lower Andesite, Albitófiro dacite, Tuff and Upper Andesite). These units underlie the Upper Valanginian to Aptian shallow marine carbonate sediments of the Chañarcillo Group (Abundancia, Nantoco, Totoralillo, and Pabellon Formations) that were deposited in the Andean back-arc Chañarcillo extensional basin. Following uplift in the middle Cretaceous, the volcanic and volcaniclastic Cerrillos Formation, which reaches a thickness of 4500 m, was unconformably deposited on the partly eroded rocks of the Chañarcillo Group (Segerstrom and Fuller 1962). In the middle Cretaceous, multiple intrusions that collectively make up the Copiapó batholith were emplaced into the western part of the Punta del Cobre belt (Arévalo 1999), and caused intense contact metamorphism (Marschik and Fontbote, 1996).

2 District architecture

Geological mapping in the district has been undertaken to characterize the different geological units and their distribution, constrain the structural-tectonic history, and define the controls on hydrothermal events and mineralization. Five regional cross-sections were constructed based on field mapping (Fig 2.), drill core logging and previous geological work by researchers and mine operators. These sections cover most of the major IOCG deposits in the district. Interpretation of stratigraphic and structural relationships on the cross-sections was complemented by geochemical and geochronological analyses. To further constrain mineralizing processes, detailed work focused on the Santos, Alcaparrosa and Candelaria deposits (Fig. 1). These three deposits cover three distinct parts of the district and show some important distinct differences in terms of the distribution of mineralization.

The Santos, Alcaparrosa and Candelaria deposits are hosted in similar stratigraphic positions within the Punta del Cobre Formation, specifically in the Lower Andesite member with lesser mineralization in the Upper Andesite member. The dacitic “Albitófiro” unit, which overlies the Lower Andesite, shows considerable variations in thickness and is interpreted to be a series of volcanic domes and related autoclastic breccias. This unit is present at Alcaparrosa and Santos where it can host significant mineralization. A fine grained rock interpreted as a volcano-sedimentary tuffaceous unit locally overlies the Lower Andesite in the Candelaria and Alcaparrosa deposits. The Upper Andesite overlies the “Albitófiro” and tuffaceous unit
and shows lithological variation from west to east. In the western part of the area the unit has an andesitic composition, whereas towards the east it becomes basaltic.

Mineralization in the Candelaria deposit is hosted at the stratigraphic level of the tuffaceous unit and top of the Lower Andesite, and also extends down into the Lower Andesite. The Santos and Alcaparrosa deposits are hosted dominantly in brecciated Albitófiro and the Lower Andesite. Alteration in the three deposits is characterized by early pervasive magnetite-biotite-chlorite, overprinted by pervasive actinolite and K-feldspar alteration in the Lower Andesite. The Upper Andesite is characterized by diopside, brown garnet, scapolite and K-feldspar alteration in the Alcaparrosa and Candelaria deposits.

The five cross-sections are oriented east-northeast – west-southwest, perpendicular to the regional strike of the main lithological units. The cross-sections extend across the sedimentary basin west into the Copiapó Batholith. The integration of drill hole lithological data and surface geological mapping indicates that the thickness of the Upper Andesite varies considerably from up to 300 m in the western part of the district to less than 80 m in the east. Similarly, the tuffaceous unit is highly heterogeneous. In the eastern part of the district it consists dominantly of a sedimentary polymictic breccia, typically less than 20 m in thickness, with clasts of the Lower Andesite and Albitófiro. Towards the western side of the district, the tuffaceous unit locally exhibits fine grained volcanic textures although the extent of these textures is difficult to define due to extensive hydrothermal alteration and contact metamorphism. The thickness of the unit can be up to 200 m. Changes of thickness within the tuffaceous and Upper Andesite units may reflect a combination of primary volcanic topography related to the existence of different volcanic centers combined with the geometry of the Chañarcillo basin and the main faults that control it.

Mineralization in the Candelaria-Punta del Cobre district is strongly structurally controlled. The major deposits are associated with faults, some of which contain and are surrounded by strong mineralization. Early faults related to basin formation trend dominantly north-northeast, but north-northwest trending faults are more important in the district and are commonly mineralized. Intersection between the faults may have been an important focus for mineralizing fluids. For example, breccia mineralization in the Albitófiro at Santos occurs at an interpreted fault intersection and mineralization exhibits both north-northeast and north-northwest orientations. Mineralization and related alteration also appears to be controlled by lithological contacts, particularly between the Lower Andesite and the overlying tuffaceous unit, and lithological permeability within the tuffaceous unit. Variations in the thickness of the tuffaceous units therefore influence the extent of mineralization.

3 Conclusions

The Candelaria-Punta del Cobre district has a complex tectonic history that includes extension during basin formation followed by inversion and compression (Martínez et al., 2013) both with potential transtensional and transpressional components (Arévalo et al., 2006). Complex volcanism occurred during basin formation and was followed by major intrusions during and post-inversion. The intrusions that make up the Copiapó Batholith at least partially, and possibly significantly postdate mineralization.

The Candelaria-Punta del Cobre district contains extensive hydrothermal alteration and mineralization that constitutes one of the largest and youngest IOCG systems in the world. The structural and volcano-sedimentary architecture in the basin appear to have influenced the location of numerous IOCG deposits and occurrences. Current research is focused on constraining the precise structural and lithological controls on mineralization, and the temporal relationships among mineralization, tectonism, and intrusive activity. There is limited understanding of the exact tectonic regime that favored the development of mineralization. Similarly, the factors that influenced variations in the styles of mineralization remain uncertain. Ongoing and future work includes geochronological research to constrain major events and whole rock geochemistry and mineral chemistry to define the extent and nature of alteration, and related temporal and spatial variations across the district.

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Figure 1. Regional geology map, modified from Arevalo (1999). Cross sections mapped are depicted in black.
Figure 2: Geological cross-sections of the district. Location and lithological legend of the cross-sections is depicted in black lines on figure 1. Dark grey lines indicate drill holes re-logged for accuracy on the sections. Red circles indicate strike and dip measured on surface.
Geochemical characteristics of magnetite from the Washan iron oxide-apatite deposit in the Ningwu ore district, East China: Implication for the ore-forming processes

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Abstract. In Chinese literature, iron oxide-apatite (IOA) deposits are referred to as “porphyrite iron deposits”, which are associated with Cretaceous sub-volcanic rocks (porphyritic diorite). The Washan deposit, located in the Ningwu ore district of East China, is a classic iron oxide apatite (IOA) deposit with 213.7 million metric tons (Mt) Fe that formed through a multi-stage ore-forming process. In-situ LA-ICP-MS trace elemental analyses of magnetite from different stages indicate that all magnetite share similar normalized trace element patterns. Concentrations of Mg, Al, Mn, Ni, and Ga increase and concentrations of Cr decrease from early to late mineralization stages and with high V and Ti contents. This implies that ore-forming conditions have a close magmatic link with increasing wall rocks (e.g., diorite and sedimentary rocks) involved into the Fe ore fluids, and suggests a magmatic-hydrothermal metallogeny. We infer that in the Washan deposit a Fe-rich liquid may have formed via liquid immiscibility and magnetite crystallized in high temperature hydrothermal environment.

1 Introduction

Iron Oxide Apatite (IOA) deposits form an important type of iron deposits worldwide and are characterized by high abundances of magnetite with low to moderate Ti-V (Dare et al. 2014) and with or without hematite and apatite. IOA deposits are also called Kiruna type deposits based on their apatite-magnetite assemblage typical of the Kiruna deposit in Sweden (Geijer 1931). The IOA deposit type was historically referred to as “porphyrite iron deposit” in Chinese literature based on the geology of the iron deposits in the Ningwu (Nanjing-Wuhu) ore district in the Middle-Lower Yangtze River metallogenic ore belt (MLYRB) of East China (Ningwu Research Group 1978). Deposits from this type locality are associated with Cretaceous sub-volcanic intrusions (porphyritic diorite) hosted by contemporaneous to slightly younger volcanic rocks and by Triassic sedimentary rocks.

The formation of IOA deposits has remained controversial worldwide in the past 50 years. One major divergence in interpretation is the magmatic or hydrothermal (metasomatic) nature of the magnetite ore. Topics being debated include 1) direct crystallization of ore from magmatic-hydrothermal fluids associated with andesite intrusions (Rhodes and Oreskes 1999; Sillitoe and Burrows 2002; Duan 2012; Dare et al. 2015), 2) the role of magmatic or non-magmatic hydrothermal fluids in leaching iron from surrounding volcanic or sub-volcanic rocks (Zhang 1980; Lu et al. 1990), 3) and ore genesis through crystallization of magma derived from liquid immiscibility, in which the iron-rich liquid (melt) was separated from an andesite parental magma (Velasco et al. 2016; Tornos et al. 2016). Actually, in most mineral deposits or deposit systems, the mineral precipitation processes are dynamic leading to different mineral assemblages or mineral abundances, including time gaps in ore-formation between two mineralization stages. Simply focusing on a single stage can thus misled on the real forming events.

In the Ningwu ore district ore bodies have a large variety of shapes that varies with hosting geological conditions. Most ore bodies share common geological-geochemical features with a similar ore-forming process (Duan 2012). Among them, the Washan IOA deposit is one of the best exposed and most representative with typical clearly multistage iron mineralization. This provides a classic case study to unravel ore-forming processes and further understand the genesis of IOA deposit.

2 Geology

2.1 Regional setting

The Ningwu ore district is located in the eastern part of the MLYRB. It extends from Nanjing (Jiangsu Province) in the northeast to the Wuhu (Anhui Province) in the southwest (Fig. 1). Cretaceous volcanic-subvolcanic rocks in the ore district are divided into four volcanic eruptive-accumulative cycles: Longwangshan Formation, Dawangshan Formation, Gushan Formation and Niangniangshan Formation from the bottom up. Each Formation started with explosive volcanic activity followed by more effusive eruptions, and ended with volcanic sedimentation. Subvolcanic rocks were formed in the late stage of each volcanic cycle, i.e. porphyritic diorite, gabbro and diorite, porphyritic gabbro and diorite, porphyritic trachyandesite, and porphyritic andesite. Subvolcanic rocks (132.6-128.2 Ma) occurring in the Dawangshan cycle are considered to have a close relationship with iron mineralization (around 130Ma) (Ningwu Research Group 1978; Duan 2012).

The IOA deposits in the Ningwu ore district are divided into three major ore fields: Meishan, Washan and Zhonggu ore fields from north to south (Fig. 1). The mineralization is mostly developed at the apical part of subvolcanic plutons or the surrounding volcanic rocks.
and form disseminated massive, breccia, stockwork and hydrothermal vein ores.

Figure 1. Simplified geological map with the distribution of IOA deposits in Ningwu ore district (after Ningwu Research Group 1978).

2.2 Deposit setting

The Washan deposit is located in the middle of Ningwu ore district (Fig. 1), with 213.7 million metric tons (Mt) Fe. The iron ore bodies at Washan mainly occur in the dome uplift area at the contact zone between the Washan porphyritic diorite intrusion and the volcanic rocks of the Dawangshan Formation (Fig. 2).

Alteration is zoned vertically and forms three main zones. The upper and light colored alteration zone with mainly kaolinite, mica and quartz, and a small amount of pyrophyllite, alunite, is distributed in the Dawangshan volcanic rocks and the upper part of the porphyritic diorite. The central, dark colored alteration zone consists mainly of albite, actinolite, magnetite,apatite, chlorite, epidote, quartz, and a small amount of kaolinite, sericite and carbonate. Economic ore bodies mainly occur in this dark colored alteration zone, followed by a small amount of chlorite, pyrite, carbonate and quartz. In the lower part of the light colored alteration zone, albite dominates the assemblages forming albittites.

Mineralization progressed in four stages: 1) disseminated, 2) breccias, 3) magnetite-actinolite vein type and 4) magnetite-apatite-actinolite vein type ores with the early stages being crosscut by the subsequent one in a regular order (Figs. 2 and 3). The earliest mineralization zone consists of disseminated ores forming a shape similar to the intrusion roof. Cryo-explosion has led to magnetite-cemented breccias in the primary ore body. Fine magnetite occurs as cement with rare apatite and actinolite. Two other iron mineralization stages (vein type ores) crosscut breccia ores. Magnetite, apatite and actinolite form the main assemblage of the four iron mineralization stages, and the magnetite content decreases from the early to late mineralization stages, whereas that of apatite and actinolite increases.

Figure 2. Typical cross section of the Washan IOA deposit (modified from Ningwu Research Group 1978).

Figure 3. Photos of iron ores showing typical ore textures and hydrothermal alteration. a Disseminated ores with earlier albite and K-feldspar alteration. b A clast of the breccia ores. The earlier pinkish albite and K-feldspar alteration was overprinted by Chl- Ep alteration at the margin. c Mt-Act vein cutting disseminated magnetite ore within porphyritic diorite. d Mt-Ap-Act vein in which Ap is showing Chl-Ap rims around F-Ap. Mineral abbreviations: Act = actinolite; Ap = apatite; Cl-Ap = chlorapatite; F-Ap = fluorapatite; Mt = magnetite; Chl = chlorite; Ep = epidote.
3 Analytical techniques and results

Magnetite ore samples were collected from the four iron mineralization stages for trace element analysis by a New Wave UP 193 Nd: YAG Laser Ablation system coupled with a Bruker Aurora M90 ICP-MS at the MRL Key Laboratory of Metallurgy and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences at Beijing. The detailed operating conditions for the laser ablation system and the ICP-MS instrument and data reduction have been described by Huang et al. (2016). Offline data reduction was performed through software ICPMSDataCal (Liu et al. 2008), including integration selection of background and analysis signals, and time drift correction and quantitative calibration.

In ore-forming processes, the contents of MgO, Al₂O₃, Co, Ni and Ga are increasing in magnetite from early to late mineralization stages, whereas the contents of Na₂O and Cr are decreasing. The contents of TiO₂ in magnetite from all the four mineralization stages are similar with a little tightly decreasing. Concentrations of P₂O₅, Sc, V, MnO, FeO, Cu, Zn, Zr, Nb, Sn, Hf and Ta do not vary much. Concentrations of K₂O, CaO, and Pb are in the same range respectively, showing no significant variations.

Figure 4. a Al+Mn vs. Ti+V magnetite discrimination diagram of magnetite in a variety of ore deposit types (after Nadoll et al. 2014), almost all samples fall in the magmatic magnetite field (Fe-Ti, V), close to the Porphyry deposit field. Some samples extent into the Porphyry and Kiruna fields (Fig. 4a). The averages of four magnetite mineralization stages plot in the magmatic magnetite field. In contrast, in the diagram of Ti against Ni/Cr diagram (Fig. 4b) proposed by Dare et al. (2014), magnetite plots across the magmatic to hydrothermal fields from the early to the subsequent ore stages.

To further characterize the origin of magnetite, the average compositions of magnetite trace elements are plotted in order of compatibility in a multi-element variation diagram following Dare et al. (2014). Here, magnetite trace-element contents fall largely within the high-temperature hydrothermal magnetite field, not the magmatic Fe-Ti-V ore field, going across their boundaries locally. The Sn-Ga contents fall within those of hydrothermal magnetite (Nadoll et al. 2014). This is also consistent with the Pb, C and Sr isotopes studies on iron ores and apatite (Yu et al. 2008; Ma et al. 2006). In contrast, the compatible elements Co, V, Ni and Cr fall within the Fe-Ti-V deposit area, with high V and high Ti contents, which indicate that conditions of crystallization fall within those of magnetite crystallizing from magmas or “inherit” magma characteristics. We interpret the iron of the Washan deposit as sourced from the porphyritic diorite intrusion and crystallizing from a fluid in a high temperature hydrothermal environment.

4 Discussion

4.1 Chemical discriminant of magnetite original

Magnetite is common in different types of deposits and its reservoirs of trace elements act as a significant petrogenetic tracer and a valuable target for geological studies (Dupuis and Beaudoin 2011; Nadoll et al. 2014). Its chemical composition concentrations are mainly controlled by temperature, fluid composition, element availability, oxygen and sulfur fugacity, silicate and sulfide activity, host rock buffering (Nadoll et al. 2014), and reflect conditions of crystallization.

Magnetite samples from the Washan deposit are plotted in discrimination diagrams of ore deposit types to extract genetic information. In the Al+Mn vs. Ti+V diagram (Nadoll et al. 2014), almost all samples fall in the magmatic magnetite field (Fe-Ti, V), close to the Porphyry

Figure 5. Multi-element variation diagrams for magnetite from the Washan deposit normalized to bulk continental crust.

4.2 Ore-forming processes

Liquid immiscibility as a source of iron enrichment has been proposed by many authors (e.g. Velasco et al. 2016; Tornos et al. 2016) and demonstrated a viable by experimental studies (e.g. Phipotts 1967). There are two type wall rocks in the Washan deposit, one is the diorite rock with minor volcanic rocks, the other one is Triassic sedimentary rocks, which as the potential one unexposed in the mining area underneath the ores and besides the diorite in deeper.

In hydrothermal magnetite genesis system, the fluid-rock interaction is one major factor which controls the composition of magnetite (like Si, Al, Mn, Mg and Ga) (Nadoll et al. 2014; Dare et al. 2014; Huang et al. 2016). It has been suggested and indicated that elements of Mg and Mn could be enriched in bearing metal hydrothermal fluid
by extensive fluid-rock interactions (Einaudi et al. 1981; Meinert 1987). Element of Al and Ga also have the similar behavior in magnetite, suggested by Huang et al. (2016). These characters are particularly prominent in the ore-forming processes of the Washan deposit, indicating the increasing degree of fluid-rock interaction.

Because of the highly compatibility into magnetite (Dare et al. 2014 and its references), Cr will be gradually consumed while the magnetite crystallization, if there is not any magmatic material and fluid involved more. For the Washan deposits, the Cr concentration of magnetite has a distinct decreasing from early to late, indicating there is less and less magmatic fluid provision from its primitive magma, in the ore-forming processes. On the other hand, more and more meteoric water have added, changing the hydrothermal fluid, which indicated by O-H isotopes character changing from magnetite, actinolite and quartz (Duan 2012). However, Ni contents is increasing which would controlled by fluid-diorite interaction.

5 Conclusion

The Washan deposit displays a multi-stage iron mineralization ore-forming process. Based on trace element compositions of magnetite grains from four iron mineralization stages, we present these remarks: Magnetite from disseminated, breccia and vein type ores have a similar root which related with magma evolution and its intrusion, there is an increasing rock-fluid interaction degree between iron-bearing hydrothermal fluid and wall rocks including diorite and sedimentary rocks, which led magnetite has increasing concentration trends of Mg, Al, Mn, Ni, Ga and decreasing concentration trend of Cr, with magmatic-hydrothermal (high temperature) feathers, showing a magmatic genesis to hydrothermal genesis trend. It confirms that the magnetite has a magmatic root, precipitated in magmatic-hydrothermal environment. And the dynamic ore-forming system should be paid more attention on the IOA deposit research.

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Orthopyroxene-bearing alteration at the roots of the Carajás IOCG mineral system, Brazil: an example from GT-34 prospect

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Abstract. The GT-34 prospect, from the Carajás Mineral Province, northern Brazil, represents an unusual nickel occurrence associated with the Carajás IOCG district. It occurs at the southern copper belt associated with regional NE-SW shear zones. Similarly to other IOCG deposits worldwide, alkali-iron alteration zones were individualized taking in consideration textural relationships and mineral chemistry. The orthopyroxene-bearing alteration is associated with the initial scapolite rich sodic metasomatism, with the first orthopyroxene occurrence related to IOCG alteration zones. The scapolite is widespread, chemically homogenous and of marialite composition, with 2.9-3.5 Cl wt%. The orthopyroxene is laden with scapolite, with composition of En68-76 and extremely low amounts of Ti, Cr, Ca and Al, similar to charnockite chemistry. Following the sodic alteration is the calcic alteration, with hornblende, oligoclase and clinopyroxene formation and subsequent brecciated nickel mineralization. Metasomatic orthopyroxene typically occurs in charnockites, under high temperature (>700°C) with a high CO2 activity fluid. On the other hand, scapolite chemistry suggest a highly saline fluid. Therefore, for scapolite-orthopyroxene formation, a mixture between those fluids is necessary. Due to CO2 known immiscibility with saline fluids, an immiscible, high temperature saline-CO2 fluid is suggested for this atypical parageneses formation.

1 Introduction

Carajás Mineral Province (CMP), northern Brazil, is the only actually known Archean IOCG occurrence, famous for its polymetallic and well-endowed world-class deposits. It lies at the southeastern portion of the Amazon craton and consists of gneissic and migmatitic basement covered by volcano-sedimentary sequences, both highly deformed and metamorphosed, and intruded by 1.88 “A” type granites (Hitzman 2000; Réquia et al. 2003; Groves et al. 2010; Moreto et al. 2015).

The Sossego-Sequerinho and Salobo deposits are currently best-documented (Monteiro et al. 2008; Xavier et al. 2010; Moreto et al. 2015). Salobo is the largest deposit and is located in the northern Carajás domain along the WNW-ESE Cinzento shear zone. Sossego-Sequerinho occurs in the southern copper belt (Moreto 2013) along the WNW-ESE Canaã shear zone, with series of known satellite occurrences (e.g. Castanha, Bacuri, Bacaba, Jatobá, Visconde) that share similar alteration zones and isotopic data suggesting mid to shallow crustal level formation (Monteiro et al. 2008; Pestilho 2011).

The GT-34 prospect occurs at the southern copper belt along a NE-SW trend, and consist of a brecciated nickel pentlandite-pyrhhotite-apatite rich mineralization. Siepierski (2008) first described GT-34 as part of the regional IOCG system formed in two phases: initial deep high temperature magnesium alteration followed by mineralization. However, proper individualization of alteration zones and orthopyroxene formation were not addressed.

Here, we characterize the parageneses of the two earliest alteration types (Na alteration and Ca alteration) within the alkali-iron metasomatic system typical of the IOCG deposit type. The crystallization of the atypical orthopyroxene-scapolite paragenesis is discussed in terms of possible fluids characteristics and crustal level.

2 Regional geology

Standing within the southeastern border of the Amazon craton the CMP (Tassinari and Macambira 2004; Vasquez et al. 2008), is limited at north by the Bacajá Domain (Fig. 1) and in the east by the Neoproterozoic Araguaia fold belt. To the south, the limit is a transitional subdomain between the CMP and the Mesoarchean Rio Maria TTG greenstone belt domain, and in the west by the Paleoproterozoic Iriri-Xingu Domain.

Figure 1. Geologic map of Carajás Mineral Province. Modified from Vasquez et al. (2008).

Basement units for the CMP consist of migmatises and bimodal syn tectonic orthogneas of the Xingu Complex (Fig. 1) dated between 3.0 and 2.83 Ga, and of the mafic to felsic orthogneas Pium Complex (3.0 Ga to 2.73
Ga; Feio et al. 2012, 2013). The supracrustal units are composed of a series of Neoarchean greenstone belts (Itacaiunas Supergroup), banded iron formation and silicilastic sedimentary rocks (Aguas Claras formation), which host the majority of the IOCG deposits at CMP. Paleoproterozoic “A” type granites (1.88 Ga) intrude both basement and supracrustal units (Ciganó, Central de Carajás and Rio Branco).

The IOCG mineralization is controlled by the main regional faults (Fig. 1; Cinzento, Carajás and Canaã faults) and occurs at two different stages: 2.71 to 2.68 Ga and 1.90 to 1.88 Ga based on ages obtained at Sossego-Sequeirinho mine (Moreto et al. 2015). Alteration zones (Montero et al. 2008), defined as sodic, sodic-calcic, Sequeirinho mine (Moreto et al. 2015). Alteration zones 1.90 to 1.88 Ga based on ages obtained at Sossego- and occurs at two different stages: 2.71 to 2.68 Ga and dominating Carajás mineralization.

(1.88 Ga) intrude both Supracrustal units are exposed due to the different crustal levels of the deposits and mineralization are similar to regional IOCG-IOA deposits at CMP and are not detailed here.

3.1 Mineral chemistry

Mineral chemistry analyses were carried out at University of Brasilia using a JEOL Superprobe JXA-8230 Electron Probe Microanalyzer (EPMA), at an accelerating voltage of 15 kV and beam current of 10 nA. Spot size was 1 μm with a 10 s analysis time. Orthopyroxene and scp were analyzed in order to better comprehend the initial Na alteration.

Scapolite is chemically homogeneous and of marialite composition (Me16.22). The Cl content is between 2.9 to 3.5 wt%, however SO3 and CO3 were not analyzed. Therefore, the exact structural formula was not obtained. Magnesium and Fe are present at relative high amounts up to 2.2 wt%, suggesting the presence of Fe-Mg during the Na alteration.

Orthopyroxene composition is En68-76 showing a Mg dominant composition with Wo 0.2 to 0.6 indicative of a low Ca composition. Titanium (≤ 0.1 wt%), Cr (≤ 0.1 wt%) and Al (0.4 to 2.1 wt%) are much lower than expected from typical igneous opx and are interpreted as indicative of a metasomatic origin. Chlorine content was constantly observed in the analyses, however the values obtained (<0.06 Cl wt%) are near the detection limit and it was not possible to determine if they are structurally bonded or micro inclusions.

4 Discussion

GT-34 prospect, despite its size when compared to major deposits, hold the first example of opx-bearing alteration associated to IOCG systems (e.g., Hitzman et al. 1992; Hitzman 2000; Xavier et al. 2010; Corriveau et al. 2016). Evidence found here suggests that opx crystallization was synchronous with Na alteration, known to be the deeper and most extensive alteration type.

Metasomatic orthopyroxene is associated with charnockites (Newton and Tsumogae 2014), displaying chemically distinct composition with low Ti, Cr, Al and Ca forming a nematoblastic texture associated with zones of increased deformation while medium to coarse grains normally appear adiablastic at the border of nickel mineralization or as cores enveloped by fine hbl. Relics of opx are partially preserved within the coarse hbl crystals. Oligoclase occurs as an alteration of scp, appearing as irregular pods forming fine anhedral to subhedral crystal typically bordered by hbl. Clinopyroxene is restricted to fine deformation bands where the alteration zones are not dominant and original host rock is partially preserved.

Nickel mineralization occurs after Ca alteration followed by two more alteration types: K-magnetite alteration and K-hematite alteration. These alteration types and mineralization are similar to regional IOCG-IOA deposits at CMP and are not detailed here.
Figure 2. Main textures and contact relationships of Na and Ca alteration at GT-34. a) Tonalitic gneiss representing the least altered host rock. b) Sodic alteration with scp bands shrouding coarse opx fragments. c) Orthopyroxene overprinted by Ca alteration forming irregular patches and fine veins. d) Calcic alteration forming fine- to medium-grained hbl replacing Na alteration. Nickel mineralization is present as late breccias. e) Orthopyroxene in irregular contact with Ca alteration. Note that hbl is subeuhedral near the contact with opx. f) Contact between opx and scp from Na alteration. g) Sodic alteration cut by Ca alteration. Scapolite at top left and opx associated with talc at top right. Hornblende forming distinct domains replacing initial Na alteration. h) Main textures of Ca alteration. Fine to nematoblastic at center to top left and coarse at the bottom right.

forming through igneous, metamorphic or dehydration process (Yang et al. 2016). Similarly, all those process occur at anhydrous conditions with a high CO₂ activity also forming, beyond opx, clinopyroxene, K-feldspar, plagioclase (Harlov et al. 2014) and a series of other Fe-Mg minerals. Different from common charnockite
processes, GT-34 opx forms with scp. Scapolite formation at CMP is known for its metasomatic origin (Moreto et al. 2008) during IOCG-related Na alteration. Mineral chemistry made here revealed a composition that would require a NaCl rich fluid for its formation. In the ideal crystal structure, scp does not show significant amounts of water on A site, which is in agreement with nearly anhydrous conditions for opx formation. Putting together a CO2 rich conditions with NaCl rich at high temperatures, fluid composition likely falls within CO2-NaCl-H2O immiscibility gap (Shmulovich and Graham 2004).

The absence of other main phases with opx, beside scp, shows that no typical charnockitic process was involved, and it is unlikely that opx formed prior to Na alteration with no other phases preserved but opx. Based on the presence of magnetite inclusions in opx and distinct Fe-Mg contents of scp, we suggest that immiscible NaCl-CO2 metasomatic fluids can form an opx-scp association at high temperatures and deep crustal levels as part of the initial Na alteration in the Carajás IOCG district.

5 Conclusion

(1) GT-34 prospect shows crucial evidence of deep crust alkali-Fe alteration, suggesting a continuum through deep-mid-shallow crustal levels.

(2) Fluids associated with the alteration zones appear to be initially anhydrous (opx-scp), most likely of CO2-NaCl affinities, with progressive H2O activity increase (hbl-olg-cpx).

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Apatite chemistry from Kiruna-type Bafq iron deposits, Central Iran: a review

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Abstract. The magnetite-apatite deposits in the Bafq metallogenic province in Central Iran, including the world-class Chadormalu and Choghart, as well as Se-Chahun and Esfard, are hosted in the Late Precambrian-Cambrian volcanic-sedimentary rocks that have undergone variable sodic, calcic, potassic, silicic, chloritic, and sericitic alterations that are characteristic of iron oxide-apatite (IOA) ore systems. Apatites from various iron deposits in the Bafq district display chondrite-normalized REE patterns characteristic of Kiruna-type deposits. The REE patterns of the apatites display similarities to those of the magmatic and sedimentary country rocks. The trace-element patterns of the apatites are comparable to those of the local granitoids and mafic bodies, as well as the iron ores, and to other Kiruna-type deposits. It can be concluded, from apatite geochemistry of major magnetite-apatite deposits in the Bafq district that both magmatic and basinal fluids contributed to the formation of the iron oxide deposits. For the Chadormalu deposit, two generations of apatite are distinguished in backscattered electron images. The lower $\Sigma$REE and Y in the earlier, and dominant, generation can be explained by local fluid aided dissolution/reprecipitation processes that led to development of monazite in close spatial association with depleted apatite. This would explain the younger monazite ages (450-250 Ma) compared with the apatite ages (533-510 Ma) obtained for Chadormalu deposit.

1 Introduction

The genesis of apatite-bearing Fe oxide deposits is controversial. The characteristics features are massive Ti-poor magnetite and the common presence of apatite, locally associated with REE-phosphates. The deposits may contain anomalous concentrations of Cu–Fe sulfides, Au, U, Ag, and Co minerals (Barton and Johnson 1996). The deposits have been classified as Kiruna-type magnetite–apatite (Frietsch and Perdahl 1995) or IOA (iron oxide-apatite) ores (Williams 2010). Some researchers consider the deposits as the Cu-poor end-member in the spectrum of the iron oxide copper–gold (IOCG) deposits (e.g., Gelcich et al. 2005; Williams et al. 2005).

The Bafq mining district lies in the Posht-e-Badam block (Stocklin 1971; Haghipour 1977) or Kashmir Kerman belt (KKB) (Ramezani and Tucker 2003) in Central Iran. The KKB is a fault-bounded structural zone, ~900 km long and 20-80 km wide (Fig. 1) with a Neoproterozoic basement of Gondwanan affinity consisting of various schists, gneisses, and granitic gneisses covered by Neoproterozoic to Triassic rocks (Stocklin 1971; Borumandi 1973; Haghipour 1977; Forster and Jafarzadeh 1994). The Neoproterozoic- Early Cambrian cover rocks consist of phyllites, slates, quartzites, and mafic volcanic rocks of the Tashk Formation (Jami et al. 2007) covered by a terrestrial to shallow marine sequence containing Ediacaran fauna (Hahn and Pflug 1980) and an Early Cambrian (528–530 Ma) bimodal volcanic unit (Ramezani and Tucker 2003).

The Bafq metallogenic province hosts large magnetite-apatite ore deposits with local REE wealth. Over 30 magnetic anomalies are identified, some well-exposed, with a total reserve of over 2 Gt of iron oxide ore with variable amounts of apatite.

Figure 1. Distribution of iron oxide–apatite deposits in the Kashmar-Kerman volcanic-plutonic belt (modified after Ramezani and Tucker 2003)

The timing of ore formation at Choghart has been constrained to be 515 ± 21 Ma and 529 ± 21 Ma (monazite Th-U-Pb total method; Torab and Lehmann 2007). Stosch et al. (2011) reported apatite U-Pb ages ranging between 527 to 539 Ma for five iron deposits in the Bafq district. These ages fall in the age range reported for felsic plutonic and volcanic rocks in the district (525–545 Ma, zircon U-Pb; Ramezani and Tucker 2003). However, Bonyadi et al. (2011) reported a U–Pb LA-ICPMS age of 510 ± 8 Ma for REE-rich fluorapatite and the associated semi-massive Ti-rich magnetite from Se-Chahun deposit. The same authors

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reported an older age (525 ± 7 Ma) for sodic alteration from the same deposit.

The Bafq district iron deposits are associated with prevalent Na- and Ca-alteration, or metasomatism, displayed by common albite and actinolite occurrences, as well as subordinate potassic, silicic, and locally sericitic and chloritic alteration types.

Similar to other magnetite-apatite deposits in the Bafq district, Chadormalu deposit is hosted by a variety of altered volcanic to subvolcanic felsic rocks, as well as mafic to intermediate intrusive bodies and various schists. Magnetite-apatite mineralization at Chadormalu occurs as two massive bodies, plus scattered magnetite-apatite veins in the greenish altered host rocks.

Apatite in the Bafq district iron deposits is closely associated with magnetite and occurs in a variety of textures and chemical compositions. In Chadormalu, apatite occurs as apatite-magnetite veins in the greenish altered rocks, as euhedral (Fig. 2a) to anhedral disseminated grains and grain aggregates mainly in the marginal parts of the main ore body, as well as irregular apatite veinlets in the internal parts of the main ore body (Heidarian 2013; Heidarian et al. 2016, 2017).

Apatite, or apatite-magnetite association, in Chadormalu locally coexists with sulphides (dominantly pyrite), quartz, and actinolite. In high resolution back scattered electron (BSE) images, the Chadormalu apatite occurs as dark and bright spots with sharp boundaries (Fig. 2b). The dark parts are mostly developed across fractures in the bright parts, and contain scattered monazite inclusions. Such textures and relations are reported from Se-Chahun (Bonyadi et al. 2011), Choghart (Taghipour et al. 2015), and Esfordi (Torab 2008).

2 Geochemistry

The composition of apatites from Bafq district iron deposits are mostly fluorapatite. Apatite from Chadormalu deposit and several other major Bafq deposits (e.g., Choghart, Se-Chahun, Esfordi) show high REE concentrations (Moore and Modabberi 2003; Jami 2007; Bonyadi et al. 2011; Sabet Mobarhan et al. 2015; this study) with high LREE/HREE ratios and negative Eu anomalies (Fig. 3a).

The chondrite-normalized REE patterns from various deposits are comparable to those of the Swedish Kirunavaara deposit, as reported by Frietsch and Perdahl et al. (1995), Harlov et al., (2002), and Mao et al. (2016) (Fig. 3a). The apatites also show some similarities in REE patterns with those of IOCG-type deposits, as reported by Mao et al. (2016) (Fig. 3b). The Chadormalu apatites show higher REE contents in the bright spots (Fig. 3a), consistent with that reported from Se-Chahun (Bonyadi et al. 2011). The high (Ce/Yb)N ratios are indicative of relative LREE enrichments (Fig. 4a), which is also characteristic of the host granitoid rocks. In this diagram, darkapatites show lower REE contents. The behavior of Ce and Eu might differ from that of the adjacent REEs due to redox sensitivity. Negative Eu anomalies appears to be a characteristic feature for the Bafq iron oxide deposits (Fig. 3a) and consistent with that in Kiruna-type deposits (Fig. 3a) and granitoid rocks (Fig. 4b). The low Eu contents can be explained by the relatively high oxidation state of the mineralizing fluids, limiting replacement of Ca²⁺ by Eu²⁺ in the apatite structure.

Parak (1975) relates the high LREE contents of the Kiruna district apatites to involvement of basinal sedimentary fluids. Apatite from Chadormalu and other Bafq iron deposits show some similarities in chemistry with that of phosphorites in the Late Precambrian-Early Cambrian Soltanien Formation (Mousavi Motlagh et al. 2015) and in the equivalent Rizu and Desu series in the Bafq area, suggesting derivation of phosphate from the sediments by circulating fluids (Torab 2008) (Fig. 3b). Sulfur isotope data from Chadormalu (Heidarian et al. 2017), Choghart (Sadeghi Davati et al. 2008), Esfordi (Jami 2008), and North Anomaly (Sadeghi 2006) suggest involvement of basinal brines in the ore systems.

Magnetites from several Bafq district iron deposits, display chondrite-normalized REE patterns similar to those of apatites. The lower REE contents of magnetites, relative to apatites, can be explained by lower REE partitioning coefficients in magnetite. A comparison of apatite and magnetite REE patterns with those from altered and unaltered host rocks, including felsic volcanic and intrusive bodies as well as gabbros, shows similar LREE enrichments (Fig. 3b) suggesting possible contribution of magmatic fluids in the apatite-magnetite mineralization in the Bafq district.
Using the Y-Sr discrimination diagram, most apatites from Chadormalu, Choghart, Esfordi, and Se-Chahun deposits fall in the granitoid field or straddle the mafic and iron ore fields (Fig. 4c). On the ternary Mn, V×10, Mg discrimination diagram (Mao et al. 2016), the Chadormalu and other magnetite-apatite deposits from Bafq district fall in the Kiruna-type domain (Fig. 4d).

The distribution of REE and abundances of certain trace elements including Sr, Y, V, Mn, and Mg in apatites from several Bafq district iron oxide-apatite deposits suggest that a combination of magmatic hydrothermal fluids, as well as basinal Cl-bearing fluids, were involved in the formation of apatites, and by corollary iron oxide ores, in the Bafq district.

The bright and dark apatites, in SEM images, are geochemically different. The dark apatites appear to have been formed due to some fluid-aided dissolution/reprecipitation (DRP) reactions, which led to depletion of REE in the original apatite and formation of REE minerals, such as monazite. KCl-enriched fluids could be responsible for these DRP reactions and monazite formation.

The maximum age range calculated from $^{238}$U and $^{206}$Pb isotopes for Chadormalu older apatite generation show an age range of 510-533 Ma, consistent with the ages reported from other deposits (e.g., Bonyadi et al. 2011; Stosch et al. 2011). The younger generation yielded U-Pb ages ranging between 450 Ma to 250 Ma. This can be explained by the DRP processes and formation of monazite, which led to Pb loss and resetting processes in the apatites.

**Figure 3.** a) Chondrite-normalized REE patterns for Chadormalu apatites (green and yellow shades, representing dark and light spots in Fig. 2, respectively); also shown are the average composition of apatites from Choghart, Esfordi, Se-Chahun, and Chadormalu deposits, as well as REE patterns of apatites from Kiruna-type and IOCG-type iron ores. b) Chondrite-normalized REE patterns (averaged) for various Chadormalu host rocks and phosphorites from late Precambrian-early Cambrian Soltanieh Formation in the Bafq district.

**Figure 4.** a) Plots of apatites from Esfordi and Se-Chahun iron oxide deposits, as well as various rocks on REE vs. $(\text{Ce}/\text{Yb})_n$ discrimination diagram of Belousova et al. (2002). Most Bafq iron district apatites plot in the granitoids field. b) Plots of apatites from Se-Chahun, and Chadormalu deposits on $\text{Eu}/\text{Eu}^*$ vs. Y diagram. Most apatites plot in the granitic and mafic rocks and iron ore fields. c) Plots of Apatites from Chadormalu, Se-Chahun (Bonyadi et al. 2011), Esfordi (Torab 2008) and Choghart, Chadormalu, and Esfordi (Taghipour et al. 2015) on Y vs. Sr diagram. d) Plots of Chadormalu, Choghart, and Se-Chahun apatites on Mg-V×10-Mn (ppm) ternary diagram, showing a Kiruna-type affinity for the deposits.
3 Implications

The spatial and temporal distribution of magnetite-apatite deposits in the Bafq district, as well as the geological and geochemical characteristics from several major deposits in the district, suggest that they developed through similar processes. The deposits are associated with a wide range of hydrothermal alteration types, including sodic (albitic), calcic or calcic-ferroan (actinolitic), potassic, silicic, sericitic, and chloritic. Apatites from the deposits are distinguished by elevated REE contents and high LREE/HREE ratios, typical of Kiruna-type deposits. The trace-element geochemistry of the apatites suggest a contribution from granitoids and (or) mafic magmas, as well as involvement of basinal fluids in the formation of the deposits. Two generations of apatites was distinguished in SEM images. The lower REE and Y contents in the earlier dark apatites can be explained by fluid-aided dissolution/reprecipitation processes, which caused REE depletion from the apatites and formation of monazite associated with the second generation. The younger ages (450-250 Ma) can be explained by this process.

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Trace element composition of iron oxides from IOCG and IOA deposits, and relationships to hydrothermal alteration and deposit subtypes

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Abstract. EPMA and LA-ICP-MS trace elemental data of magnetite and hematite from fourteen well-studied iron oxide–copper–gold (IOCG) and iron oxide–apatite (IOA) deposits are used to test the relationships between trace element geochemistry and their host alteration types and deposit subtypes. The data furthers the development of discrimination diagrams. Iron oxides from HT Ca-Fe alteration type are relatively rich in Mg, Ti, Co, V, and Ni, whereas those from HT K-Fe type are rich in Mn and Cr. Those from LT K-Fe type have relatively high Si, Ca, Y, Pb, Zr, Ge, W, Sn, Ta, Nb, Cu, and Mo. The consistency of the relative enrichment of specific elements in iron oxides with that in altered rocks indicates that iron oxide geochemistry can serve as a proxy of hydrothermal alteration types. Iron oxides from magnetite IOCG deposits have relatively high Ga, Mn, Zn, Ni, and Cr, a signature distinct from those from hematite IOCG deposits. Iron oxides from magnetite IOA deposits show relatively high Mg, Zn, Ni, Co, and V, whereas those from magnetite + hematite IOA deposits contain high W, Sc, and Ti. Plots of Si+Ca vs. Mn+Cr, Mn+V and Mn+Mg+V+Ni are proposed to discriminate different alteration and deposit subtypes.

1 Introduction

Iron oxides such as magnetite and hematite are very common in igneous, sedimentary, and metamorphic rocks, and in various types of mineral deposits. Trace elements in iron oxides such as magnetite and hematite have been used in provenance studies of sediments (Razjigaeva and Naumova 1992), petrogenesis (Dare et al. 2014), mineral exploration (Boutroy et al. 2014; Makvandi 2015), and deposit genesis (Dupuis and Beaudoin 2011; Huang et al. 2010, 2016). However, the scarcity of large geochemical data across IOCG and IOA systems that encompass the entire spectrum of IOCG alteration types impedes the development of discriminant diagrams that characterize individual alteration type signatures. In addition to different alteration types, IOCG and IOA deposits can be subdivided into hematite, hematite + magnetite and magnetite groups based on the nature of the principal iron oxides present (Williams 2010). The genetic differences among these deposits remain unknown. Trace element composition of magnetite and hematite from fourteen well-studied IOCG and IOA deposits were determined by EPMA and LA-ICP-MS. The geochemistry of different hydrothermal alteration types and deposit subtypes are characterized and discriminated by trace element composition of magnetite.

2 Methodology

A total of fifty samples are chosen from fourteen IOCG and IOA deposits, including Igarapé Bahia, Sossego, and Salobo from Brazil, Olympic Dam, Ernest Henry, and Savage River from Australia, Candelaria from Chile, and Kwyjibo from Canada, Kiruna and Rektor from Sweden, El Romeral from Chile, Pilot Knob, Pea Ridge and Adirondacks from USA. All samples were carefully described at hand specimen scale and their thin sections are observed by optical microscope and scanning electron microscope. Alteration names are given according to the mineral assemblages of analyzed samples and the alteration description of individual deposits. Here, three alteration types are used, i.e., HT Ca-Fe, HT K-Fe and LT K-Fe. Four deposit subtypes are defined according to the major iron oxides in the deposit. IOCG deposits include magnetite (MagIOCG) and hematite IOCG (HemIOCG) deposits, whereas IOA deposits include magnetite (MagIOA) and magnetite-hematite (MagHemIOA) IOA
Minor/trace elements in iron oxides were analyzed at Laval University by a CAMECA SX-100 Electron Probe Micro-Analyzer, equipped with five wavelength-dispersive spectrometers, using a 10-μm diameter beam with a voltage of 15 kV and a current of 100 nA. Part of samples were analyzed by a RESOlution M-50 193 nm Excimer Laser Ablation system coupled with an Agilent 7700x ICP-MS at Université du Québec à Chicoutimi (UQAC). Line analyses were carried out using a beam size of 25 to 80 μm with a speed stage of 3 to 15 μm/s and a laser frequency of 10 Hz and a power of 5 mJ per pulse. The detailed methods for EPMA and LA-ICP-MS analyses are available in Boutroy et al. (2014).

3 Results and discussion

Magnetite and hematite grains were discussed together because their chemical compositions in individual deposits do not show significant differences. The minimum, maximum, average composition, afforded by EPMA, of iron oxides from different alteration types and deposits subtypes are shown in Fig. 1. Iron oxides from the HT Ca-Fe alteration type have relatively high Mg, V and Ni but relatively low K and Al contents (Fig. 1a). Iron oxides from HT K-Fe alteration type have relatively high Mn and Cr contents, whereas those from LT K-Fe alteration type have relatively high Si, Ca, Sn, Cu, and Ti contents but low Mn, Mg, V and Ni contents (Fig. 1a). Iron oxides from the MagIOCG deposits are characterized by relatively high Mn, whereas those from the HemIOCG deposits have relatively high Si, Ca, Al, Sn, Cu, and Ti contents but low Mn, Mg, V, and Ni contents (Fig. 1b). Iron oxides from the MagIOA deposits have relatively high Mg, Zn, V, and Ni contents and low Si, Ca, and Ti contents, whereas those from MagHemIOA deposits are characterized by relatively high Ti but low Al (Fig. 1b).

LA-ICP-MS analyses show that iron oxides from HT Ca-Fe alteration type have relatively high Mg, Ti, Co, V, Ni and low Ge, Sn, and Mo contents. Iron oxides from HT K-Fe alteration type have relatively high Mn and Cr but low Ca, Y, P, Pb, Zr, W, Sn, Ta, and Nb contents, whereas those from the LT K-Fe alteration type have relatively high Si, Ca, Y, P, Pb, Zr, Ge, W, Sn, Ta, Nb, Cu, and Mo but lower Ga, Mn, Mg, Ti, Zn, Co, V, Ni, and Cr (Fig. 2a). Iron oxides from MagIOCG deposits are characterized by relatively low Si, Ca, Y, P, Pb, Zr, and Hf and high Ga, Mn, Zn, Ni, and Cr, whereas those from the HemIOCG deposits are characterized by high Si, Ca, Y, P, Pb, Zr, Ge, W, Sn, Ta, Nb, Cu, and Mo but lower Ga, Mn, Mg, Ti, Zn, Co, V, Ni, and Cr (Fig. 2b). Iron oxides from MagIOA deposits show relatively high Hf, Mg, Co, and V and low Si, Ca, Y, Ge, W, Sn, Ta, Nb, and Mo contents, whereas those from the MagHemIOA deposits have relatively high W, Sc, and Ti but low Pb, Al, Mg, and Zn contents (Fig. 2b).

In summary, EPMA and LA-ICP-MS data show that iron oxides from the HT Ca-Fe alteration type have relatively high Mg, Ti, Co, V, Ni contents and low K, Al, Ge, Sn, and Mo contents (Figs. 1a and 2a). Iron oxides from HT K-Fe alteration type have relatively high Mn and Cr but low Ca, Y, P, Pb, Zr, W, Sn, Ta, and Nb, whereas those from the LT K-Fe alteration type have relatively high Si, Ca, Y, P, Pb, Zr, Ge, W, Sn, Ta, Nb, Cu, and Mo but lower Ga, Mn, Mg, Zn, Co, V, Ni, and Cr (Figs. 1b and 2b). The relative enrichment of Mg, Co, and Ni in iron oxides from the HT Ca-Fe alteration type is consistent with documentation that fluids for Ca-Fe alteration are rich in Ca, Fe, Mn, Mg, Zn, Ni and Co (Montreuil et al. 2013). The relative enrichment of Si, Zr, Ta and Nb in iron oxides from LT K-Fe alteration type is consistent with that of fluids leading to K-Fe alteration being rich in K, Al, Ba, Si, Rh, Zr, Ta, Nb, Th and U (Montreuil et al. 2013). This indicates that the trace element composition of iron oxides can serve as a proxy of alteration types to some extent.

Figure 1. Multi-element box and whisker plots for EPMA trace element data of iron oxides. a. From different alteration types. b. From different deposit subtypes. The whisker represents the range from minimum to maximum values. The circle filled by black means the average composition. The short horizontal line within the box represents the median value and separates box with 25% values greater and 25% smaller than the median value, respectively.
Based on the average trace element composition of iron oxides, discrimination diagrams for different alteration and deposit subtypes are proposed. Plot of Si+Ca vs. Mn+Mg+V+Ni can discriminate LT K-Fe alteration from HT Ca-Fe and HT K-Fe alteration types, but cannot discriminate HT Ca-Fe alteration type from HT K-Fe alteration type (Fig. 3a). Plot of Si+Ca vs. Mn+Cr can discriminate three alteration types from each other in spite of minor overlapping (Fig. 3b). Individual analyses for each grain are also plotted in these diagrams to test the precision of the defined boundary. Results show that the defined boundary by average composition is also appropriate for individual compositions (Fig. 3c, d).

Plots of Ca+Al+Mn vs. Ti+V and Ni/(Cr+Mn) vs. Ti+V were proposed to discriminate IOCG, IOA, banded iron formation, skarn, and porphyry deposits from each other using trace element composition of iron oxides (Dupuis and Beaudoin, 2011). Larger dataset of EPMA and LA-ICP-MS analyses for IOCG and IOA deposit allows complementing these diagrams and developing new discrimination diagrams for deposit subtypes. Plot of Si+Ca vs. Mn+V is proposed for discriminating HemIOCG, MagIOA, MagHemIOA deposits from each other (Fig. 4a). Plot of Si+Ca vs. Mg+Mn+V+Ni is used to discriminate MagIOCG deposits from HemIOCG deposits in spite of minor overlapping (Fig. 4b). The individual analyses of iron oxides also plot within the field defined by the average composition (Fig. 4c, d). But both of these diagrams cannot discriminate MagIOCG deposits from MagIOA and MagHemIOA deposits.
Conclusions

Iron oxides from different alteration types and deposit subtypes of IOCG and IOA deposits show distinct trace element compositions. Geochemistry of iron oxides can to some extent reflect the fluid compositions responsible for their formation. Diagnostic elements or element assemblages can be used to discriminate different alteration types from each other as well as different deposit subtypes.

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Figure 4. Discrimination diagrams for different subtypes of IOCG and IOA deposits defined by EPMA data. Data points in a and b are average trace element compositions of iron oxides, whereas those in c and d are individual analyses. Dashed lines in a and c are used to distinguish HemIOCG, MagIOA, and MagHemIOA deposits, whereas lines in b and d are used to distinguish MagIOCG and HemIOCG deposits.
Abstract. The Island Dam prospect is located within the Mesoproterozoic Olympic Cu-Au Province, South Australia. Banded iron formation (BIF)-style mineralization is overprinted by amphibole-magnetite alteration we refer to herein as 'skarns'. Iron oxides within BIF and skarn lithologies display textures and geochemical signatures defining the two contrasting mineralization styles. Iron oxide layers in BIF are composed of martite, which features relative enrichment in Ni, Co, Mn, As, Sb, U, Y and REE. Skarn lithologies contain cm-scale laths of hematite that are markedly enriched in W and Sn (thousands of ppm, and compositionally zoned with respect to these elements). Iron oxide-copper-gold (IOCG) mineralization is associated with skarn alteration in some parts of the Olympic Cu-Au Province and is linked to a ~1.6 Ga magmatic-hydrothermal event, which generated the World’s largest concentration of iron oxide-copper-gold (IOCG) deposits. Skarn alteration at Island Dam can be attributed to the same event. Iron oxides are ideal tracers of alteration processes in iron oxide-bearing ore systems. At Island Dam, recognition of distinct signatures in iron oxides highlights their capacity to distinguish protolith from alteration products and trace hydrothermal history. Moreover, interpreting the evolution of iron oxide mineralogy may be an important step for understanding the spatial-temporal relationships between BIF and IOCG mineralization.

2 Geological background

The Island Dam prospect is located in the eastern Gawler Craton, ~90 km southeast of the World-class Olympic Dam IOCG deposit within the Olympic Cu-Au Province (Fig. 1; see also Ehrig et al. this volume). Mineralization in the Olympic Cu-Au Province is spatially and temporally linked to volcanism and plutonism during generation of a ~1.6 Ga siliceous large igneous province. In contrast to the granite-hosted, hematite-brecia deposit at Olympic Dam, the Cu prospect at Island Dam is hosted within metasedimentary and volcanic rocks of the Wallaroo Group (WG). These were deposited, at 1765-1740 Ma, onto older (~1850 Ma) gneissic granites of the Donington Magmatic Suite (Cowley et al. 2003 and references therein). The WG sequences include impure limestone and dolostone horizons, as well as thin BIF-like layering, which is also observed/inferrred, for example, in the northern part of the Olympic Dam district (Fig. 1). These clearly pre-date ~1600-1585 Ma Hiltaba Igneous Suite (HIS) equivalents.

The formation extends from the Mt. Woods Inlier in the northern Gawler Craton to the upper Yorke Peninsula in the south, but paleo-reconstruction and district correlation of WG sequences is hampered not only by younger cover sequences but also by superimposed alteration, including alkali-(calcic) + Fe metasomatism with regional expression in the Moonta area (Conor et al. 2010; Kontonikas-Charos et al. 2014), as well as calcic skarn formation in prospects such as the Groundhog Zn-Cu skarn in the Punt Hill area (Reid et al. 2011), or the Cu-Au skarn at Hillside, Yorke
Peninsula (Conor et al. 2010; Ismail et al. 2014). Thick (~500 m) sequences of interbedded garnet skarn and banded calc-silicate-feldspar rocks are intersected between the Gawler Range Volcanics and Donington Granite in drillholes (e.g. SAR9) west of the Punt Hill area, where meter-scale intervals rich in iron oxides with a BIF-like appearance also occur as horizons within the skarn in SAR9. Mineralization within prospects hosted by the WG are dated at ~1.6 Ma, e.g. Sm-Nd dating of pyroxene-garnet skarn at Groundhog (Reid et al. 2011), or accessory minerals elsewhere (Skirrow et al. 2007).

This study focuses on a selection of ~25 samples containing iron oxides from lithologies with BIF and WG-like appearance, as well as several specimens of specular hematite. Polished blocks were analyzed using scanning electron microscopy in back-scatter electron mode (BSE), and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) for trace elements using BHVO-2G, GSD-1G and NIST610 as reference standards. All instrumentation is housed at Adelaide Microscopy, The University of Adelaide.

4 Results

Distinct generations of iron oxides within the two main lithologies of interest here, BIFs and skarns, are recognized based on textural and compositional variations. Iron oxides within the BIFs are dominantly a martite, readily recognizable from granular shapes, inclusions of magnetite, and often the presence of acicular-shaped mineral relicts that are marked by fine-grained chlorite within the martite mass (Fig. 3a) and could represent original actinolite grains.

Quartz, carbonates (mainly siderite) and chlorite are abundant gangue minerals in the BIFs. There is clear evidence for K-Fe alteration as 10-20 μm K-feldspar grains rimmed by film-like hematite within quartz (Fig. 3b). What we refer here to as skarn is recognized by the presence of actinolite (Fig. 4a), phlogopite, magnetite, apatite, titanite, calcite, fluorite and tourmaline, lending the rocks a green color with patchy alteration domains that may display banding (Fig. 2b, c). Massive or banded actinolite skarn varieties are progressively altered,
particularly by pseudomorphic replacement during the retrograde skarn stage.

**Figure 3.** BSE images a. martite (Mrt) in BIF. Note hematite replacing a previous lath-shaped mineral with contours marked by chlorite (Chl). b K-feldspar (Kfs) with a film of hematite around the margin as inclusions within quartz (Qz).

In contrast to martite from the BIF, euhedral magnetite in the actinolite skarn displays oscillatory zoning with respect to Si and Ca, and may contain inclusions of quartz, calcite and chlorite (Fig. 4b). Thin lamellar aggregates of hematite are also noted. In the actinolite skarn there are numerous pseudomorphs of rutile + calcite after coarse, lozenge-shaped titanite. In detail, the rutile also shows tiny inclusions of scheelite at the boundaries between W-poor cores and W-richer rims.

**Figure 4.** BSE images from amphibole-magnetite (skarn) lithologies showing a actinolite (Act) with Fe-rich (bright) domains. b Si- and Ca- (dark and bright) zoned magnetite (Mt). c and d BSE image and LA-ICP-MS element map showing W-zonation in coarse-grained Hm. Scale: parts per million (x10³).

A close relationship between hematite and sulfides is seen in samples from altered skarn and/or of BIF affiliation. The majority of iron oxides are represented by aggregates comprising martite-magnetite intergrowths with irregular and/or scalloped mutual boundaries.

Sulfides, chalcopyrite, pyrite, and minor bornite occur as patches throughout carbonate + quartz + chlorite assemblages interstitial to the iron oxides, as well as hosted along the aforementioned magnetite margins. A distinct generation of hematite, occurring as small lamellae, occurs within areas of sulphides. This hematite also displays zonation with respect to W. The coarse-grained (as large as 4 cm) specular hematite (Fig. 2d), features polysynthetic twinning as well as strong zonation with respect to W. This is expressed as W-rich and -poor sectors along the lamellae as shown by the LA-ICP-MS map for W (Fig. 4c, d). There are also various overprinting aspects marked by W depletion, either along grain boundaries (as in Fig. 4d) or within brecciation domains in other samples.

The existing trace element dataset for magnetite is small and will not be discussed here; only that for hematite is presented. Martite, representing BIF mineralization, and the coarse lamellar hematite within amphibole-magnetite assemblages show distinct differences (Fig. 5).

**Figure 5.** Binary plots of As vs. Sb (top left), Ni vs. Co (top right), U vs. W (lower left) and Sn vs. W (lower right) showing discriminant fields of hematite in Island Dam. CG-Hm - coarse-grained hematite.

Chalcophile elements, As and Sb, (average 39 and 9 ppm, respectively) and transition metals such as Ni, Co and Mn, are higher (tens of ppm) in martite than in coarse-grained hematite. Uranium concentrations in martite average 6 ppm. In contrast, coarse-grained hematite contains higher concentrations of high-field strength elements (HFSE), such as Sc and Nb, than martite. Most interestingly, coarse-grained hematite features a high Sn content (average 240 ppm), and still higher (several thousands of ppm) concentrations of W. In addition to its enrichment in hematite, W is also present in zoned rutile and as inclusions of scheelite, and sometimes in hematite. Martite contains higher ΣREE and Y (ΣREY) than coarse-grained hematite (means 2.6 and 0.38 ppm, respectively). Chondrite-normalized REY fractionation patterns for distinct hematite textures (Fig. 6) also differ. Martite is enriched in LREE relative to HREE whereas coarse-
grained hematite displays a relatively flat trend.

Figure 6. Chondrite-normalized REY fractionation trends of the two textural types of hematite as marked.

5 Discussion and implications

The distinct textural and compositional character of iron oxide populations suggests at least two generations of Fe-mineralization in the Island Dam area. The relative enrichment in transitional metals, chalcophile elements, U and $\Sigma$REY in the BIF lithologies, characterized by a martite texture, is most likely attributable to superimposed fluid-rock interaction from sedimentary deposition to supergene enrichment followed by interaction with hydrothermal fluids (IOCG event at ~1.6 Ga), a scenario comparable to that suggested by Ciobanu et al. (2015) for the deposit margins at Olympic Dam. In contrast, the younger skarn lithologies represented by the coarse-grained hematite are rich in HFSE and granitophile group elements and can be directly related to hydrothermal fluids affiliated with Hiltaba magmatism. The W-Sn-rich signatures are attributable to the major 1.6 Ga IOCG event since such signatures are recognized in most deposits and prospects across the region, either in iron oxides (Olympic Dam, Prominent Hill), or in garnet skarns when suitable protoliths are present (Hillside and Punt Hill).

In contrast to other, potentially analogous terranes, such as the Great Bear Region, where alteration sequences can be directly mapped over large distances (Corriveau et al., 2016), at Island Dam, and in general in the Olympic Cu-Au province, this is not the case. Because of the cover, geological interpretation is almost entirely dependent on available drillcores. Moreover, the present work at Island Dam is carried on drillholes adjacent to the Andamooka fault system, likely with a multiple reactivation history.

Attempts to date the two hematite types from Island Dam via LA-ICP-MS using GJ-1 zircon as primary standard gave an indication of two age groups: (i) older than 1.6 (WG for BIFs); and (ii) ~1.6 Ga or younger (~1.2 Ga) for coarse-grained hematite. These data show, however, large errors either due to the high common Pb, or the low-U concentration. Future work targets alternative dating methods such as (U-Th)/He dating of hematite.

The distinct martite signatures presented here are inferred to represent pre-skarn mineralization, as they lack HFSE and W + Sn element signatures of the coarse-grained, skarn-type hematite. This suggests that iron oxides retained primary signatures despite overprinting. The capacity to retain primary signatures shows the potential for iron oxides to not only distinguish protolith from alteration products, but also trace hydrothermal processes. If BIFs are found as protoliths in terranes where IOCGs also occur, then geochemical signatures should still be recognizable when, the textures, of the sedimentary protoliths are retained.

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Trace element composition of iron oxide ores from the El Laco magnetite-apatite deposit, northern Chile

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Abstract. The trace element geochemistry of six representative types of iron oxide mineralization from the El Laco magnetite-apatite deposit, located in northern Chile, are compared to each other and to magnetite from the unaltered host rock andesite. Two groups of results correspond to the two types of magnetite that formed with relatively constant Ti contents, and successive depletion of other minor and trace elements. These two types likely correspond to two separate stages of magnetite formation; e.g., magmatic and hydrothermal crystallization. Dominant unzoned and monotonous, relatively Ti-rich, magnetite is interpreted as magmatic while only the magnetite coating vesicle pipes as sub- to euhedral crystals and showing fine-scale zoning is interpreted as precipitated directly from the exsolving hydrothermal fluids.

1 Introduction

The El Laco volcano is a unique magnetite-apatite deposit located in the Central Volcanic Zone, in the Atacama Desert region of northern Chile. The host rocks for the iron oxide ore orebodies are calc-alkaline andesite flows and related pyroclastic rocks with K-Ar ages from 5.3 +/-1.9 Ma to 1.6 +/-0.5 Ma (Naranjo et al. 2010).

Iron oxide mineralization occurs predominantly as stratabound lenses with massive vesicular and friable structures that have been interpreted as lava flows (Henríquez and Martin 1978; Nyström and Henríquez 1994; Naslund et al. 2002; Nyström et al. 2016; Tornos et al. 2016). The main ore mineral is magnetite; however, it is commonly overprinted by late-stage hematite.

Genesis of this deposit has been widely debated by many authors. Crystallization from Fe-rich melts and emplaced at different depths or erupted at the surface (e.g., Henríquez and Martin 1978; Nyström and Henríquez 1994; Naslund et al. 2002; Nyström et al. 2008). Alternatively, replacement of the host rocks by iron-rich hydrothermal fluids was proposed (e.g., Sillitoe and Burrows 2002; Dare et al. 2015). Tornos et al. (2016) suggested that this crystallization took place with exsolution of large amounts of magmatic-hydrothermal fluids.

Recently, a magmatic-hydrothermal genesis has been proposed for the nearby Los Colorados mine, in which an early generation of individual phenocrysts of magnetite was separated and floated from a crystallizing andesite melt and was later overgrown by hydrothermal magnetite, giving rise to grains with an internal magmatic core and an hydrothermal rim (e.g., Knipping et al. 2015).

The main objective of this study is to investigate the trace element geochemistry of the different ore types at El Laco and track the existence of zoning that could help to elucidate its origin.

2 Samples and methodology

2.1 Iron oxide ore samples

The following six types of iron oxide mineralization were identified and collected in the southern part of the deposit (e.g., Laco Sur):

Vesicular magnetite is the typical facies of the stratabound magnetite bodies and shows different types of porosity. The magnetite occurs as subhedral crystals that often contain minor hematite veinlets and in some cases fractures that are filled with Fe phosphates and concentric globules that are a mixture of siderite, Fe phosphate, and Fe oxides.

Contact between magnetite dyke and andesite host rock consists of small euhedral magnetite crystals that commonly contain tiny hematite veinlets. Hematite and a Fe phosphate mineral occur as overgrowths on the magnetite crystals or in fractures within the magnetite crystals.

Magnetite tubes have rounded concentric degassing structures with euhedral magnetite crystals (up to 1 cm) growing into the void space in subvertical vesicle pipes. The sample selected was cut from a cross-section of a hand sample in a perpendicular orientation to the lava tube.

Pyroclastic ore is a very fine grained generally unconsolidated mineralization type composed of anhedral magnetite with rare hematite veinlets that is thought to represent ejected lapilli (Nyström et al. 2016).

Diatreme magnetite consists of euhedral or subhedral magnetite crystals cementing a breccia. It is intergrown with hematite in irregular aggregates and elongated crystals.

Elongate hematite ore has crystals that are up to 10 cm in length. The crystals investigated were perpendicular to the length, and no signs of earlier replaced magnetite were recognized.
We have compared the trace element geochemistry of magnetite from the six types of mineralization above and magnetite from the host andesite at the same locality that was that previously reported by Broughm et al. (2017). The magnetite from the host andesite is very different to that of the ore mineralization. It has relatively high Ti-contents and reveals ilmenite exsolution lamellae that were not identified in any of the samples from the present study.

2.2 Analytical methods

Polished 25 mm diameter epoxy mounts were investigated using reflected light microscopy to identify magnetite and hematite. BSE images documented internal zoning in some samples. EPMA-WDS analyses were done to obtain the Fe content in selected magnetite crystals, which was used as the internal standard for data reduction for trace elements by LA-ICPMS. X-ray maps were done on selected magnetite grains from each of the type of ore investigated for Al, Si, Ca, Mg, and Ti.

Electron microprobe analyses for Fe and Ti and X-ray maps were done using a JEOL JXA 8230 SuperProbe EPMA at Memorial University of Newfoundland. The following conditions were used: accelerating voltage of 15 kV, sample current of 100 nA, a beam diameter of 1μm, and peak and background times of 40 and 20 ms, respectively. Natural magnetite and kaersutite were used as standards for Fe and Ti, respectively.

The X-ray maps were acquired using 15 kV, 250 nA, and 200 msec acquisition times. The step size used varied depending on the size of the magnetite crystals being mapped.

The LA-ICPMS analyses were done at the Micro Analysis Facility – Bruneau Innovation Centre (MAF-IIC) at Memorial University using a Finnigan Element XR high-resolution double focusing magnetic sector inductively coupled plasma mass spectrometer (HR-ICPMS), coupled to a GeoLas 193 nm Excimer laser system. A laser energy density 4 J/cm² was applied with a pulse frequency of 5 Hz. The background measured was about 30 s, followed by 50 s of laser ablation using a laser spot diameter of 30 μm. The primary standard used was NIST-610 and the secondary standard used was USGS BCR-2G. Data reduction was done using the Iolite software program (Paton et al. 2011).

3 Results

Aluminium, Mg, and Si, occur in relatively high concentrations, and for most of the samples are minor elements. Titanium, V, Ni, and Co are the most abundant trace elements. Chromium is below the minimum detection limit for most of the analyses, so is not considered further.

All of the results obtained can be divided into two groups depending on the Ti content. The first group includes the diatreme magnetite and the magnetite from the contact between the magnetite dyke. The second group includes the pyroclastic magnetite, magnetite from the magnetite tube, and the vesicular magnetite. The elongate hematite sample has similar trace element chemistry to the second group, however, is significantly depleted in most of the trace elements measured.

Most of the samples studied are chemically homogeneous and the trace elements do not reveal appreciable zoning. However, BSE imaging reveals that chemical growth zoning is obvious in the magnetite crystals lining the vesicle pipes (Fig. 1).

The Ti and V concentrations in the internal zones (with numerous diopside inclusions) are similar in composition to the diatreme magnetite, and magnetite from contact with andesite samples, whereas the most external zones have compositions close to that of the vesicular and pyroclastic magnetite.

Although, the P content is generally uniform in all of the samples analyzed, it is worth noting that in two samples (e.g., the contact with the andesite host and the vesicular magnetite) Fe-phosphate minerals occur as veinlets or along grain boundaries and is evidence for late precipitation of P and Fe-bearing minerals (Fig. 2).

Figure 1. Back-scattered electron image and X-ray maps of euhedral magnetite crystal (mt) growing in the internal part of the vesicle pipes. Magnetite in the inner zone hosts numerous pyroxene (px) inclusions.

On the binary plots (Fig. 3) the two groups described above plot in different fields. Hematite veinlets present in some spots analyzed do not influence the magnetite composition and do not stand out from the other analyses done on this sample.

In the plots of Ti vs V (Fig. 3 A), the analyses done on
the diatreme magnetite and magnetite from the contact with andesite, can be separated from the rest of the results at the level above 100 µg/g Ti. These points also plot in a separate area on the V/Ti vs Ni/Ti (Fig. 3B) diagram. Magnetite in the host rock andesite is enriched in Ti, however, the enrichment is caused by the ablation of ilmenite lamellae (that could not be avoided during the LA-ICPMS analyses), and not by Ti substituting for Fe in the magnetite. The sum of the \( \Sigma \text{REE} \) content differs by a wide range (e.g., 0.05 up to almost 2,700 µg/g, that could be related to nanoinclusions). The \( \Sigma \text{REE} \) content is independent of the type of magnetite analyzed (Fig. 3C).

Ternary plots reveal two groups of magnetite in terms of the Ti contents. Two separate trends are clearly visible for some minor elements, such as Ca, Al, Mg and Si (Fig. 4A). The Ti-V-Fe plot shows that some of the magnetite of the vesicle pipes (from the inner pyroxene-rich layer) tracks the same trend as the diatreme magnetite and magnetite from the contact with the andesite host rock.

4 Magmatic or hydrothermal origin?

Among the ore samples studied there are no magnetite grains with high Ti contents that have been proposed as indicative of magmatic magnetite (e.g., Dare et al. 2014).

The magnetite also does not show cores that could resemble magnetite of the host andesite rimmed by low Ti magnetite; thus, there are no evidences that the flotation model proposed by Knipping et al. (2015) operated at El Laco.

The monotonous chemical composition of magnetite suggests a common origin for all the types of magnetite, except for that lining the tubes. The trace element geochemistry alone does not help to discriminate between magnetite precipitated from an iron-rich melt or from cooling aqueous fluids. However, geological and geochemical considerations (see Naslund et al. 2002 and Tornos et al. 2016) suggest that the bulk of the magnetite has a magmatic origin and only that infilling the vesicle pipes could be of hydrothermal origin.

Figure 2. Back-scattered electron image and X-ray maps of magnetite (mt) crystals from the contact with andesite. Fractures are filled with Fe-rich phosphate.

Figure 3. Binary plots showing composition of various magnetite types. a V vs Ti, b V/Ti vs Ni/Ti, c Ti vs \( \Sigma \text{REE} \). Broughm et al. 2017 did not measure the \( \Sigma \text{REE} \) content.
Figure 4. Tertiary plots showing composition of various magnetite types. a Ti vs Ca vs Fe, b Ti vs V vs Fe, c Ti vs ΣREE vs Fe. Dashed lines suggest possible substitution trends in two types of magnetite. Legend to symbols is the same as in Figure 3.

There are multiple lines of evidence for the presence of low Ti magnetite in igneous rocks (occurring as tiny micro-inclusion within plagioclase and pyroxene phenocrysts and daughter crystals in melt inclusions) and related mineralization (see Velasco et al. 2016). The evolution from magmatic Ti-rich magnetite to magmatic Ti-poor magnetite is not always due to cooling and probably is due to partitioning of Ti between aqueous fluids, melts and minerals, or simply to a gradual decrease of Ti during the crystallization in a limited Ti reservoir as is suggested by the data; in fact, intrusive magnetite has higher Ti contents than their extrusive counterparts.

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Comparisons on alteration, mineralization and fluid evolution between the Qiaoxiahala and the Laoshankou Fe-Cu-Au deposits, Chinese Altay, NW China

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Abstract. The Qiaoxiahala and the Laoshankou deposits are two important Fe-Cu (-Au) deposits in the northern margin of East Junggar terrane and hosted by the Middle Devonian Beitashan Formation. Six hypogene hydrothermal stages are observed at Qiaoxiahala, and four stages are identified at Laoshankou. Field study and microscopic observation show that they have some similarities and differences in alteration and mineralization types, including 1) two-stage mineralization, magnetite formed prior to chalcopyrite; 2) chalcopyrite is associated with Au mineralization; 3) typical skarn alteration minerals are more widely present in Qiaoxiahala; 4) magnetite and chalcopyrite in Qiaoxiahala and Laoshankou have different related alteration minerals. Fluid inclusion studies including laser Raman spectroscopic analysis, integrated with sulfur, oxygen, hydrogen and carbon isotope analyses of minerals with well-defined paragenetic relationships, were used to clarify the fluid evolution in Qiaoxiahala and Laoshankou: 1) various sources of ore-fluids, especially external fluids (e.g., seawater, formation water and meteoric water) were involved; 2) an external fluid, probably the Early Carboniferous seawater exchanging with organic-rich host rocks, added into the main magnetite mineralization stage; 3) fluid in pyrite-chalcopyrite mineralization stage has higher δ^{18}O-water and more variable δD-water in Qiaoxiahala, indicating more exchanges with Beitashan Formation organic-rich wallrocks.

2 Alteration and mineralization

Six hypogene hydrothermal stages are observed at Qiaoxiahala (Fig. 2a), include early skarn (Stage Q-I), late skarn (Stage Q-II), magnetite mineralization (Stage Q-III), magnetite-pyrite mineralization (Stage Q-IV), chalcopyrite mineralization (Stage Q-V) and late veins (Stage Q-VI). These six stages represent three major mineralization events, as represented by the Stage Q-III magnetite- epidote-K-feldspar-quartz-calcite, Stage Q-IV magnetite- pyrite-garnet-quartz-calcite and Stage Q-V chalcopyrite- chlorite assemblages. Four hypogene hydrothermal stages are identified at Laoshankou (Fig. 2b), including Ca-silicate alteration (Stage L-I), amphibole-epidote-magnetite stage (Stage L-II), pyrite- chalcopyrite stage (Stage L-III) and late veins (Stage L-IV), in which two major mineralization events are represented by stage L-II- B magnetite-epidote-amphibole and stage L-III-B chalcopyrite-amphibole-chlorite.
Comparisons of alteration and mineralization between these two deposits show that: 1) two-stage mineralization, magnetite formed prior to chalcopyrite in both deposits; 2) chalcopyrite is associated with Au mineralization in both deposits; 3) typical skarn alteration minerals are more widely present in Qiaoxiahala; 4) magnetite in Qiaoxiahala relates to epidote, K-feldspar, quartz and calcite, but in Laoshankou magnetite only relates to epidote; 5) chalcopyrite in Qiaoxiahala is only associated with chlorite, without late-stage amphibole, which exists in Laoshankou.

3 Fluid evolution

Fluid inclusion studies including laser Raman spectroscopic analysis, integrated with sulfur, oxygen, hydrogen and carbon isotope analyses of minerals with well-defined paragenetic relationships, were used to document the fluid evolution of the two deposits.

At Qiaoxiahala (Fig. 3a), the stage Q-I prograde skarn alteration formed by high temperature (~700°C) magmatic fluids with \( \delta^{18}O_{\text{water}} \) values of 8.0‰ – 9.2‰. The stage Q-III magnetite formed at high temperature (~350°C), medium-low salinity, Mg-Fe-rich fluid, which is probably derived from the Early Carboniferous seawater (Veizer et al. 1999) exchanging with the Beitashan Formation organic-rich limestone or tuff. This is supported by the common occurrence of \( \text{C}_4\text{H}_6 \) and \( \text{CH}_4 \) vapor phase in fluid inclusions and high \( \delta^{18}O_{\text{water}} \) (9.7‰ – 11.2‰) and \( \delta^{18}D_{\text{water}} \) (28.7‰ – -24.6‰) values. The stage Q-IV magnetite-pyrite mineralization and stage Q-V chalcopyrite mineralization were interpreted to have formed by the addition of medium temperature, low-medium salinity and Ca-rich organic-rich sedimentary formation water. This is supported by decreasing \( \delta^{18}O_{\text{water}} \) (-141‰ – -92‰), increasing \( \delta^{18}D_{\text{water}} \) (8.9‰ – 11.1‰; 7.2‰), negative \( \delta^{34}S_{\text{fluid}} \) (-1.7‰ – -0.2‰; -4.2‰) and more vapor phases of \( \text{SO}_2 \), \( \text{C}_2\text{H}_2 \) and \( \text{CH}_4 \) in fluid inclusions. The large decrease of \( \delta^{18}O_{\text{water}} \) and unaltered \( \delta^{18}D_{\text{water}} \) values for Stage Q-VI indicate a large input of meteoric water.

At Laoshankou (Fig. 3b), the stage L-I Ca-silicate alteration was inferred to have crystallized from a ~590°C magmatic fluids with \( \delta^{18}O_{\text{water}} \) values of 9.2‰ to 9.7‰. The stage L-II-B magnetite-epidote-amphibole assemblage was subsequently precipitated from ~530°C mixing fluids of the high temperature magmatic fluid and the seawater, which was modified through reaction with the host rocks with \( \delta^{18}O_{\text{water}} \) values of 9.5‰ – 10.6‰ and \( \delta^{18}D_{\text{water}} \) values of -25.4‰ – -23.7‰. The noneconomic stage L-III-A pyrite-epidote-quartz-garnet assemblage was deposited at ~420°C from fluids with \( \delta^{34}S_{\text{fluid}} \) of -3.7‰ – -0.5‰ and \( \delta^{18}O_{\text{water}} \) values of 7.9‰ – 8.9‰. Lower temperature and organic components may record the involvement of meteoric water modified with organic matter in the host strata. Two groups of fluids were possibly involved in the Cu mineralization stage (Stage L-III-B), including those dominated by meteoric water (medium Th, low salinity, Na-rich) and Ca-rich formation water (medium Th, medium salinity, Ca/Fe-Mg-rich), with \( \delta^{34}S_{\text{fluid}} \) value of -2.6‰, \( \delta^{18}O_{\text{water}} \) values of 5.8‰ to 6.0‰, \( \delta^{18}C_{\text{water}} \) values of -3.3‰ to -3.1‰ and \( \delta^{18}D_{\text{water}} \) values of -110‰ to -94‰. During the end of fluid evolution, the amount of meteoric water continued to contribute to the system at low-temperature, low-salinity, Na-rich fluids without ore precipitation.

Comparisons on the fluid evolution between the two deposits indicate that: 1) various sources of ore-fluids, especially external fluids (e.g., seawater, formation water and meteoric water) were involved in both deposits; 2) an external fluid, probably the Early Carboniferous seawater exchanging with organic-rich host rocks, added into the main magnetite mineralization stage in both deposits; 3) fluid in pyrite-chalcopyrite mineralization stage has higher \( \delta^{18}O_{\text{water}} \) and more variable \( \delta^{18}D_{\text{water}} \) in Qiaoxiahala, indicating more exchanges with Beitashan Formation organic-rich wall-rocks.

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**Figure 1.** Simplified tectonic division of the CAOB (a) and Chinese Altay-East Junggar (b); (c) Regional geological and metallogenic map of the northeastern Junggar terrane.
Figure 2. Alteration and mineralization paragenesis: a Qiaoxiahala and b Laoshankou deposits.

Figure 3. Calculated $\delta D_{\text{water}}$ and $\delta^{18}O_{\text{water}}$ values of fluids responsible for alteration and mineralization at the Qiaoxiahala a and the Laoshankou b deposits. Fields for primary magmatic water are from Taylor (1997); organic water are from Rotherham et al. (1998); formation water derived from meteoric water are from Clayton et al. (1966) and Kharaka and Hanor (2003).
Multiple origins of iron oxides in regional rhyolites and the Pea Ridge IOA-REE deposit, SE Missouri, USA

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Abstract. We compared the paragenesis, textures, and chemical compositions of magnetite and hematite in host and regional rhyolites across the St. Francois Mountains terrane, southeastern Missouri, to those in mineralized rocks in order to understand the origin of iron oxides in the Pea Ridge IOA-REE deposit. Trace element compositions, determined by EMP and LA-ICP-MS, were used to discriminate between igneous and hydrothermal sources.

The igneous magnetite and ilmenite phenocrysts in the rhyolites were oxidized to form submicron-hematite ± rutile pseudomorphs and hematite laths during eruption. Hematite was partially recrystallized and coarsened by hydrothermal fluids. Hematite in host rhyolite at the Pea Ridge deposit was replaced and/or overgrown by hydrothermal magnetite during IOA mineralization and then replaced and/or overgrown by hydrothermal hematite during breccia pipe formation. Evidence for precipitation of igneous magnetite from an iron oxide melt or transport of microphenocrysts of igneous magnetite in an aqueous emulsion is lacking. The Pea Ridge deposit formed by magmatic-hydrothermal processes.

1 Introduction

The Mesoproterozoic St. Francois Mountains terrane of SE Missouri, USA, contains several iron-oxide-apatite (IOA) ± rare earth element (REE) deposits for which a variety of genetic models have been proposed. Nold et al. (2013) suggest that magnetite crystallized from an immiscible iron-oxide-rich melt and was overgrown by hydrothermal magnetite. Childress et al. (2016) surmise that magnetite crystallized from a silicate melt and was overgrown by hydrothermal magnetite after transport to the site of ore formation in an aqueous emulsion (Knipping et al. 2015). Alternatively, the magnetite may have a magmatic-hydrothermal origin (Hofstra et al. 2016, and the references therein).

Textures, paragenetic relations, and trace element chemistry were used to distinguish magnetite and hematite of igneous and hydrothermal origin in the massive iron oxide deposit at Pea Ridge (Dupuis and Beaudoin 2011; Nadoll et al. 2014; Dare and Barnes 2015). Our results indicate that the iron oxides present in the rhyolite host rocks and Pea Ridge IOA deposit have multiple origins.

2 Geology

Compositionally, 1.5-1.3 Ga igneous rocks in the St. Francois Mountains terrane consist of subalkaline/ferroan rhyolite ignimbrites and flows underlain by coeval granite plutons. Regional rhyolites consist of porphyritic flow-banded and homogenous flows and flow-banded crystal-rich and crystal-poor tuffs. Some of the tuffs contain abundant lithic fragments and/or pumice. Volumetrically minor tholeiitic basaltic andesite and dacite are also present. Geologic relations suggest that all of these rocks formed in an intracratonic rift setting (Day et al. 2017, and du Bray E. (U.S. Geological Survey), unpublished data).

The Pea Ridge IOA deposit is hosted in high silica rhyolite tuff underlain by an inferred granitic pluton and is surrounded by a mafic to intermediate ring intrusion (Day et al. 2016). The northeast-striking, steeply dipping, tabular magnetite ore body is enveloped by magnetite-cemented, amphibole-rich, pseudo and heterolithic breccias that are surrounded and/or overprinted by silicified and potassically altered zones. On the northwest side of the deposit, a magnetite-rich zone is mantled and capped by a hematite-rich zone. REE-rich breccia pipes crosscut the NW side of the deposit (Seeger et al. 2001).

The rhyolites dip steeply and were termed “porphries” by miners, who designated units for the mine levels (in feet) where they were first encountered: 1975, 2275, 1825, and 1675 (Sidder et al. 1993). A black “porphyry” was also noted which appears to be a darker equivalent to the 1675 “porphyry.” The 1975 and 2275 “porphries” are the principal IOA deposit hosts. The 1975 and 1825 “porphries” seem to be less welded than the 2275 “porphyry.” The 1675 and black “porphries” are massive, crystal-rich rhyolites that lack pumice and may represent flows or hypabyssal intrusions.

3 Samples and methods

Regional rhyolite tuffs and flows were sampled in the Ironton (i.e., Shepherd Mountain, Cedar Hill, Pond Ridge, Crane-Lookout Tower, Grassy Mountain, Lake Killarney, and Royal Gorge) and Eminence areas (Upper and Lower Coot Mountains and Stegall Mountain). Some regional samples are more proximal to known iron mineralization than others. At Pea Ridge, samples were collected from each of the aforementioned alteration zones, breccia types, and rhyolite “porphries.”

Magnetite and hematite were analyzed using reflected light microscopy, Raman spectroscopy (Das and Hendry 2011; relative to U.S. Geological Survey reference materials), electron microprobe (EMPA), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS; Longerich et al. 1996). In reflected light, hematite is greyish-white, whereas magnetite is brownish-grey. Hematite typically has five distinct Raman peaks at:
4 Petrography of Fe-Oxide stages

In regional rhyolites, distal to iron mineralization and in the host rhyolites at Pea Ridge, three stages of Fe oxides are most prominent. Stage 1 consists of 100-500 µm, phenocrysts of tabular ilmenite and equant magnetite (± ilmenite lamellae; Fig. 1a) pseudomorphically replaced by stage 2 micron-sized, hematite and rutile, which often exhibit hatched patterns in ilmenite and triangular domains in magnetite (Fig. 1b, 1c, 1d). Finely zoned, subhedral to anhedral, 25-100 µm crystals of hematite and rutile also formed during stage 2. This hematite and rutile often form micron-sized lamellae/hatched patterns. Stage 2 hematite and rutile were recrystallized and/or overgrown by coarser grained stage 3 hematite that is rutile-poor (Fig. 1b, 1d). Recrystallized hematite often has void spaces ± rutile along pre-existing exsolution bands (Fig. 1c). Rare recrystallized magnetite is also present. Euhedral, 25-500 µm, laths and ‘spongy’, 2-20 µm, aggregates of hematite grew in open spaces during stage 3 (Fig. 1c).

In rhyolites proximal to iron mineralization at Pea Ridge, stage 1 is absent, and stage 2 and 3 are overprinted by up to three additional stages. Stage 2 and 3 hematite are overgrown by anhedral to subhedral, 25-250 µm, stage 4 magnetite with mineral inclusion-rich cores and inclusion-poor rims (Fig. 6d in Hofstra et al. 2016). Coarser-grained ≥500µm magnetite is present locally. Stage 4 magnetite is replaced by stage 5 hematite along grain boundaries and in the mineral inclusion-rich cores (Fig. 1e). Stage 6 consists of 25-500 µm sized laths of euhedral hematite that grew in open fractures and vugs (Fig. 1f) in the hematite zone and REE breccia pipes. Anhedral to subhedral hematite also replaces stage 4 magnetite grains and clasts. Some of the regional rhyolites proximal to other iron deposits also contain stage 4 magnetite and stage 5 hematite.

5 Chemistry results

Magnetite and hematite compositions are plotted on Al+Mn vs. Ti+V discrimination diagrams (Figs. 2, 3). Stage 1 magnetite phenocrysts from regional rhyolites plot in the magmatic Fe-Ti and V field (Fig. 2a; dark grey), which is consistent with an igneous origin.

Compositions of stage 2 hematite from the magnetite zone, adjacent host “porphyries” (i.e., 1975, 2275, and 1825), and the regional rhyolite tuffs and flows are similar to magnetite phenocrysts (Fig. 3a; light grey). Stage 2 hematite pseudomorphs after ilmenite contain variable Mn compositions and plot above and below data defined by stage 2 hematite pseudomorphs after magnetite (Fig. 3a). Stage 2 hematite compositions are consistent with formation by oxidation of magnetite and ilmenite phenocrysts during or soon after rhyolite eruption. Compositions of finely zoned hematite, stage 2, crystals
are also consistent with formation under magmatic conditions (Fig. 3b; light grey) and may represent vapor phase crystallization minerals.

Compositions of stage 3 hematite from the magnetite and hematite zones, host “porphyries” (i.e., 1975, 2275, and 1825), and certain rhyolite tuffs and flows typically extend from the magmatic field into the Porphyry, Kiruna, and IOCG fields (Fig. 3a; lime green). Similarly, compositions of stage 3 hematite pseudomorphs after magnetite and ilmenite form distinct clusters (i.e., Porphyry field and below the Kiruna and IOCG fields) while those of open space hematite crystals plot in either cluster (Fig. 3a, 3b). Stage 3 hematite seems to reflect hydrothermal processes associated with regional potassic alteration and/or early IOA alteration. Likewise, compositions of most stage 3 magnetite in the 1675 and black “porphyries” cluster in the magmatic field and some trend through the Kiruna field toward stage 4 magnetite compositions (Fig. 2a; lime green). This shift into the hydrothermal field may indicate that magnetite phenocrysts in these units were recrystallized.

Compositions of stage 4 magnetite from the magnetite, amphibole-rich, and hematite zones plot within or below the IOCG field (Fig. 2b; light blue). Magnetite that grew in open spaces (i.e., veins/breccia fill) contains slightly lower Mn concentrations than that replacing host rock silicate minerals. Although, magnetite grains are zoned with respect to mineral inclusion abundances, their chemical compositions are homogeneous. Compositions of stage 4 magnetite within the adjacent “porphyries” (i.e., 1675 and black) and regional rhyolite tuffs and flows broadly overlap with those of magnetite from Pea Ridge deposit. All of the Stage 4 magnetite is therefore interpreted as having a hydrothermal origin.

Compositions of stage 5 hematite from the hematite, magnetite, amphibole zones, and regional rhyolite flows contains low Ti, V, Al, and Mn concentrations and is coincident with the lower portions of the IOCG field and extends below both the Kiruna and IOCG fields (Fig. 3a, 3b; light red). Compositions of most stage 5 hematite overlap those of stage 4 hydrothermal magnetite and part of the stage 3 hematite field (Fig. 3a, 3b). Stage 5 hematite appears to have formed by oxidation of hydrothermal magnetite.

Stage 6 hematite from the REE-breccia pipe and hematite zone typically contains more Al than stage 5 hematite and plots in the upper part of the IOCG field (Fig. 3b; purple). The difference in composition suggests that the fluids responsible for REE-breccia pipe formation were distinct from those that formed the IOA deposit.

Stage 1 magnetite and Stage 2 hematite often contain detectable ± Sn, Ga, Nb, Zn, Sb, Pb, Ta, W, Zr, Mo, Ni, and Co, whereas many stage 3 hematite grains contain lower concentrations of these elements. Most of these elements are assumed to have been derived from the rhyolite host rocks. Stage 4 magnetite and Stage 5 hematite typically have the lowest concentrations of these elements, which is consistent for their iron being sourced from a subjacent intermediate to mafic intrusion. Compositions of stage 6 hematite related to the REE-breccia pipes is distinguished by detectable Sn, Ga, Zr, Sb, Mo, W, Nb, and ± Ni contents, possibly derived from a subjacent rhyolite intrusion.

6 Conclusions

The textures and compositions of iron oxides in the regional rhyolites suggest that igneous magnetite and
ilmenite phenocrysts in the representative magmas were oxidized to form submicron-hematite ± rutile pseudomorphs and finely zoned hematite laths that formed during eruption and lithification. This hematite was partially recrystallized and coarsened by hydrothermal fluids that infiltrated regional rhyolites.

In the Pea Ridge IOA-REE deposit, hematite in the rhyolite host was replaced and overgrown by hydrothermal magnetite during the IOA mineralization and in turn replaced and overgrown by hydrothermal hematite during formation of the hematite zone and REE breccia pipes.

This study suggests that Stage 2 or 3 hematite has been mistaken (e.g., Mercer et al. 2015; Childress et al. 2016) for igneous magnetite, which would invalidate some of the interpretations presented therein. Importantly, evidence for precipitation of igneous magnetite from an iron oxide melt or transport of micro-phenocrysts of igneous magnetite in an aqueous emulsion is absent. Our results support a magmatic-hydrothermal origin for the Pea Ridge IOA-REE deposit.

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The IOA type occurrences of the Neoproterozoic Santa Quiteria magmatic arc, Borborema Province, northeast Brazil

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Abstract. IOA (iron oxide-apatite) and IOCG (iron oxide-copper-gold) deposits are known in all continents. In Brazil, records of these deposits, particularly of the IOCG-type, have been restricted to the Carajás Mineral Province, while the IOA types were unknown. However, important occurrences of Fe-P (±Cu) have also been identified on the western edge of the Neoproterozoic Santa Quiteria magmatic arc. These are hosted by metadiorites, a bimodal metavolcanic sequence and metasedimentary rocks crosscut by post-collisional biotite granite intrusions. Five Fe-P (±Cu) occurrences are recognized: (1) banded or stratabound magnetite-apatite-monazite; (2) massive magnetite-(specular hematite)-apatite; (3) disseminated and vein-type magnetite-apatite in metadiorite; (4) massive hematite bodies; and (5) skarn-type with magnetite, garnet, clinopyroxene and amphibole. These occurrences also contain mineral assemblages formed by sodic-calcic, potassic and propylitic alteration. Mineral chemistry data show that: (i) except for vein types, apatite in all the mineralization styles is F rich (2.4 ≤ F ≤ 4.4%), low in Cl (<0.5%); and (ii) magnetite contains different concentrations of Ti, V, Cr and Ni attributed to both igneous and hydrothermal environments. However, the low sulphide content and high concentration of apatite indicate that the investigated Fe-P (±Cu) occurrences are of the IOA type.

2 Iron oxide-apatite-(copper) mineralization

Five types of Fe-P-(Cu) occurrences have been described in the SQMA and in order of decreasing importance, they are as follows: (i) banded - stratabound Fe-P; (ii) massive magnetite-(specular hematite)-apatite; (iii) disseminated and vein magnetite-apatite in albitized metadiorite; (iv) massive hematite bodies; and (v) skarn-type. The banded - stratabound Fe-P occurrence is associated with amphibolite-metamorphosed bimodal (basalt- andesite-rhyolite) volcanic rocks. It presents a deformed banded structure, foliation trace oriented in the N-S direction, and intrafolial folds oriented along the same direction. It follows the contact zones in these rocks, along with sodic, chloritic, and less commonly potassic alteration. Mineral composition includes magnetite (50-70%), with or without ilmenite exsolution (Fig. 2a, b), apatite (<8%), monazite and subordinate copper sulphides (~2%). Magnetite with ilmenite exsolutions contains 84.1-95.1% FeO, 0.1-0.63% TiO2 and 0.04-0.23% V2O3, whereas the ilmenite exsolutions exhibit 19.4-78.7% FeO, 14.2-52.44% TiO2 and 0.23-0.46%V2O3. This suggests that magnetite was originally richer in titanium, which by oxy-exsolution processes evolved to intergrowths of pure magnetite and ilmenite, a characteristic feature of magmatic magnetite (e.g., Grant 1984). Crosscutting centimetre to metre-wide biotite granite dykes and apophyses cause significant textural modifications to this occurrence type, with formation of
biotite and precipitation of chalcopyrite and bornite, now partially altered to limonite and / or goethite (~ 5%) and malachite (~1%) (Fig. 2c,d).

The fine-grained massive magnetite-(specular hematite)-apatite type is hosted in paragneisses but occurs as loose centimetre to meter blocks in the field (Fig. 2e). It commonly shows cavities that resemble volatile escape vesicles, a primary feature of volcanic activity (Fig. 2f). It consists essentially of magnetite (~ 60%), apatite (≤30%) and accessory clinopyroxene. Blocks containing specular hematite also contain significant concentrations of actinolite, epidote, and quartz as products of hydrothermal alteration.

The disseminated and vein-type magnetite is hosted essentially by albitized metadiorite. It is composed of albite plagioclase, clinopyroxene, actinolite, and disseminated and agglomerate magnetite (annealing texture).

The massive hematite occurrence type outcrops poorly and is generally associated to topographic highs in the field. It consists predominantly of rhombohedral hematite (~ 95%), of polygonal granular texture, with subordinate magnetite (~ 2%), apatite and gorceixite (BaAl₃(PO₄)(PO₃OH)(OH)₆) as accessories (Fig. 2g). The magnetite is mainly xenocrystal (Fig. 2h).

The skarns occur as loose blocks next to the metaleucodiorite (exoskarns). It contains magnetite (40%) and garnet (35%), with subordinate clinopyroxene, quartz, amphibole, epidote and chlorite, the latter three attributed to retrograde alteration.

3 Chemical mineral compositions

Apatite from the vein magnetite occurrence type is fluorine-poor (F≤0.33%) and Cl-rich (1.92-2.89%), and classified as chloroapatite. Apatite in the other occurrences tends to be F-rich (2.4 ≤F≤ 4.4%) and contain low Cl concentrations (≤0.5%), typical of fluorapatite (Figs. 3 and 4). Sr, Y and Mn in apatite show variable concentrations in all the different occurrence types (Fig. 5). Taking into account the Sr-Y correlation, most of the apatite from the stratabound type fall within the field of the Kiruna deposit type, while apatite from the other occurrences is distributed between the fields of granitoids and alkaline rocks (Fig. 5).

Al + Mn vs Ti + V concentrations have been used to compare magnetite from the different investigated Fe oxide-P occurrence types and magnetite from other mineral systems of hydrothermal and magmatic origins, including skarns, IOCG, Kiruna and Porphyry Cu deposits (Fig. 6) (Dupuis and Beaudoin 2011; Nadoll et al. 2014; Dare et al. 2015; Knipping et al. 2015).

Figure 2. Sample photos and photomicrographs of the different occurrences: a Stratabound type showing finely deformed banded structure marked by b the alternation of crystals of magnetite and apatite. c Biotite granite cutting the occurrence of stratabound type. The contact is marked by potassic alteration with coarse-grained biotite and d chalcopyrite, bornite and microfractures filled by chalcocite. e Massive magnetite type with apatite (brown) and clinopyroxene (blue-green) aggregates. f Massive magnetite with volatile escape vesicles. g Geminated hematite with polygonal texture. h Martitized magnetite xenocrystal. Note that the magnetite is microfractured and martitized and its fractures do not propagate through the geminated hematite.
conditions of crystallization. The magnetite disseminated in the metadiorite is attributed to magmatic crystallization, whereas vein magnetite may have precipitated from high-temperature hydrothermal fluids. The stratabound type magnetite has similar Ti + V values as that of the metavolcanic host rocks (metabasalt-andesitic). It is also richer in these elements than the magnetite xenocrysts and host rhombohedral hematite ore. In addition the magnetite xenocrysts hosted in the rhombohedral hematite ore present practically the same Ti + V values as the host hematite, which may indicate that they were submitted to common formation processes.

Finally, the disseminated magnetite of the metadiorite, the metavolcanic host rock of the stratabound ore, and part of the stratabound ore are concentrated in the Porphyry Cu and Kiruna compositional fields (Fig. 6). The magnetite of the veins, skarns, magnetite xenocrysts and rhombohedral hematite record compositions within the metasomatized rocks field, and the exsolutions of ilmenite, as expected, plots in the field of magmatic rocks.

In this diagram, vein magnetite is more enriched in Al + Mn and depleted in Ti + V than magnetite in the host metadiorite, which suggests different origins or different conditions of crystallization. The magnetite disseminated in the metadiorite is attributed to magmatic crystallization, whereas vein magnetite may have precipitated from high-temperature hydrothermal fluids. The stratabound type magnetite has similar Ti + V values as that of the metavolcanic host rocks (metabasalt-andesitic). It is also richer in these elements than the magnetite xenocrysts and host rhombohedral hematite ore. In addition the magnetite xenocrysts hosted in the rhombohedral hematite ore present practically the same Ti + V values as the host hematite, which may indicate that they were submitted to common formation processes.

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4 Preliminary conclusions

The styles of mineralization combined with petrographic, mineralogical and mineral chemistry data suggest that the five Fe-P-(Cu) occurrences defined in the SQMA are the product of several different ore-forming episodes.

The stratabound and metadiorite magnetite exhibits magmatic affiliation, whereas magnetite grains from the other occurrences are associated with fluids of magmatic hydrothermal origin, probably with crustal contamination. The stratabound occurrence type is deformed and appears to represent the oldest event. Its association with a deformed and partially modified metabasalt-andesitic and metarhyolite rocks suggests a close relationship with this bimodal magmatism, indicating shallow crustal formation. This allows the
comparison to the stratiform or stratabound deposits of Kiruna (Sweden), El Laco (Chile) and Bafq (Iran). The copper sulphide mineralization is localized and seems to be genetically related to the biotite granite that crosscuts the stratabound ore, indicating a late process in relation to that ore.

The fine-grained massive magnetite-apatite type, with and without specular hematite, appear to develop at epizonal levels and form part of the same magnetite-apatite system that gave rise to the stratabound ore. In this case, one can treat it as a product of evolution of a continuum of the Fe-P system.

The disseminated and vein-type magnetite ores in metadiorite rocks have the same magmatic affiliation, but in different crystallization conditions. The first is igneous and the second is magmatic-hydrothermal in origin. The skarn occurrences develop in contact zones between metadiorite rocks and calc-silicate rocks.

The massive hematite ore, dominated by rhombohedral hematite with polygonal texture, remains of unknown origin, although this type of hematite in IOA and IOCG deposits has been treated in the literature as magmatic hematite (Nold et al. 2013, 2014). However, by the current level of knowledge, it can be assumed that the studied hematite ore is of magmatic-hydrothermal origin, and highlights another generation of iron ore within the local geological context. On the other hand, except for the iron deposits of Pilot Knob and Iron Mountain in Southeastern Missouri (USA) and Grängesberg in Sweden, examples of deposits containing rhombohedral hematite seem to be rare which makes this occurrence an exceptional case.

The characterization of IOA occurrences in the Santa Quiteria magmatic arc is of great importance, mainly because it is the first description of IOA deposits with Fe-Ap- (Cu) in the SQMA, northeast Brazil.

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IOCG Sin-Quyen deposit, LaoCai, N-Vietnam

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Abstract. The geology, mineralogy and geochemistry of the IOCG Sin-Quyen deposit are described in the paper. The combined mineralogical and geochemical studies constrain the stages of ore mineral crystallization, and establish the timing of uraninites. A special attention is paid to the allanite group of minerals which contain the bulk of the REE.

1 Introduction

The studied copper deposit is located in the Sin-Quyen district, province of Lao-Cai in North Vietnam. Exploitation, enrichment and smelting of the copper metal are active since 2006. During field work in 2014, 45 samples from the operating open pit and waste disposal were collected.

2 Geological setting

The IOCG Sin Quyen deposit is hosted by altered amphibolite and biotite gneiss located in the metamorphosed sedimentary rocks of the Proterozoic Sin Quyen Formation, which fills the wide Red River regional fault zone (Fig. 1). The deposit consists of dozen ore bodies forming lens of several tens of meters in width and a few hundred meters in length trending in the NW-SE direction (Fig. 2) (Ishihara et al. 2011). The deposit can be divided into two zones, the first consists of least-altered rocks and ores, the second of weathered rocks.

In the deposit massive skarn ores, disseminated and vein types of ore have been described. Based on local geology and ore mineralization and recognized processes, the deposit is classified as an IOCG type. The deposit was passed through a complicated multistage mineralogical composition. The mineralized zone is several meters up to 30 meters of wide, NW-SE trending and is dipping almost vertically. Verticality facilitated penetration of oxidizing surface waters in the ore body leading to an oxidation zone that reaches over 100 m in depth. Macroscopically visible oxidized minerals include malachite, azurite and Fe-hydroxides. Mineralogical and geochemical description of the deposit is based on 42 samples collected through the deposit section crossing the ore body and from the concentrates and wastes.

3 Mineralogy of the IOCG deposit

The bulk chemical analyses show a high concentration of copper (above 1 wt%), iron (above 40 wt%) and gold (2.36 ppm) in massive sulphide ore and elevated uranium (56 ppm). Concentration of copper in the waste ranges between 0.03 wt.% and 0.05 wt.%. The concentration of sulfur is also relatively high - 0.60-0.77 wt.%. The major minerals are chalcopyrite and magnetite, clinopyroxene, allanite, epidote, biotite, titanite and some quartz in hydrothermally altered sequence of the Sin Quyen Formation. Other ore minerals consist of pyrite, pyrrhotite, sphalerite, ilmenite, marcasite, tennantite, cubanite, arsenopyrite, galena, Bi-native, bismuthinite, electrum, native gold, and tellurides (Tab. 1). Microscopic studies of ore led to the identification of magnetite, ilmenite, pyrite, pyrrhotite, chalcopyrite, sphalerite, marcasite, tennantite, cubanite, arsenopyrite, galena, native bismuth, bismuthinite, and electrum and native gold. Small inclusions of gold (up to a few microns...
in size) occur in massive chalcopyrite. Thiosulphate replacing pyrrhotite and Fe-oxides have also been found in the dry waste samples. Thiosulphates are a result of pyrrhotite oxidation.

4 Measurements and results

Generally all collected samples are rich in rare earth elements (REE) and their concentration ranges from dozens of ppm to more than 5400 ppm, the average concentration of uranium and thorium amounts to 20.2 ppm (250 Bq/kg) and 17.9 ppm (72.6 Bq/kg) respectively (Nguyen et al. 2016). Uraninite crystals occur in the copper-massive iron ore samples. Uraninites are inhomogeneous in both optical properties and chemical composition (Fig.3). Inhomogeneity of uraninites is also confirmed by two different ages determined, using Jeol 8230 Super Probe. The uraninites with high REE content are older, and those with low REE content are much younger. Based on uraninites dating two stages of mineralization are proposed for this deposit. The major stage is related to the skarn-metasomatic alteration of the Cambrian age, the younger stage was associated with late Cretaceous-Paleocene (82-42 Ma) tectonic activity. Weathering was recognized as the final stage in evolution of the deposit. The absolute age of these uraninites was calculated as 458-522 Ma (500 Ma average, for n= 36 and σ = 33 Ma) and as 82-78 Ma.

Microscopic observation let to distinguish two different minerals from the allanite group (Fig. 4). Chemical composition of both varieties was described Nguyen et al. (2016). The bands at 1041, 1033, 958, 920, 907 and 876 are attributed to SiO2 stretching vibrations. The other bands are found over 750-350 cm\(^{-1}\) spectral range. These bands occur at 685, 650, 631, 610, 601, 586, 559, 509, 449, 425, 413, 382, and 375, cm\(^{-1}\) (Fig. 5), and are connected with siloxane bending modes. The Raman active bands appearing below 350 cm\(^{-1}\) regions, i.e. 310, 268, 219, 192, 126 cm\(^{-1}\) are described as lattice vibrations (López and Frost 2015).
The localization of bands attributed to SiO$_2$ stretching vibrations is shifted towards higher wave numbers for crystal point Viet-5-002. The main bands at this region occur at 1052, 1045, 971, 909, and 871 (Fig. 6). The bands coming from siloxane bending modes for Viet 5-002 crystal occur at 685, 597, 563, 455, 440, 432, 419, 383 and 351 cm$^{-1}$ (Fig. 6) and are also sifted towards higher wavenumbers than for Viet-5-001 crystal (Fig. 5). The position of these bands appears to vary depending on the type of cations in allanite-Ce structure. Distribution of major cations confirms position of both allanite faces (Fig. 8a, b, c, d). Based on mineralogical observations and absolute age dating, three mineral stages have been documented.
Two major are presented in Table 1. The third, last stage is composed of malachite, azurite, Fe-hydroxides and thiosulphates, and is developed in the oxidation zone. These minerals have been also recognized in the telling pond.

Table 1. Stages of mineral assemblage (partly after Ta Viet Dung et al. 1975 and McLean 2001).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Skarn-Metasomatic stage</th>
<th>Hydrothermal stage 82-42 Ma</th>
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<tbody>
<tr>
<td>Albite</td>
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<tr>
<td>Biotite</td>
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<td>Hedenbergite</td>
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<td>Hematite</td>
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<td>Quartz I</td>
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<td>Titanite</td>
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<td>Rutile</td>
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<td>Apatite</td>
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<td>Quartz II</td>
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<td>Cubanite</td>
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<td>Molybdenite</td>
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<td>Galena</td>
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<td>Native gold</td>
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<td>Bi-native</td>
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<tr>
<td>Bismuthinite</td>
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Tellurobismuthite  --

1) after Gaskov 2011; mineral in bold are described by the authors.

5 Conclusions

Three stages of ore mineralization have been documented in the deposit. Timing of two major stages was confirmed by absolute age determination using U–Pb–Th quantitative measurement. The skarn-metasomatic stage was developed in age range of 575-430 Ma, and the younger in the age range of 82-42 Ma. In the deposit two different minerals from the allanite group have been documented and contain different amounts of major ions like Ca, Al, Ce and La.

Acknowledgements

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Timing and tectonic setting of host rocks to the Malmberget AIO deposit, Sweden

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Abstract. Host felsic and intermediate meta-volcanic rocks to the Malmberget apatite iron ore (AIO) deposit have been investigated geochemically and geochronologically, the latter using the U-Pb method on a set of zircons. Results indicate emplacement age of 1.9 Ga for the felsic and intermediate volcanic rocks, potentially in an extensional environment. The zircon U-Pb radiometric ages are among the first conclusive ages with implicit constraint on the geological evolution of the northern Norrbotten ore district and Malmberget deposit.

1 Introduction

Malmberget, the world’s second largest underground apatite iron ore (AIO) operation, is located in the vicinity of the Gällivare town in the northern Norrbotten ore district, Sweden. The current annual production is 16 Mt of ore and reserves are estimated at >378 Mt of ore with 40% Fe (LKAB 2015).

Limited studies on the origin of the host rocks have been carried out (Martinsson et al. 2013 and references therein). Few attempts to constrain ages of the Malmberget host rocks returned partly inconclusive results with low precision (Sköld et al. 1988; Storey et al. 2007). This work presents conclusive U-Pb radiometric ages based on a larger set of zircons in addition to geochemical data fingerprinting the origin and tectonic setting of the Malmberget host rocks.

2 Geological background

Bedrock in the northern Norrbotten ore district is the result of complex geological events that include several plume-related rifting events of the Archean craton, and macro and micro-continent collision with intense crustal growth related to Proterozoic subduction events (Martinsson et al. 2016 and references therein). The remnant nuclei’s of the Archean craton constitute the lower-most part of the stratigraphy and is overlain unconformably by a Paleoproterozoic cover comprising Karelian (2.5 to 2.0 Ga) and Svecofennian (1.90 Ga) units (Martinsson 2004).

Active subduction processes at 1.90 Ga along the SW border of the Archean craton resulted in the generation of calc-alkaline volcanic successions such as the Porphyrite Group (1.91-1.88 Ga) and co-magmatic Haparanda Suite (1.89-1.86 Ga, Bergman et al. 2001; Martinsson 2004). The compressional regime (subduction) was shortly followed by an extensional environment leading to the generation of more alkaline magmatism (Martinsson 2004). The extensional environment gave rise to a generation of intrusions belonging to the Perthite Monzonite Suite (PMS, 1.88-1.86 Ga) and comagmatic volcanic rocks referred to as the Kiirunavaara Group (1.91-1.88 Ga, Bergman et al. 2001; Martinsson 2004; Westhues et al. 2016). These rocks were later intruded by Lina-type granitoids covering a large part of northern Norrbotten (Bergman et al. 2001, Fig. 1).

Volcanic, volcaniclastic and volcano-sedimentary rocks belonging to the Porphyrite Group are found along the Nautanan deformation zone (NDZ), in the Aitik and Liikavaraa deposits, and are described in detail by several authors (Lynch et al. 2015 and references therein, Fig. 1). Rocks belonging to the Kiirunavaara Group host the Malmberget AIO deposit (Martinsson et al. 2013, Fig. 1). Host rocks to the Malmberget deposit have been previously described by Martinsson et al. (2013) as felsic metavolcanic rocks of dacitic to rhyolitic in composition and mafic volcanic rocks of basaltic-andesitic, and andesitic-trachyandesitic in composition. These rocks are intruded by granitic bodies in addition to felsic and mafic dikes of several generations (Martinsson et al. 2013). These rocks were later deformed and metamorphosed up to amphibolite facies conditions (Bergman et al. 2001). Intense hydrothermal alteration is common within the Gällivare area. An assemblage comprising amphibole-garnet-biotite represents peak metamorphism whereas quartz-sericite-epidote-chlorite-calcite represents retrograde conditions. Scapolite, sericite, muscovite, tourmaline, apatite, K-feldspar, epidote, and magnetite are interpreted as magmatic-hydrothermal alteration (Lynch et al. 2015 and references therein).

3 Methods

Samples were collected during a field campaign in 2014 both underground and from outcrops. Fresh, unaltered samples were targeted. Polished thin sections were prepared and a detailed examination was performed using conventional optical microscopy. Major and trace elements were analyzed by ALS Chemex laboratories, Canada. The zircon extraction and analytical procedure is similar to the procedure described in Sarlus (2016).

4 Results

A brief description of samples from the felsic volcanic and basaltic-andesitic units subjected to radiometric dating and geochemical studies is provided below.

4.1 Petrography
The felsic volcanic rock has a reddish pink to pinkish gray color, a fine grain size, and an equigranular texture. The mineral assemblage comprises quartz, two generations of plagioclase, K-feldspar, biotite and muscovite with accessory titanite, zircons, and opaque phases. Zircon content is moderate to abundant within this rock. Zircon crystals are pinkish to clear transparent, mostly euhedral but few subhedral grains are observed.

The basaltic-andesitic unit has a dark gray color and a fine to medium grain size mainly composed of plagioclase and ferromagnesian silicate minerals (hornblende and biotite). Zircon content is low and the few crystals found exhibit anhedral shapes with inclusions.

4.2 Geochemistry

Rocks of the Malmberget AIO deposit have been subjected to several types of alterations and regional scale IOCG-overprint (Martinsson et al. 2013, Bauer et al. unpublished data). Using the IOCG alteration indices and discrimination diagram of Montreuil et al. (2013, Fig. 2a) samples from felsic volcanic units show weak signs of alteration apart from a few samples showing Na-enrichment (6.0 wt%) and K-depletion. Two samples from the andesitic unit show weak Na-enrichment while one sample is strongly enriched in Fe (19 wt%) in addition to Na and depleted in Si (51wt%; Fig. 2a).

Samples from the felsic volcanic unit plot close to the defined field of unaltered rocks in Figure 2a, hence considered unaltered. Based on the outcome from Figure 2a, geochemistry of the metavolcanic rocks allows the use of major element classification diagrams such as the Total Alkali versus Silica (TAS) diagram (Fig. 2b). However, scatter across the fields of the TAS diagram using major elements for the andesitic unit is expected as they show signs of Si depletion and Na enrichment. Samples from the felsic volcanic rocks cluster tightly within the rhyolite field while the andesite samples show a dispersed pattern between andesite, basaltic trachyandesite, and trachyandesite fields. Using the immobile element ratio of Zr/TiO2 versus SiO2 (Fig. 2c) allows for a more reliable classification of the andesite samples, which gives similar results as the TAS diagram. The spider plot after Pearce (2008, Fig. 3a), using trace element chemistry, shows a declining pattern for the LREEs (La-Nd) but a rather flat pattern for the HREEs.

A spike in Th-content and a negative Nb-Ta anomaly is observed for most of the samples apart from the two samples subjected to radiometric dating. A negative anomaly for titanium and a positive anomaly for zirconium are observed for all samples. For tectonic discrimination of the andesitic unit using the immobile element ternary diagram of Wood (1980, Fig. 3b), samples plot within the E-MORB, WPT and VAB fields (see figure caption for abbreviations).

4.3 Geochronology

U-Pb radiometric dating of the felsic volcanic rock yielded a concordia (Tera-Wasserburg) date of 1895±10 Ma (MSWD of concordance + equivalence = 0.70). Data from homogenous, fresh and fracture free parts of the crystals were chosen for concordia age calculation. Based on the character of the zircon crystals and spot locations, the 1895±10 Ma date is interpreted to represent the emplacement age of the unit (Fig. 4a).

The set of zircon crystals from the basaltic-andesitic unit yield an upper regression date of 1895±14 Ma MSWD = 0.83, n=8, Fig. 4b). The best fit regression is obtained using Tera-Wasserburg graph. The pattern of lead loss is clearly observable in the Figure 4B. The regression date is interpreted to best represent the crystallization age of the unit.

5 Discussion and conclusions

Geochemical data suggest sodic alteration mainly affected the andesitic rocks, while felsic volcanic rocks show weak potassic alteration apart from a single sample which is enriched in sodium (Fig. 2a). Sodium enrichment in andesitic samples affects the classification using major element resulting in the dispersed pattern seen in the TAS diagram (Fig. 2b). However, combining the immobile element Zr/TiO2 vs SiO2 graph (Fig. 2c) with the TAS diagram give means for a more reliable classification of these rocks.

The REE and HFSE group normative diagram (Fig. 3a)
shows a correlation in negative Nb-Ta and negative Ti anomalies. The negative Nb-Ta anomaly is observed for most samples apart from one sample belonging to the andesitic unit and another to the felsic volcanic unit. The negative Nb-Ta anomaly is observed for most samples apart from one sample belonging to the andesitic unit and another to the felsic volcanic unit. In general, a negative Nb-Ta anomaly is considered a typical signature of subduction generated magmas (Pearce 2008). However, a negative Nb-Ta anomaly associated with a negative Ti anomaly give rise to multiple interpretations: i) the Nb and Ta are incorporated into Ti-rich phases such as titanite, ilmenite, and rutile in the residue during magma generation, ii) fractionation of Ti-rich minerals such as titanite, ilmenite, and rutile have depleted the magma in Ti, Nb and Ta, or iii) hydrothermally remobilized. Martinsson et al. (2013) have reported ilmenite as the dominant Fe-Ti oxide phase and titanite as a common accessory mineral in the andesitic unit of the Malmberget deposit. The three scenarios proposed above will have implications for fingerprinting the tectonomagmatic environment for these rocks and assigning them to regional volcanic suites of the Kiirunavaara and/or Porphyrite Group described Martinsson et al. (2016 and references therein), a discussion that is out of the scope of this abstract. However, the andesite sample in Figure 3b plots within the E-MORB WPT field, indicative of an intraplate setting. Martinsson et al. (2016 and reference therein) have suggested a bimodal, intraplate setting due to the extension of a mature continental arc for the Kiirunavaara group rocks. This chemical and radiometric data suggest that the andesitic unit of the Malmberget deposit is most likely a product of an extensional environment.

Crystallization age of the felsic volcanic unit at 1895±10 Ma (Fig. 3a) is well in the range of the Kiirunavaara

**Figure 2.** a Alteration index and discriminant diagram after Montreuil et al. (2013). Grey field: range of weakly altered rocks of the Great Bear magmatic zone and the Andes. b Total Alkali versus Silica diagram after Le Maitre et al. (1989) for classification of volcanic rocks. c Immobile trace element ratio versus Silica (Zr/TiO₂ vs. SiO₂) classification diagram proposed by Winchester and Floyd (1977) for volcanic rocks.

**Figure 3.** a MORB normalized spider plot after Pearce (2008). Note the absence of Nb-Ta anomaly for the felsic- and intermediate volcanic sample respectively. b Tectonic discrimination diagram mainly for basalts, after Wood (1980). Field are Island-arc Tholeites (IAT), Calc-alkaline Basalts (CAB), N-type Mid Ocean Ridge Basalts (NMORB), E-Type Mid- Ocean Ridge Basalts (EMORB), Within-Plate Tholeites (WPT) and Alkaline Within-Plate Basalts (WPB). Symbol colors in Figure 2.

**Figure 4.** a Reverse concordia (Tera-Wasserburg) diagram for the felsic volcanic rock based on the five most concordant analysis. b Reverse concordia (Tera-Wasserburg) diagram for the andesite unit with all analyzed spots and a regression line through part of the data set (red ellipses).
group rocks (1.91-1.88 Ga, Bergman et al. 2001). However, the obtained concordia age of 1895±10 Ma is the oldest recorded age to date through means of robust radiometric dating using U-Pb method on zircons. The upper limit of the Kiirunavaara group rocks at 1.91 Ga in Bergman et al. (2001) is based on work by Sköld and Cliff (1984) where two samples of quartz porphyries c. 45 km apart from each other were combined and dated in addition to a syenite porphyry from the Malmberget area. The crystallization ages were calculated in a single concordia space using a regression through the dataset (see Fig. 2 in Sköld and Cliff 1984). The upper intercept age of 1909±7/16 was interpreted as the upper limit for the Kiirunavaara group and the Malmberget syenite age was estimated to 1860 Ma. The 206Pb-207Pb ages for the analyzed quartz porphyries ranged between 1858-1762 Ma and the Malmberget syenite porphyry 1821-1804 Ma (Sköld and Cliff 1984). The age calculation method used by Sköld and Cliff (1984) is regarded as not reliable. A recent study by Westhues et al. (2016) on mafic-intermediate and felsic volcanic rocks of the Kiirunavaara deposit returned U-Pb zircon ages in the range of 1884-1872 Ma. Samples from the felsic porphyry of the Kiirunavaara hanging-wall returned concordant ages of 1872±7, 1876±7, 1879±7, 1880±5 Ma (Westhues et al. 2016). Emplacement age for the mafic-intermediate footwall rock of the Kiirunavaara deposit is set at 1884±4 Ma (Westhues et al. 2016). The calculated concordant ages by Westhues et al. (2016) for the felsic volcanic and mafic-intermediate rocks of the Kiirunavaara group are in range (within error) of the obtained concordant ages of the felsic volcanic and mafic-intermediate rocks hosting the Malmberget deposit. This implies, if accepting the error overlap, the felsic and mafic-intermediate rocks at Kiirunavaara and Malmberget were coevaly emplaced from a similar source. On the other hand, if disregarding the error overlap this implies, either, a prolonged magmatic episode with multiple pulses from a common source, where the felsic volcanic at Malmberget is generated earlier than the felsic porphyries of the Kiirunavaara deposit, or, that these rocks were formed from separate sources. Comparison and evaluation of the zircon crystals dated within the study by Westhues et al. (2016) and this study would be highly interesting. To further address this issue, studies of the Sm-Nd or Lu-Hf isotopic systems would probably reveal important questions.

Acknowledgment

LKBAB are acknowledged for data supply and support during sample collection. We thank Louise Corriveau for his constructive comments and revision. This work is based on results from the SIP-STRIM project “Multi-scale 4-dimensional geological modeling of the Gällivare area” financed by VINNOVA, Boliden AB and LKBAB.

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Integrated SWIR spectral and XRD studies on core samples from Gadarwara, Central India craton, Madhya Pradesh, India—footprints for IOCG mineralisation

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Craig Hart
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Abstract. High-quality spectra short wave infrared wavelength (SWIR) spectra and X-Ray diffraction (XRD) studies were obtained with an ASD Terraspec Spectroscope on core samples to identify and characterise IOCG type mineralisation from the Gadarwara prospect in the Central Indian craton. The samples consist largely of banded hematite jaspilite (BHJ) and magnetite (BM) iron formation with pervasive carbonate alteration. Clay minerals such as illite, kaolinite, and montmorillonite along with siderite, ankerite, Fe chlorite, albite and actinolite were identified by SWIR. After data reduction and correction, the XRD spectra peaks correspond to Fe-oxides, copper, gold, platinum and REE. These results provide the first integrated report of SWIR and XRD spectral studies on core samples and the reported mineralogy and geological and geophysical footprints bear some similarities with IOCG mineralisation.

1 Introduction

A government airborne geophysical survey flown in the late 1970s detected a large magnetic anomaly at Gadarwara, Madhya Pradesh, in north-central India. Despite the size and intensity of this anomaly, it was never investigated in detail, most probably because the IOCG model was not developed and the region is covered by considerable thicknesses of alluvium. A recent mineral exploration program drilled through the alluvial cover into the basement and intersected magnetite- and hematite-rich basement rocks which potentially represents the first discovery of IOCG-type mineralisation in India (Raju PVS et al. 2014). This paper provides the first report on core samples using SWIR and XRD to characterise these rocks and provides new constraints on the nature and significance of this mineralisation.

2 The Gadarwara magnetic anomaly

In 1979, the National Geophysical Research Institute carried out regional aeromagnetic surveys in three blocks along the Narmada Son Lineament for the Geological Survey of India. The data was acquired at a nominal line spacing of 2000 m and at an altitude of 1000 m. This area is mostly covered by thick alluvium probably overlying the Vindhyan sediments, outcrops are sparse with a few exposures of Mahakosal Fm. south of the survey area and underlain by the Archean-Proterozoic Bijawar Group. The aeromagnetic survey discovered and defined a conspicuous anomaly in the central block (Atchuta Rao et al. 1992; Ram Babu 2003). The anomaly has a magnitude of about 600 nT above background and covers an area of about 40 km², south of Gadarwara (22.552° N, 78.472° E). This Gadarwara magnetic high is elongate, trends to the east-northeast and is about 1,800 m wide and 20 km long.

Figure 1. Geologic map of the Gadarwara area, India.

A subsequent ground magnetic survey better constrained the anomaly to an amplitude of about 1200 nT. Interpretation of
airborne and ground magnetic profiles using a thick dike model provided the depth, width, dip, and susceptibility of the causative source as 200 m, 4000 m, 42°N, and 0.004 CGS, respectively (Atchuta Rao et al. 1992). A self-potential (SP) survey along the same traverse recorded an anomaly of about –50 mV amplitude. An electromagnetic (EM) survey using a Maxmin-II apparatus recorded weak conductive responses at the edges of the source. The weakness of the EM response may be attributed to a deeper nature of the source (Atchuta Rao et al. 1992).

The geological reasons for this anomaly are not apparent from the sparse and poor quality field constraints. The most proximal rocks are lower Cretaceous coal-bearing sedimentary rocks to the south (~ 900 km) but otherwise the region’s uppermost stratigraphy north of Gadarwara is dominantly represented by thick accumulations of volcanic strata of the Cretaceous Deccan Traps (Fig. 1).

3 Drilling

In 2007, Adi Gold Mining Pvt. Ltd. initiated a North to South exploration program of three vertical diamond drill holes (1.4 km total) across the centre of the geophysical anomaly. DDH-1 (Fig. 2) was drilled near the northern edge of the anomaly, went through 309 m of alluvium before intersecting bedrock and then cored 303 m of bedrock for a total depth of 612 m. DDH-2 advanced through 288.8 m of alluvium before being abandoned. DDH 3, near the southern edge of the anomaly, went to 307.0 m depth before being lost in alluvium. DDH-3A (adjacent to DDH-3) intersected bedrock at 312 m and retrieved 118.4 m cores within bedrock. These are presumed to be the first deep drill holes to intersect Precambrian bedrock in the Narmada son lineament.

4 Petrography

Rock units encountered in the drill cores include felsic tuff, metasedimentary rocks dominated by banded chert, and various BIF facies, such as cherty BIF, hematite BIF, magnetite BIF and carbonate BIF. Mineralogy was assessed petrographically and by short wave infrared spectroscopy (SWIR) using ASD Terraspec instrument. Siderite, ankerite, Fe chlorite, illite, kaolinite, montmorillonite, albite and actinolite were identified.

4.1 Cherty BIF facies

The cherty BIF facies consists of alternating bands of crypto-crystalline to microcrystalline chert and anhedral hematite (Fig. 3) with little or no clastic contamination. The thickness between iron layers varies from 10 to 50 meters. Sericite and chlorite-ripdolite are common. The hematitic facies BIF is the dominant lithology and typically consists of specularite and less frequently of massive steely hematite and fine-grained hematite replacement of other minerals, especially silicates and magnetite. Specularite is typically variably replaced by magnetite, such that the rocks locally hosts up to 50% magnetite. Hematite contains inclusion of ilmenite as triangular pits. The common gangue mineral phases include quartz, Ca(Mg-Fe) carbonates, chlorite, sericite and apatite. Hematite facies rocks have higher sulphide contents than the magnetite facies (Fig. 3). REE and U enrichments occur as discrete mineral phases. Accessory zircon and apatite occur as hexagonal and elongated needles. The hematite jaspelite consists of jaspelite bands intercalated with iron rich layers less than 1 mm thick.

Figure 2. Litholog of DDH-1 borehole.
5 Analytical methods

5.1 Short wave infrared studies

Clay alteration minerals were determined in on rock surfaces in real time using an ASD Terraspec Spectroscope to obtain high-quality spectra short wave infrared wavelengths (SWIR) based at Mineral Deposit Research Unit at The University of British Columbia. This help in understanding the alteration chemistry useful for mineral exploration.

The XRD analysis was conducted at CSIR-NGRI, India X Ray facility, using a Bruker D-8 advance model. It is equipped with a source of Cu Ka radiation with high precision LYNXE detector and used Ni Kβ filter. The samples were pulverised using a McCrone XRD mill and were back-loaded into PMME mounts of 25x8 mm diameter. The diffraction patterns collected using knife edge to reduce air scatter by scanning from 5 to 70 reduce 0.02° 2θ steps and counting for ≈ 3177 s/step for a total scan time of reduce 0.02° 2θ steps diffraction patterns were evaluated using the Bruker Diffmac. Suite EVA V 4.0, software released in 2016. Each diffraction pattern was corrected for background. Instrumental shifts in 2θ were corrected by reference to the 100% intensity (104) Ka peak of corundum at 35.149 2θ position. Mineralogical identification was facilitated by using the Crystallography Open Database (COD), and the International Centre of Diffraction Data (ICDD) data base.

6 Results and discussion

The minerals identified by SWIR are quartz, clay minerals, white micas, Fe bearing minerals and carbonates, which are consistent with the mineralogy identified by XRD analysis (Fig. 4a, b). The SWIR and XRD data sets were comparable for 90% of samples in DDH-1 and DDH-2 boreholes. Chlorite-group minerals had the least disagreement between the two characterisation techniques. For the samples selected for validation of XRD analysis, the kaolin group minerals identified by SWIR occurred mainly within low-grade oxidised core and consisted of montmorillonite and kaolinite in good agreement with XRD results, although SWIR results returned only montmorillonite and dickite. It was difficult to distinguish between kaolinite and dickite groups in diffraction patterns and, hence, spectral SWIR data is corroborating in this case.
variations may have caused a regional transformation of kaolin group minerals and smectites to mica and chlorite. The hydrothermal footprint is expressed by intense silicification related to pervasive quartz veinlets. The oxidation of primary sulphides and iron oxides, such as hematite, magnetite, iron carbonates (e.g., ankerite, siderite etc.). The common U and Th minerals include uraninite, thorite and allanite with apatite, titanite, xenotime and epidote. The presence of tourmaline is reported and the compositions fall in mineral fields where schrol-dravite join. This mineral suite is comparable to IOCG alteration assemblages but is not exclusive to IOCG mineralisation.

8 Conclusion

Overall, the SWIR and XRD integrated mineral identification method provides very rapid characterisation of drill hole mineralogy and alteration trends typical to IOCG mineralisation at Gadarwara, India

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Figure 4. a, b, sample at 312 m depth in borehole DDH-1show SWIR (hematite) and XRD (hematite and quartz) X-ray Diffraction (XRD) analysis.

7 Footprints of IOCG mineralisation

The mineral footprints in the core samples investigated from Gadarwara suggest that samples have undergone hydrothermal, and oxidation alterations of primary mineralisation. The potential indicator minerals comprise sheet silicates (i.e., kaolinite, montmorillonite, dickite, mica, chlorite), iron oxides, quartz and carbonates. The PT-
Trace element signatures in U-W-Sn-Mo zoned hematite from the IOCG deposit at Olympic Dam, South Australia

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Abstract. Hematite is the dominant gangue component of the Olympic Dam Cu-U-Au orebody, South Australia. A distinct oscillatory-zoned hematite, conspicuously rich in ‘granitophile’ elements (U, W, Sn, Mo) is recognized throughout the ~2 km vertical extent of deposit zonation, from deep pyrite-chalcopyrite to shallow bornite-chalcocite orezones, as well as throughout the entire NW-SE strike of the orebody. Concentrations of granitophile elements are retained, albeit at lower concentrations, in later replacement hematites. Comparison of trace element datasets for U-W-Sn-Mo-zoned hematite relative to replacement hematite provides evidence for localized fluid-mineral reaction and for the importance of reactions coupling dissolution with reprecipitation rates in driving element exchange. The oscillatory-zoned hematite is analogous to that previously dated by LA-ICP-MS, confirming that this generation of hematite was formed at ~1.6 Ga during the onset of the IOCG mineralising system. Such ‘granitophile’-rich hematite may be common in other IOCG deposits, and typifies precipitation from fluids rich in these elements during the main hydrothermal stages. Lack of evidence for this type elsewhere is most likely attributable to advanced overprinting in which such signatures are largely obliterated.

1 Introduction

Inherent to all iron-oxide copper gold (IOCG) deposits is the abundance of Fe-oxides as hematite (α-Fe2O3) and/or magnetite (Fe3O4). The increasing volume of published trace/minor element data for minerals from hydrothermal ores (Cook et al. 2016 and references therein) include studies of Fe-oxides for fingerprinting mineral deposits of different types (e.g. Dupuis and Beaudoin 2011). Trace element signatures of magnetite from end-member IOCG deposits sensu lato such as Kiruna (Sweden) and El Laco (Chile) have been obtained to support debates around their magmatic versus hydrothermal origins (Dare et al. 2015; Knipping et al. 2015). In contrast, trace elements in Fe-oxides from sensu stricto IOCG-systems, and specifically hematite, have not been studied in detail despite being the main products of alteration closely associated with mineralising processes. Among the exceptions is hematite from the IOCG deposit at Olympic Dam (OD), South Australia (S.A.), which was found to incorporate a wide range of trace elements, including HFSE, REE+Y (REY) and is particularly rich in U, W, Sn, and Mo (hereafter ‘granitophile’ elements) (Ciobanu et al. 2013; 2015; Cook et al. 2016). Incorporation of U and its decay products within grains showing oscillatory zonation patterns facilitates its use as a mineral geochronometer for directly dating hydrothermal ore-forming processes in IOCG deposits from S.A. and elsewhere (Ciobanu et al. 2013; Courtney-Davies et al. 2016). Hematite from OD shows incredible textural diversity including pseudomorphic replacement of pre-existing minerals and/or rock fragments, overgrowths of hematite with distinct trace/minor element signatures, as well as cycles of (inter)conversion with magnetite, all of which is mirrored by a complexity of preserved trace element signatures (Ciobanu et al. 2013; 2015; Cook et al. 2016). Hence, studies of hematite signatures and their variation can offer insights into the processes responsible for the genesis and overprinting of IOCG-deposits, as well as providing a temporal context for regional metallogenic events.

2 Geological background

Olympic Dam is a giant, Cu-U-Au-Ag deposit (10,400 Mt @ 0.77 % Cu, 250 ppm U3O8, 1 ppm Ag and 0.32 ppm Au; BHP Billiton 2016) located on the eastern margin of the Gawler Craton. It belongs to the Olympic Cu-Au Province (e.g. Skirrow et al. 2007) in which IOCG mineralisation is associated with ~1.6 Ga magmatism (Hiltaba Intrusive Suite; HIS and Gawler Range Volcanics, GRV), although ongoing work at OD shows the importance of subsequent overprinting events to account for the spectacular metal endowment of the deposit. The deposit is hosted within the Olympic Dam Breccia Complex (ODBC), which is confined to the Roxby Downs Granite (RDG; Fig. 1), a HIS granitoid. Latest, high-precision U-Pb dating of magmatic and hydrothermal zircon in RDG and ODBC shows that brecciation and hydrothermal alteration (at least the early stage) is coeval with RDG crystallisation at ~1595 Ma (e.g. Jagodzinski 2005 and unpublished data). U-Pb geochronology of oscillatory-zoned hematite from two locations in the deposit shows overlaps with the zircon ages (Ciobanu et al. 2013; Courtney-Davies et al. 2016).

The RDG displays a gradational continuum from altered, through fractured to brecciated lithologies, associated with an increase in Fe-metasomatism and
multiple episodes of brecciation and displacement. OD is mineralogically zoned at the deposit scale, characterized by an inwards-, roughly concentric and quasi-continuous Cu-(Fe)-sulphide zonation that spans vertically and horizontally from pyrite-chalcopyrite (Py-Cp) through chalcopyrite-bornite (Cp-Bn) to bornite-chalcocite (Bn-Cc) dominated assemblages (Ehrig et al. 2012), a pattern considered to represent a primary feature of hypogene ore precipitation (Ciobanu et al. 2017). Hematite is the main Fe-oxide within the orebody, even though at depth and along the deposit margins magnetite is also present and shows various, complex replacement textures with hematite (Ehrig et al. 2012; Ciobanu et al. 2015).

3 Sampling approach and methodology

The present study is undertaken on ~50 samples collected from drillholes intersecting different parts of the OD orebody along its ~6 km strike and throughout the entire ~2 km vertical zonation in the SE lobe. These were selected to represent the lithological complexity, e.g. (i) presence of blocks of sediments and brecciated felsic volcanics in the SE lobe; (ii) sediments in the ‘barren core’ from the middle part of the deposit (>20 wt.% Fe); (iii) high-grade chalcocite and bornite ores from the middle (RU34-8889-8891) and NW arm of the deposit, respectively. Polished blocks were analysed using reflected light microscopy, scanning electron microscopy in back-scatter electron mode (BSE), electron probe microanalysis (EPMA) and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) for trace elements using BHVO-2G and NIST610 as reference standards. All instrumentation is housed at Adelaide Microscopy, The University of Adelaide.

4 Results

Oscillatory zonation in hematite with respect to concentrations of U+W+Sn+Mo is recognised throughout most samples from across the deposit area, including from the shallow Bn-Cc orezone in the SE lobe, in hematite-richest breccias from the ‘barren core’, and in high-grade bornite ores from the NW arm of the deposit (Fig. 1). This type of hematite (GpZ-Hm; Fig. 2) occurs as single grains of variable size (tens to hundreds of µm), and more rarely as lamellar aggregates. Remarkable concentrations of granitophile elements, routinely measured by LA-ICP-MS (see below), are confirmed by EPMA analysis (e.g. up to wt.% levels of UO₃ and WO₃; Fig. 2a). Overprinting of such hematite is recognised, including marginal corrosion and replacement, brecciation, porosity, fields of discrete inclusions (U-, W-, or REE-minerals), as well as cross-cutting veinlets. In most cases, GpZ-Hm grains display varying degrees of pseudomorphic replacement, leading to overgrowths of hematite poor in granitophile elements (Fig. 2a). There are, however, also grains with a clast-like morphology, little apparent replacement, and excellent preservation of compositional zoning (Fig. 2b). These are specific to samples from the ‘barren core’, or from entrapped sediments from the SE lobe.

Although the abundance of GpZ-Hm is higher in samples analysed here from the SE lobe, this type of hematite is relatively minor on the deposit-scale (~10 vol.% within a given sample) relative to other hematite types. These include porous aggregates, and fine-grained hematite filling single grains of other minerals (feldspars in RDG or volcanic rocks), other rock fragments, or the dominant fine-grained hematite that makes up the matrix for breccias, notably in samples from the ‘barren core’ of the deposit. One type of replacement hematite is defined by fine aggregates of hematite filling coarser lamellae (mm-size) arranged within an overall rhombic outline (RC-Hm). The pre-existing mineral may have been a carbonate. Importantly, such aggregates host abundant chalcocite and define high-grade chalcocite-only ores in the middle part of the deposit.

Figure 1. Sketch map of OD showing sampled drillholes. Different categories of hematite (Hm) as follows: red: oscillatory-zoned (GpZ-Hm); green: carbonate replacement (RC-Hm); blue: replacement, undifferentiated. After Ehrig et al. (2012).

Figure 2. BSE images showing oscillatory-zoned hematite and styles of overprinting.
Trace element data for zoned hematite show variation with respect to REY, HFSE (particularly Nb and V), as well as in the relative proportions of the granitophile elements, e.g. U vs. W+Sn+Mo (Fig. 3). Concentrations of U and W can both reach up to several wt.%; in some cases, hematite grains rich in U and W co-exist in the same sample (e.g. in the Cp-Py zone at depth in the SE lobe). Sn and Mo concentrations are generally subordinate: up to hundreds of ppm (exceptionally thousands of ppm Sn in samples from the SE lobe). Such variation is, however, neither systematic with respect to location within the deposit nor throughout its vertical extent. Replacement hematite, particularly in samples from the middle part of the deposit (included here for comparison) can also be relatively rich in granitophile elements, albeit 1-2 orders of magnitude lower than in GpZ-Hm (Fig. 3). There is an apparent decrease in the U content of hematite from SE to NW. GpZ-Hm in samples from the SE lobe and ‘barren core’ appear the poorest in HFSE relative to other types.

Figure 3. LA-ICP-MS maps of carbonate replacement hematite (see text for further detail). Scales in counts-per-second x 10^3.

The relatively homogenous distribution of granitophile elements and HFSE in the RC-Hm type (Fig. 4) seems to map out the coarse lamellae rather than fine-grained nature of the hematite filling. RC-Hm also stands out by having the highest, consistent Nb+V concentrations (Fig. 4c). In contrast, ΣREY concentrations display a relatively constant spread, with a wide range across several orders of magnitude, irrespective of hematite type (Fig. 4a).

Chondrite-normalised REY fractionation trends (Fig. 5) show that GpZ-Hm is, for the most part, poor in REY, but nevertheless displays a consistent pattern defined by relative LREE enrichment. Other REY trends, including flat to slightly concave profiles, are obtained from grains with higher-ΣREY throughout all categories of hematite. RC-Hm is an exception, however, and shows conspicuous, concave, HREE-enriched trends throughout all analyses.

Figure 4. Scatter plots showing variation in trace element signatures of different types of hematite.

Figure 5. Chondrite normalized REY fractionation trends of different types of hematite.
5 Discussion and implications

‘Granitophile’-rich, oscillatory-zoned hematite previously reported from a couple of locations in the OD deposit (Ciobanu et al. 2013; 2015) is now recognised as present throughout the ~2 km vertical extent of deposit zonation (from deep Py-Cp to shallow Bn-Cc orezones), as well as throughout the entire NW-SE strike of the orebody. Such hematite has been also dated by LA-ICP-MS, using GJ-1 zircon as primary standard, and shows the same ~1.6 Ga age (Courtney-Davies et al. unpublished data), firmly indicating that this generation of hematite was formed during the onset of the IOCG mineralising system.

GpZ-Hm is a poor host for REY; higher ΣREY are mostly attributable to discrete inclusions of REE-minerals. The change in REY fractionation trend from LREE, dominant throughout most hematite types, to HREE-enriched, as documented here for RC-Hm, can be related to pH variation, as this parameter can strongly impact on REE solubility (Midgisov et al. 2016 and references therein). This is concordant with the interpretation of replacement of a pre-existing carbonate, strongly reactive to the acidic fluids leading to hydrolytic (sericite-hematite) alteration, and could also account for the formation of high-grade chalcocite ore. One of the interesting findings is that the potential that HFSE may have for understanding primary deposit zonation, or the importance of different protoliths relative to granitophile-rich hydrothermal fluids.

The fact that concentrations of U and other granitophile elements are retained throughout all replacement hematites, some of which are clearly formed on behalf of the oscillatory-zoned type, suggests the importance of reactions coupling dissolution with reprecipitation rates (CDRR) throughout the ODBC, retaining such elements close to the sites of fluid-mineral interaction. The data for U-W-Sn-Mo-zoned hematite can be considered as evidence for localised fluid-mineral reaction throughout the ODBC and the importance of CDRR in driving element exchange as was shown for OD uraninite (Macmillan et al. 2016a, b) and for feldspar alteration in the RDG outside the orebody (Kontonikas-Charos et al. 2017).

Comparative compositional zonation with respect to W+U was shown for hematite from other deposits in the Olympic Cu-Au Province and from Carajas, Brazil (Courtney-Davies et al. 2016), irrelevant of host lithologies (granitoid hosted or not). It is likely that ‘granitophile’-rich hematite is one of the main types in IOCG deposits, and typifies precipitation from fluids rich in these elements during the main hydrothermal stages, assuming no other minerals that are normally good ‘granitophile’ carriers are formed at the same time (e.g. skarn calc-silicates). A lack of evidence for this type elsewhere is most likely attributable to advanced overprinting (obliteration of such signature), and/or poor mineralogical/petrological studies.

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Mineralisation paragenesis of the Liikavaara Cu-(W-Au) deposit, northern Sweden

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Abstract. The Liikavaara Cu-(W-Au) deposit is located in the Gällivare ore district in northern Sweden, a few kilometres east of the renowned Aitik Cu-(Au) deposit. Its enrichment in Critical Raw Materials and its scheduled production for the near future make the Liikavaara deposit ideal as the subject of a case study on improved ore characterisation using various micro-analytical techniques. Here we present a general overview of the mineralogy in Liikavaara to provide a base for future micro-analytical studies. The deposit lies within Palaeoproterozoic volcanosedimentary rocks of andesitic composition. A unit of biotite schist hosts the ore. Mineralisation in Liikavaara is mainly controlled by quartz-(calcite)-(tourmaline) veins. Aplitic dykes and calcite veinlets also cut the deposit. Ore minerals are chalcopyrite, pyrrhotite, pyrite, sphalerite, galena, and molybdenite. Non-sulfide sources include scheelite and minor magnetite. The deposit is affected by alteration such as sericitisation, calcification, tourmalinisation, epidotisation, and chloritisation. The genesis of the deposit is up to today not determined and studies are few. However, the deposit's spatial proximity to a mineralised granodiorite dated at ca. 1.87 Ga offer some similarities to the Aitik deposit and its 1.89 Ga quartz monzodiorite. A primary magmatic origin with later IOCG overprint could therefore be a possibility.

1 Introduction

In 2010 the EU introduced a methodology to define Critical Raw Materials (CRMs), i.e. materials with a high economic importance to the EU and with a high risk associated with their supply. A list of these CRMs was published in 2011 and revised in 2014 (European Commission 2014).

Despite many CRMs occurring as traces in active mines throughout Europe, there is a dependency on import for most of these raw materials. This is largely due to their low abundance in the European mines but also simply because the content and distribution of additional low-grade by-products has not been economically viable to promote. Often CRMs are treated as waste or even penalty metals rather than sellable by-products. While we have to accept the uneven distribution of the CRMs throughout the world we can make an effort to use what little is offered.

Naturally, there needs to be an economic viability for companies to treat their by-products as commodities rather than waste. Increasing the geological and mineralogical knowledge of the occurrence and distribution of the CRMs can help to bridge this gap. A better understanding should aid to increase efficiency of various metallurgical processes for metal separation and recovery. This could make the production of low abundant CRMs viable as well as improve purity of the main product.

Due to advancements in micro-analytical techniques over the last few decades, new and promising opportunities for mineralogical studies with much higher detail than previously is now possible.

This extended abstract marks the beginning of a case study on the Liikavaara Cu-(W-Au) deposit. Its goal is the development of chains of micro-analytical methods for analysis of trace CRMs, fit to the specific needs of professionals in the fields of geology, mineral processing, and metallurgy.

To provide a base for further studies we here present a brief geological and mineralogical overview of the deposit based on the results of drill core logging and thin section analysis with the petrographic microscope.

2 District and deposit geology

The Liikavaara Cu-(W-Au) deposit is situated in the Gällivare ore district in northern Sweden (Fig. 1). This district is host to numerous small- to large-scale deposits, predominantly epigenetic Cu-Au and some Fe (Bergman et al. 2001). Most notable are the actively producing Malmberget Fe deposit (LKAB) and the world-class Aitik Cu-(Au) deposit (Boliden AB), the latter located just a few kilometres west of the Liikavaara Cu-(W-Au) deposit (Fig. 1). Many of the Cu-Au deposits are structurally controlled by the Nautanen Deformation Zone which runs north-northwest through the ore district.

In northern Sweden, a 2.7 to 2.8 Ga Archaean basement is unconformably overlain by a Palaeoproterozoic succession of Karelian greenstones, and Svecofennian porphyries and elastic metasedimentary rocks (Bergman et al. 2001). In the Gällivare area the supracrustal rocks are mainly of volcanoclastic and volcanic origin. They are intruded by diorites (Haparanda and Perhitie monzonite suite) and ca. 1.8 Ga old granites and pegmatites (Bergman et al. 2001).

The Liikavaara Cu-(W-Au) deposit lies in the eastern limb of a syncline in volcanosedimentary rocks of andesitic composition that form the upper part of the Muorjevaara Group (Zweifel 1976). The mineralized zone is hosted by biotite schist (Fig. 1). It extends for approximately 1 km at a width of 100 m striking NW.
and dipping 80°W (Zweifel 1976). The deposit has a volume of 56 Mt at 0.24 % Cu (cut-off grade 0.08 %). It is also weakly enriched in Au, Ag, Zn, Pb, As, Bi, Mo, Sn, and the CRMs W and Sb (Zweifel 1976). Main ore constituents are chalcopyrite, pyrrhotite, and pyrite with minor amounts of magnetite, sphalerite, galena, and molybdenite. The main source for tungsten is scheelite. Gangue and vein minerals are quartz, calcite, and tourmaline (Zweifel 1976).

Due to a lack of surficial exposure, most geological data comes from drill core logging and geochemical analysis. All drill cores are property of Boliden AB who holds the exploration permits and mining concession for the Liikavaara Cu-(W-Au) deposit and plans for production towards 2021-22.

**Figure 1.** Top left) Location of the Aitik and Liikavaara deposits. Right) Geological map of the Liikavaara deposit. Lower left) Geological profile through the Liikavaara deposit.

### 3 Sampling and methods

Three drill cores from Boliden AB, two central and one distal to the deposit, were logged and sampled for the various vein- and mineralisation styles in the Liikavaara Cu-(W-Au) deposit. The samples were prepared into 30 µm polished thin sections by Vancouver Petrographics LTD. A total of 20 thin sections were analysed with the petrographic microscope.

Additionally, zircons from a granodiorite intrusion just north of the deposit were U/Pb dated with a MC-LA-ICP-MS at the Vegacenter in Stockholm. The geochronological analysis was carried out to investigate a possible connection between the intrusion and deposit formation.

### 4 Results

#### 4.1 Mineralogy

Mineralisation in the Liikavaara Cu-(W-Au) deposit is mostly vein-controlled, although sulphides and magnetite are sporadically disseminated in the host rocks as well.

The deposit is intruded by metre-wide aplitic dykes consisting of quartz, microcline, and plagioclase (Fig. 1). Quartz-(calcite)-(tourmaline) veins of millimetre to decimetre thickness occur within the aplitic dykes and in the host rocks where they usually follow the biotite foliation. Calcite also forms micrometre to millimetre wide veinlets. They crosscut foliation in the host rocks as well as other veins and dykes (Fig. 2a).

The host rocks and to some extent also the dykes are affected by hydrothermal alteration with sericite, chlorite, epidote, calcite, and tourmaline (Fig. 2a, 2b, 2f).

Metals are mainly contained in sulphides such as chalcopyrite, pyrrhotite, pyrite, sphalerite, galena, and molybdenite. Other sources include magnetite and scheelite (Fig. 2c-f). The sources for Au, Ag, Bi, Sb, and Sn were not clearly identified in this study. However, Au and Ag seem to occur in association with sulphides in quartz veins and/or thin fingers from the aplitic intrusions. Bismuthinite likely is the major Bi mineral.

The drill cores show zonation for some of the ore minerals. Chalcopyrite is the most abundant sulphide in the central part of the ore while pyrite dominates in the distal parts. Sphalerite and galena are most concentrated higher up in the ore zone. Scheelite is confined to the central ore body while magnetite is mostly found distally in the deposit.

Chalcopyrite, pyrrhotite, and pyrite are the most abundant ore minerals. They occur both disseminated and in accumulations especially in quartz-(calcite)-(tourmaline) veins. Grain sizes range from a few micrometres to millimetres. Chalcopyrite is often found replacing pyrrhotite which itself occasionally contains pyrite remnants (Fig. 2c). Pyrite also occurs as smaller euhedral grains with skeletal-growth texture (Fig. 2d). Sphalerite and galena are minor in abundance. They usually occur together, partly intergrown with chalcopyrite (Fig. 2c). These three minerals are also found in cross-cutting calcite veinlets (Fig. 2a). Magnetite is scarcely distributed but locally enriched. Its grains are disseminated in host rocks and veins, usually broken, and partly replaced by sulphides (Fig. 2e). Scheelite is found exclusively in veins. The anhedral to subhedral grains vary in size but are often much coarser then the surrounding minerals (Fig. 2f). They are commonly associated with calcite and sulphides. The occurrence and distribution of molybdenite and other trace metal minerals is not yet studied.
Figure 2. Petrographic microscope images of selected samples from the Liikavaara Cu-(W-Au) deposit. 

a. Chalcopyrite in a calcite vein crosscutting a quartz vein in biotite schist. 
b. Alteration minerals sericite, epidote, and tourmaline in a quartz-tourmaline vein within aplite. 
c. Intergrowth of pyrrhotite, chalcopyrite, galena, and sphalerite. 
d. Assemblage of pyrite (skeletal growth texture), marcasite, chalcopyrite, and pyrrhotite. 
e. Quartz-calcite vein containing magnetite, pyrite, and chalcopyrite. 
f. Large scheelite grains in a quartz vein; dark-greenish to reddish tourmaline in the host rock. 

4.2 Geochronology

Many of the zircons analysed with the MC-LA-ICP-MS were zoned and some had radiation fractures. A common Pb correction was necessary for about 40% of the measurements (all discordant). Ages were determined following the strategies of Spencer et al. (2016).

The plotted U and Pb ratios outline a discordia with a lower intercept at approximately 387±32 Ma (app. age of the Caledonian orogeny). The concordant data (20 of 66 measurements) deliver a concordia age of 1873.0±5.3 Ma based on the assessment method of Ludwig (1998, 2003) within Isoplot. The according weighted average age is 1874.4±1.7 Ma with a MSWD of 1.5. This indicates that the data conform to a single population as the MSWD is within 1±2√(2/(n−1)), i.e. 0.3511-1.6489 for a data volume of 20. It should be noted that for age assignment the 207Pb/206Pb system was used over the 206Pb/238U due to the lower intercept at approximately 21.43±0.3 Ma (app. age of the Caledonian orogeny). The concordant data (20 of 66 measurements) deliver a concordia age of 1.89±1.7 Ma with a MSWD of 1.5. This indicates that the data conform to a single population as the MSWD is within 1±2√(2/(n−1)), i.e. 0.3511-1.6489 for a data volume of 20. It should be noted that for age assignment the 207Pb/206Pb system was used over the 206Pb/238U due to the ages being above 1.5 Ga.

5 Discussion

Crosscutting relationships suggest aplitic dykes to be older than the veins. Calcite veinlets appear to be youngest.

Replacement textures and inclusions infer a paragenetic sequence for the ore minerals. Magnetite is likely oldest followed by pyrite, pyrrhotite, and chalcopyrite. A second generation of pyrite probably occurred later (euhedral grains with skeletal-growth texture) as did scheelite. Sphalerite and galena might be even younger as they are found in crosscutting calcite veinlets and surrounding chalcopyrite.

The Liikavaara Cu-(W-Au) deposit lies spatially close to the renowned Aitik Cu-(Au) deposit. The latter has been described as a porphyry-type deposit with IOCG overprint (Wanhainen 2005; Wanhainen et al. 2012). According to Wanhainen et al. (2012) primary mineralisation is associated with a 1.89 Ga quartz monzodiorite (Haparanda type), and post-ore modification lasted at least 160 Ma including an IOCG-type overprinting event at ca. 1.8 Ga.

If similar processes were responsible for the formation of the Liikavaara Cu-(W-Au) deposit is unclear. The proximal granodiorite intrusion dated to 1.87 Ga in this study is somewhat younger than the 1.89 Ga quartz monzodiorite at Aitik and likely belongs to the Perithite monzonite suite. Disseminated sulphides in the host rocks common for Aitik are rarely observed in Liikavaara, where vein-controlled mineralisation dominates. It is possible that hydrothermal fluids remobilised an older mineralisation of magmatic-hydrothermal origin from the host rocks into the veins but a purely hydrothermal origin for the metals is plausible too. Either way, hydrothermal fluids were likely involved in the current distribution of metals in Liikavaara. Furthermore, they could be related to the IOCG overprinting event as it was of regional scale and affected many deposits in the whole of the Norrbotten district (Martinsson et al. 2016). For a complete ore genetic model more work is necessary such as structural and fluid inclusion studies. The current knowledge will, however, suffice as a base for forthcoming trace element and CRM studies.

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Trace element geochemistry of magnetite from Ernest Henry IOCG deposit, Australia

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Abstract. Trace element geochemistry of magnetite was used to consider mineralisation processes and vectors around the pipe-like Ernest Henry IOCG hydrothermal breccia deposit. Although EMPA mapping shows that individual magnetites are not zoned with respect to trace element distribution, LA ICP-MS results show that different magnetites from the same or nearby samples may vary widely in composition, and the variability in composition itself is of genetic importance. The most abundant trace elements in magnetite are Mg, Al, Ti, V, Cr, Mn, Co, Ni and Sn. There are no clear patterns that relate to paragenesis or adjacent mineral assemblages. Regional magnetites and those on the flank of the orebody show a high standard deviation in abundance of Mn, Ti, Al and V, for both replacive types and vein/breccia hydrothermal cement. In the core of the orebody, magnetite shows lower standard deviation of all these elements and tends to be lower in Al and higher in Mn, particularly towards the deep core of the orebody. This zonation is interpreted as a predominant influx of primary Mn-rich ore fluids from depth with the breccia, interacting upwards and outwards with both wall rocks and another fluid as the orebody precipitated.

1 Introduction

Magnetite, widespread in igneous, sedimentary and metamorphic and hydrothermal rocks, is sensitive to temperature, pressure, sulphur and oxygen fugacity, cooling rate, silica activity as well as whole rock, magma or fluid compositions. Advances in the trace element analysis of sulphides provides encouragement for magnetite microchemistry as a petrogenetic indicator; however, magnetite has proven more problematic. Although magnetite chemical zonation has begun to be interpreted within igneous rocks and orthomagmatic ore deposits, many problems remain with interpretation of magnetite chemistry in hydrothermal rocks (Dare et al. 2014). Magnetite from Ernest Henry IOCG deposit and nearby was selected for this study, as it is intimately associated with mineralization at Ernest Henry (together with pyrite, chalcopyrite, and calcite) and also with quartz, calcite and K-feldspar from barren and adjacent mineralized systems. Laser ablation ICP-MS provided the basis for in situ analyses on magnetite, from which we attempt to use the trace element geochemistry to vector to the orebodies or to distinguish between barren and mineralized hydrothermal systems. Given the difficulty of performing experiments on trace element partitioning on hydrothermal magnetite formation, we present here natural data from this well-known IOCG deposit as a way to improve the understanding of connections between ore genesis models and relationships to magnetite chemistry.

2 Geological background

Ernest Henry is a magnetite-dominated IOCG deposit in the Cloncurry District of the Mount Isa Block in northern Australia, with 226 Mt at average 1.10% Cu and 0.51g/t Au (Williams and Pollard 2003). The pipe-like orebody is hosted by the Mount Fort Constantine Volcanics, a ~1740 Ma sequence of metamorphosed intermediate volcanic rocks of the uppermost Corella Formation. The orebody extends > 1400 metres down-dip, largely bound by two northwest trending shear zones that dip ~50° toward the southeast. Copper and gold mineralization occurs primarily within hydrothermal matrix of a breccia body dominated by rounded clasts of potassically altered Mount Fort Constantine Volcanics (Mark et al. 2006). The matrix is dominated by magnetite, pyrite, chalcopyrite, calcite and quartz, with minor apatite, actinolite, fluorite, barite and biotite. Ore genesis is thought to be controlled, at least partly, by pressure changes accompanying collapse of a fluidized breccia pipe at several km depth (Rusk et al. 2010; Oliver et al. this conference).

Near Ernest Henry, magnetite is found in a) regional pre-ore Na-Ca alteration (Mark et al, 2006; Oliver et al, 2008), b) pre-ore K-Fe-(Mn-Ba) alteration represented by intensive biotite-magnetite alteration and shear zones proximal to ore, with less common K-feldspar-garnet (Mn-rich), c) K-feldspar alteration within the altered clasts of the orebody, d) as a major component of hydrothermal infill within the deposit (Mark et al. 2006; Rusk et al. 2010), and e) as a main ingredient of a second generation breccia present as discordant, fluidized magnetite-rich seams and patches overprinting the main orebody in the deeper holes (EH 554 and below, Oliver et al. 2005).
3 Sampling and analyses

185 drill core samples from eight drill holes were logged during this study, from which we analysed over 412 spots on magnetite in 47 samples. Visual examination and petrographic observation under microscope suggested 18 types of magnetite, marked by distinct morphology, texture, paragenesis and origin. Twelve individual magnetite grains from six samples in drill hole EH554 were selected to show transitions from shallow to deep parts of the orebody, mapped using EPMA before the LA ICP-MS analyses.

Analyses were performed at the Advanced Analytical Centre (AAC) at James Cook University. Trace element concentrations and elemental distribution in magnetite (and some related pyrite) were investigated using a Joel JSM5410 LV superprobe, with a 20 kV accelerating voltage and 100 ms dwell time on steps ranging from 1 to 5 μm to produce mm-scale maps. We then used a GeoLas 193 nm Excimer Laser Ablation System coupled to a Varian 820-MS series quadrupole ICP-MS, on samples in a sealed cell constantly flushed with a mixture of high purity Ar and He. Spot size ranged from 32 to 60 μm, with a laser repetition rate of 10 Hz, laser beam energy at the sample around 8 J/cm², 30s measurement of background initially (laser off) and a 35s analyses signal. We used NIST SRM610 and 612, and iron, as standards. For data reduction we used GLITTER 4.4.4 software ( Longerich et al.1996). Signals were manually screened for heterogeneities such as micro-inclusions or contamination in the process of data reduction.

4 Results

4.1 Overall magnetite geochemistry

Electron microprobe trace element maps indicated that all selected magnetite individual crystals are weakly- or un-zoned (Figure 1), allowing some reliance on subsequent laser spot analyses to characterize whole magnetite grains. The homogeneity may be a consequence of rapid diffusion at the inferred 400 to 500°C temperatures of ore genesis (Mark et al. 2006).

The most abundant trace elements in magnetite at Ernest Henry are Al, V, Ti, Cr, Mn, Co, Ni, Zn, and Ga. Despite individual grain homogeneity, magnetite compositions vary widely across the deposit and most trace elements vary over two to three orders of magnitude among samples (Fig.2) or even among grains within a single sample, challenging any global magnetite classification scheme presented to date (e.g. Dare et al. 2014). We initially attempted to classify different trace element chemistry in magnetite using different paragenetic stages, host rock bulk geochemistry, adjacent mineral assemblages, and whether clast or matrix, but clear relationships were not apparent, until we considered position within the orebody together, with copper grade.

Figure 1. Trace element mapping of V and Mn in magnetite by EMPA shows homogeneous grains, similar to all other elements detected (that were not inclusions). (a) and (b) are one grain from 551.3m, and (c) and (d) show another grain from 680.0 m, all from drill hole EH554.

Figure 2. Typical limits of detection (LOD), mean, and maximum and minimum values (blue shading) of trace elements from over 400 individual analyses in magnetite from the Ernest Henry IOCG deposit.

4.2 Spatial variation of magnetite geochemistry

We analysed magnetite from regional albite-rich breccias (up to 30km from Ernest Henry), regional prospects (Mt Fort Constantine Pit “Mt Pit” and Little Eva, and the Erebus satellite orebody under Ernest Henry. Most samples were from Ernest Henry, classified as “core” or “flank” relative to the radial aspects of the ore pipe, and as shallow
mid or deep, relative to the length of the ~ 50° dipping pipe from near the current surface. Two features are most prominent in this analysis. Firstly (Fig. 3a), there is a trend in Mn content of magnetites, increasing from relatively low values regionally, to intermediate values in the upper and flanking parts of the Ernest Henry orebody, to highest in the deep core of Ernest Henry and the deep satellite deposit, Erebus. Although complex, the progressive Mn-enrichment is matched by depletion in Ti, V and Al. Secondly, we considered the “noise” in trace element signal from any one sample, by assessing the standard deviation of the element abundance as a % of the mean abundance of that element. Regional magnetites and those on the flanks of Ernest Henry have higher variability in Ti, Mn and (arguably) Al and V content than those within the higher grade core of the Ernest Henry orebody and Erebus. There are some sub-trends, not statistically strong, that also suggest the magnetites become progressively less variable (or simpler in composition) down-dip along the orebody, both in the flanks and in the core.

5. Discussion and conclusions

Magnetite has an inverse spinel structure with the general stoichiometry AB₂O₄, where A is a divalent cation such as Mg, Fe²⁺, Mn²⁺, Co, Ni, and Zn, and B is a trivalent cation such as Al, Fe³⁺, Cr, V, or Ga, rarely Mn³⁺ or Sn or Ti with a 4⁺ charge (Nadoll et al. 2014). The degree of substitution relates to temperature, as well as pressure, oxygen fugacity, sulphur fugacity, oxidation and reduction etc. Within and around the Ernest Henry IOCG deposit, the overall low Ti contents in magnetite are consistent with predominantly hydrothermal origins, and we infer that the Mn is occurring mostly on the divalent site as Mn²⁺. The high variability (standard deviations) of magnetite trace elements away from the orebody could partly relate to multiple fluid-rock interactions (not necessarily ore-related). However it should be noted that many of the variable magnetites at Ernest Henry come from hydrothermal cement to the main (upper or outer) ore and in veins, so the processes controlling the diverse chemistry are more likely due to fluid compositional variability than the direct degree of wallrock interaction. Also, the decrease in complexity, and increase in Mn content of magnetites in the core of the deposit and with depth, suggests that the system was driven primarily by an influx of reduced, Mn-bearing fluids, and that the upwards and outwards decrease in Mn and increase in “noise” was a function of upflow, dispersal and mixing of this primary fluid during ore precipitation (Fig. 4). The proposed model derived from the magnetite chemistry is in accordance with the physical models for ore deposition at Ernest Henry (Mark et al. 2006, Rusk et al. 2010) whereby rapid fluidized upflow of rock fragments and fluid in the pipe was slowed by interaction with fluids and rocks in the upper parts of the system.

Figure 4. Schematic cross-section for orebody formation based on interpretation of magnetite chemistry and complexity, looking approximately east.

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The Heijianshan Fe-Cu (-Au) deposit in the eastern Tianshan, NW China: a Paleozoic IOCG deposit?

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Abstract. The Paleozoic Heijianshan Fe-Cu (-Au), a typical Fe-Cu deposit of the Eastern Tianshan district, is hosted in Upper Carboniferous volcanic/volcaniclastic rocks. The early epidote alteration stage is characterized by a mineral assemblage of epidote-calcite-tourmaline-sericite, indicating a Ca-Mg alteration event before magnetite and Cu (-Au) mineralization. Based on fluid inclusion and stable isotopes (H-O-S) studies, types and sources of ore-forming fluids for the epidote alteration are shown to be distinct from the subsequent magnetite and Cu (-Au) mineralization stages. Magnetite mineralization formed from high temperature, medium–high salinity, Na-Ca-Mg-Fe-rich, magmatic-hydrothermal fluids and Cu (-Au) mineralization from low temperature, Ca-Mg-rich, hydrothermal fluids. The mineralization contexts of the Heijianshan deposit, combined with alteration types, chemical data (EPMA and LA-ICP-MS) on magnetite and tectonic setting are similar to those of the Mesozoic central Andean IOCG deposits. The Heijianshan deposit represents the first IOCG deposit identified in the Eastern Tianshan and a Paleo Zoic IOCG deposit example in the world.

1 Regional and deposit geology

The Eastern Tianshan of the Central Asian Orogenic Belt (CAOB) is subdivided, from north to south, into the Dananhu-Tousuquan island arc belt, Kangguer shear zone, Aqishan-Yamansu island arc belt and Central Tianshan terrane with their boundaries being respectively the deep, E–W-trending Kangguer, Yamansu and Aqikekuduke faults (Fig. 1).

The Aqishan-Yamansu belt contains Carboniferous volcanic, volcaniclastic and elastic rocks over lain by Permian elastic and volcanic rocks with local carbonate interbeds (Mao et al. 2005). This belt develops plenty of Late Carboniferous to Early Triassic felsic intrusions (Li et al. 2002; Zhou et al. 2010) and many significant Fe and Fe-Cu deposits, including Hongyuntan, Bailingshan, Chilongfeng, Heijianshan, Yamansu and Shaquanzi (Fig. 1).

As a typical Fe-Cu deposit of the Aqishan-Yamansu belt, the Heijianshan Fe-Cu (-Au) deposit is hosted in the Upper Carboniferous Matoutan Formation. The Heijianshan orebodies are largely tabular or stratabound and have mixed oxide and oxide-sulfide ores. Metallic minerals at Heijianshan are dominated by magnetite, hematite, and minor chromite, electrum and sulfides (including pyrite, pyrrhotite and chalcopyrite). Non-metallic minerals include mainly epidote, calcite, amphibole, chlorite, and minor K-feldspar, quartz, titanite, albite, barite, tourmaline and sericite. Magnetite ores commonly occur as massive, disseminated, magnetite clasts, and occasionally as veinlets. Pyrite and chalcopyrite (-electrum) ores are disseminated, in veinlets or occasionally massive.

2 Alteration/mineralization paragenesis

Based on the space-time relationships among pervasive alteration types, mineral assemblages and veins, the Heijianshan alteration/mineralization paragenetic sequences can be sequenced as follows: an early chromite stage, epidote alteration, magnetite mineralization, pyrite alteration, Cu (-Au) mineralization, late veins and supergene alteration.

Chromite stage (Stage I) consists of irregular chromite in the core of magnetite grains that are replaced and cut by magnetite, indicating pre-magnetite formation.

Epidote alteration (Stage II) has a mineral assemblage of epidote-calcite-tourmaline-sericite, indicating a Ca-Mg alteration event. Those minerals, representing Ca-Mg alteration, are commonly replaced/cut by later-stage magnetite and amphibole (Fig. 2a).

Magnetite in magnetite mineralization (Stage III) coexists with amphibole + quartz + K-feldspar + titanite + pyrite (Fig. 2b). A hematite sub-stage (Stage III-A), replaced subsequently by magnetite (i.e., “mushkeotvite”), may have occurred before the main magnetite mineralization (Stage III-B), indicating a rapid $\mathrm{O}_2$ drop at the beginning of the main Fe mineralization.

Pyrite alteration (Stage IV) includes abundant quartz and pyrite, with minor hematite, pyrrhotite and chalcopyrite.

Cu (-Au) mineralization (Stage V) is characterized by a mineral assemblage of quartz-chalcopyrite-chlorite + electrum ± hematite to replace/cut former-stage minerals (Fig. 2c, d).

Late veins (Stage VI) are comprises numerous hydrothermal veins, filled with epidote, amphibole and/or calcite.

Supergene alteration is mainly represented by supergene Cu minerals, such as atacamite and chrysocolla.
3 Magnetite geochemistry

Magnetite in massive, disseminated and clasts ores shows an obvious hydrothermal origin: (a) depletions in Zr, Nb and Ta; (b) low Ti (<2 wt.%) and Al (<1 wt.%); and (c) Ni/Cr ≥1 (Zhao et al. 2016a). Magnetite grains in these different ores can be clearly distinguished by trace elements, e.g., diagrams of Cr vs. Co/Ni, Cr vs. Ti, V vs. Cr and Ni vs. Cr, which are mainly controlled by: (a) fluid and host rock compositions; (b) precipitating of coexisting minerals; and (c) physicochemical properties (e.g., temperature, pressure and $f_O^{2}$) (Zhao et al. 2016a). Furthermore, the Heijianshan magnetite geochemistry shows certain affinity of IOCG-like deposit in the Ti/V vs. Ti and (Ca + Al + Mn) vs. (Ti + V) discriminating diagrams (Zhao et al. 2016a).

4 Comparison with central Andean IOCG deposits

4.1 Alteration/mineralization paragenesis

The Heijianshan epidote alteration stage represents a Ca-Mg alteration event before mineralization, comparable to the widely developed pre-mineralization Na-Ca alteration in the central Andes (Williams et al. 2005; Chen 2013), and the alteration style differences (Na, Ca or Na-Ca) may have been attributed by the different types of host rocks

Figure 1. a Tectonic framework of the Central Asian Orogenic Belt (CAOB; modified after Sengör and Natal 1996). b Tectonic map of North Xinjiang (simplified after Chen et al. 2012). c Geological map of the Eastern Tianshan Orogenic Belt and distribution of major ore deposits (modified after Wang et al. 2006; Deng et al. 2014).
The distinct Fe and Cu (-Au) mineralization are respectively associated with amphibole + K-feldspar and chlorite + hematite alteration, also comparable to the central Andean IOCG deposits, especially in the quartz/calcite-chalcopyrite-hematite assemblage for the Cu (-Au) mineralization.

**4.2 Nature and sources of ore-forming fluids**

Fe mineralization at Heijianshan is high temperature (~590 °C, constrained by magnetite-actinolite oxygen isotope geothermometry; Zhao et al. 2016b), medium–high salinity, Na-Ca-Mg-Fe-rich with magmatic-hydrothermal origin, whereas the Cu (-Au) mineralization is low temperature (~240 °C, constrained by chlorite geothermometer), Ca-Mg-rich, and of hydrothermal origin. The quite different characteristics of the ore-forming fluids for the distinct Fe and Cu (-Au) mineralization stages are similar to those documented for the central Andean IOCG deposits, e.g., Mina Justa (Chen et al. 2011) and Raúl-Candestable (Perú) (Ripley and Ohmoto 1977), Mantoverde (Rieger et al. 2012) and La Candelaria (Chile) (Marschik and Fontboté 2001).

**4.3 Tectonic settings**

The Aqishan-Yamansu belt was a back-/intra-arc basin at ~350–325 Ma during the southward subduction of the Kangguer oceanic plate beneath the Yili-Central Tianshan block (Zhang et al. 2016). As the southward subduction took place, the Aqishan-Yamansu back-/intra-arc basin began to close, accompanied with arc-related magmatism. During the Aqishan-Yamansu basin inversion (~325–300 Ma), Fe and Cu (-Au) mineralization formed at Heijianshan, similar to other Fe (-Cu) deposit in the Aqishan-Yamansu belt, e.g., the Bailingshans, Duotoushan, Chilongfeng, Heifengshan (pyrite Re-Os age: 301.5 ± 5.4 Ma; Huang et al. 2013), Shuangfengshan (pyrite Re-Os age: 292.4 ± 4.8 Ma; Huang et al. 2013) and Shaquanzi deposits (294.5 ± 6.4 Ma and 303 ± 12 Ma for pyrite and magnetite Re-Os ages, respectively; Huang et al. 2013, 2014). The Aqishan-Yamansu belt (such as Heijianshan in this case; Zhang et al. 2016) shares similar tectonic settings (~170–120 Ma for intra-back basin) followed by economic and regional Fe (-Cu) or IOCG mineralization (~120–100 Ma for basin inversion) to the central Andean IOCG belt (Chen et al. 2013).

**5 Conclusion**

The Heijianshan Fe-Cu (-Au) deposit shares many similarities with the central Andean IOCG deposits in alteration, mineral assemblages, nature and sources of ore-forming fluids and tectonic settings. All these similarities and magnetite geochemistry suggest that Heijianshan is probably an IOCG deposit, which may imply further exploration potential for IOCG deposits in the Paleozoic Aqishan-Yamansu belt of the Eastern Tianshan, NW China.

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**References**

Late Paleozoic base and precious metal deposits, East Tianshan, Xinjiang, China: Characteristics and geodynamic setting.


S07 – Developments of geochronological methods and their application to date ore forming events

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Application of U-Pb ID-TIMS geochronology to the geology of mineral deposits: future possibilities and current limitations

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Abstract. Advances in methodologies for U-Pb ID-TIMS geochronology have resulted in improved precision and accuracy such that better dates are now transforming geological interpretations of areas that host mineral deposits. Isolation of closed system components in zircon by thermal annealing followed by partial dissolution, called chemical abrasion (Mattinson 2005), has led to a dramatic improvement in our ability to produce concordant dates. Precision has been enhanced by ever lower background Pb levels, use of isotopic tracer solutions that permit internal mass fractionation corrections, improved ionization efficiency, and more sensitive instrumentation for measuring isotopic ratios. In combination with field observations, application of such methods to zircon and baddeleyite in pyroxenites and gabbronorite of the Rustenburg Layered Suite in the Bushveld Complex, South Africa, and to differentiated gabbro sills of the Cape Smith Belt, Quebec, has led to our reinterpretation of the prevailing view of the geology of these areas. In plate reconstruction efforts, with the objective of providing a more complete context for mineral districts, enhanced accuracy and precision of dates for mafic dykes and sills by using chemically abraded zircon, and relying less on baddeleyite, has helped provide a new level of robust temporal correlations between ancient cratons.

1 Introduction

A major impediment to accurate dating of minerals by U-Pb methods has been the partial loss of radiogenic Pb from the crystals over time. In the case of zircon, accumulation of radiation damage, or ‘metamictization’, renders the crystal open to potential alteration and removal of radiogenic Pb. Early in the development of U-Pb ID-TIMS geochronology, Krogh and Davis (1975) and Krogh (1982) recognized that etching zircon crystals in hydrofluoric acid and mechanical abrasion, respectively, could reduce discordance by removal of altered portions of the grains affected by Pb loss. In 2005, Mattinson described a pre-treatment procedure for zircon called ‘chemical abrasion’ that produced more concordant systems more consistently. This involves thermal annealing of the crystals at 900-1000°C to restore crystallinity, followed by a multi-step etch procedure to remove zones that have partially lost Pb. Most labs report a simplified single etch step in hydrofluoric acid that follows annealing. After more than a decade of community-wide testing of chemical abrasion, most modern ID-TIMS labs report its routine use. Such a pre-treatment for other common geochronometers such as baddeleyite remains elusive, although Rioux et al. (2010) reported progress in extracting end member ages in composite zircon-baddeleyite crystals with a two-step partial dissolution procedure.

In a typical U-Pb ID-TIMS analysis, the largest source of analytical uncertainty is usually associated with the correction for instrumental mass dependent fractionation, unless the amount of radiogenic Pb relative to background Pb is low, in which case the isotopic composition of the blank begins to dominate analytical uncertainty. In U-Pb ID-TIMS dating, isotopic tracer solutions with precisely determined U/Pb are added to each isotope analysis. Known quantities of the tracer isotopes are measured against sample isotopes during mass spectrometric analysis. Tracer solutions that contain two isotopes each of Pb and U permit within-run measurement of fractionation during the mass spectrometric sample analysis of these elements, significantly reducing the analytical uncertainty. The EARTHTIME Project provided a series of such calibrated isotopic tracer solutions to the U-Pb geochronological community (206-205Pb-233-235U, 205Pb-232-235U spikes). This has been a major step towards improved precision while at the same time it has reduced analytical bias among dates reported from different labs.

Further improvement to precision in U-Pb geochronology has been gained through the use of an improved Pb emitter (Gerstenberger and Haase 2004), which enhances ionization efficiency, and a gradual reduction in levels of background Pb contamination now in the 0.2-0.5 picogram (1x10^-12 g) range in some laboratories. Better instrumentation in recent years has also aided precision. Many labs have acquired collector systems with higher sensitivity (i.e., 10^12 and 10^13 ohm resistor amplifier boards for Faraday cups), which allow static measurements that require less analysis time and give exceptionally high precision.

Modern U-Pb ID-TIMS geochronology remains challenging because it requires maintenance of a clean lab with ultra-low Pb background levels, constant monitoring of mass spectrometers and potential interferences, and considerable skill. But it is worth the effort because it...
produces dates with the highest precision of any U-Pb technique or other isotopic dating method. Most U-Pb dates published today are acquired by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), which is less costly than TIMS, has rapid throughput, and offers spatial control (typically ~30-50 micron scale), but usually with precision of >1%, which does not provide the resolution that some geologic problems demand. Herein, we describe recent examples where improved accuracy (concordance) and precision in U-Pb ID-TIMS dating has led to proposed revision of the geological development of well-known mineral deposits, or provided an exacting temporal correlation between cratons to target potential mineral exploration sites.

2 Examples of mineral deposits with proposed geological re-interpretations based on field observations and modern U-Pb zircon ages

2.1 Bushveld Complex, South Africa

The archetypal mafic-ultramafic Bushveld Layered Complex of South Africa contains the richest chromium and platinum group element deposits on Earth. Studies of its formation influence our basic concepts of how igneous bodies crystallize and magmatic ore deposits form. No consensus exists on the details of its formation, but it is generally assumed that the layered rocks represent an upward-aggrading pile of crystals that were deposited on the floor of a vast long-lived, repeatedly replenished magma chamber (Wagner 1929; Cameron 1980; Kruger 2005). Recently, we reported new U-Pb geochronological results on pyroxenites and gabbronorite from the Upper Critical Zone and Lower Main Zone of the Rustenburg Layered Suite of the complex (Mungall et al. 2016). Resolution of the ages of discrete layers required uncertainties of ~200 Kyrs on 2.05 Ga rocks, or ~0.01% precision. Our results demonstrate that there is an age reversal in the lower part of the Upper Critical Zone with the UG1 pyroxenite being slightly older (2057.04 ± 0.15 Ma zircon and 2057.24 ± 0.29 Ma baddeleyite) than the underlying, discrete, MG2 (2056.84 ± 0.15 Ma zircon) and MG2 (2056.48 ± 0.20 Ma zircon) pyroxenite layers (see Fig. 1). These results therefore suggest that at least part of the Rustenburg Layered Suite formed by lateral injection of sills into pre-existing cumulates, an idea previously suggested by Truter (1955), Lee and Butler (1990), Mitchell and Scoon (2007, 2012). This conclusion was based on field observations in combination with the U-Pb ID-TIMS ages, and the textural-chemical character of partial melts of the host gabbronorite. The study forces us to reconsider a long-held interpretation of fundamental igneous processes of how layered mafic intrusions form, and therefore on processes by which associated mineral deposits are generated.

Figure 1. Schematic chronostratigraphy of lithologies intersected by diamond drill hole TF3 in the Western Lobe of the Rustenburg Layered Suite, Bushveld Complex, South Africa. Weighted mean $^{207}$Pb/$^{206}$Pb zircon and baddeleyite ages are shown (BR is Bastard Reef; MR is Merensky Reef; UG2, UG1, MG2-4 are chromitites; LCZ is Lower Critical Zone; UCZ is Upper Critical Zone; MZ is Main Zone). Crosses in the section show locations of dated samples. Error bars show 2s errors. Figure from Mungall et al. (2016).

2.2 Cape Smith belt, Québéco

The Cape Smith belt of northern Québec hosts the Raglan Ni-Cu-PGE sulphide ore district, among the richest in the world, and is another example of where field evidence and high precision dates support a re-interpretation of a long-held view of the geology of the area. Here, a generally north-dipping sequence of volcanic and sedimentary rocks has long been viewed as a multiply-imbricated thrust pile (see Fig. 2a). In broad outline, from south to north, the (tectono) stratigraphy comprises autochthonous to paraautochthonous lower Povungnituk sedimentary rocks, a thick pile of Povungnituk basaltic lavas, additional sedimentary rocks, numerous mafic-ultramafic sills, more Mg-rich and primitive Chukotat volcanic rocks, further sedimentary panels, and a complex of overlying tectono-
Formation at the top of Povungnituk Group and also the around 1883 Ma. Sills of this age cut the Nuvilik sedimentary rocks, from the base of the Povungnituk Group; and 3) overlain, along a regional thrust contact, by the volcanic dominated and more primitive lavas of the Chukotat Group (e.g., St-Onge et al. 2000). Multiple thrusts have been interpreted based primarily on the reapparance of clastic sedimentary rocks in the volcanic-dominated pile. If these tectono-stratigraphically higher panels of clastic sedimentary rocks indeed represent structural repetitions of lower Povungnituk sedimentary rocks, from the base of the stratigraphic section, then such thrusts are required. However, as shown in Figure 2b, an alternative interpretation is that many of the higher sedimentary intercalations, particularly the mostly deep water Nuvilik Formation, are unique stratigraphic units, each with their own character, rather than structural repetitions.

Our new U-Pb ID-TIMS ages on differentiated mafic-ultramafic sills that intrude the critical part of the sequence (i.e., above and below the Raglan horizon), show that most, if not all, were intruded in a short time interval around 1883 Ma. Sills of this age cut the Nuvilik Formation at the top of Povungnituk Group and also the Chukotat Group. The Cross Lake sill, which has a previously determined anomalously older age of 1918+9/-7 Ma (Parrish 1989), has been re-dated in this study using single chemically abraded zircon grains and can now also be included in this group (preliminary 1882.4 ± 1.5 Ma age). The main “Footwall Gabbro” sill below one of the main Ni-sulphide ore bodies at Raglan and a sill that intruded above some of the main ore lenses within the Chukotat Group also give this age.

Some of the main Ni-sulphide ore lenses at Raglan occur in thermo-mechanically eroded komatiite lava channels that have eroded down into the Nuvilik Formation turbidites and mudstones, and into the top of the Footwall Gabbro sill (Lesher 2007), thus welding the Chukotat Group lavas to the underlying Nuvilik Formation and therefore the Povungnituk Group, which indicates a stratigraphic rather than thrust contact (Bleeker and Ames 2017, and references therein). The similarity of the sills both below and above the Povungnituk-Chukotat boundary support a stratigraphic relationship along this first order contact, and their ages bracket the onset of Chukotat magmatism and ore formation along the Raglan horizon to a ~1.2 Myr interval at ca. 1883-1882 Ma. Given that the mafic-ultramafic sills bracket the onset of komatititic volcanism and are spatially correlated, they must be part of a (proximal?) feeder system that gave rise to the Chukotat lava pile and its contained Ni-sulphide endowment.

The Nuvilik Formation turbidites and mudstones in the footwall of the Raglan horizon represent deep water sediments deposited after the Povungnituk magmatic event, probably during thermal subsidence following a first phase of rifting. The sulphidic mudstones at the top of the Nuvilik Formation provided the local sulphide source for the Raglan horizon ore bodies (Lesher 2007; Mungall 2007; Bleeker and Ames 2017).

3 Improved dating of the LIPs record and implications for plate reconstructions

Baddeleyite (ZrO₂) in dykes and sills is an essential, widely used primary geochronometer for establishing the timing of mafic igneous events. It occurs widely among mafic-ultramafic rocks, from alkalic compositions to quartz-saturated tholeitic or even intermediate compositions. Examples of inherited baddeleyite are extremely rare, which is an advantage over co-occurring zircon in these rocks. But it is less robust during post-crystallization deformation and metamorphism. Before eventual break-down, it commonly develops thin zircon overgrowths (Heaman and LeCheminant 1993), which adds significantly to the complexity of the U-Pb systematics. At high metamorphic grade, progressive recrystallization to granular zircon is common (e.g., Davidson and van Breemen 1988). Presently, there is no effective pre-treatment that eliminates or reduces Pb loss in baddeleyite (see Rioux et al. 2010) and most U-Pb baddeleyite results indicate some Pb loss (~0.5-2.5% Pb loss), often with no single well-defined Pb-loss line, rendering a unique upper intercept age difficult. In rocks that contain both baddeleyite and magmatic zircon, the mineral of choice is zircon. Previously, mechanical air abrasion on zircon from mafic rocks was not feasible due to their often delicate, platy habit. But with chemical abrasion on such grains, reproducible and concordant results can be expected. In testing paleo-geographic reconstruction, i.e. among now dispersed cratonic fragments, we have focussed our efforts during sample collection on targeting differentiated portions of dykes and sills with the specific intent of recovering zircon. Through this effort we have correlated the Wind River dykes on the Wyoming craton with the Biscotasing dykes of the southern Superior craton to better than ~0.05% (or ~1 Myr). Improved precision has helped provide an exacting correlation, first proposed by Roscoe and Card (1993) based on stratigraphic correlations, and further refined using dyke swarm orientations by Ernst and Bleeker (2010). Global scale correlation of multiple extensive dyke swarms using highly precise ages at the typical duration of ~1 Myr of large igneous province events sets the stage for a fully integrated geological and metallogenic compilation of the joined cratons.

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Figure 2. Tectono-stratigraphic columns for the Raglan area, Cape Smith Belt. a) Previous interpretation of a strongly thrust-imbricated tectono-stratigraphic pile, with north-dipping thrust bringing back lower Povungnituk sedimentary rocks at various levels throughout the pile (after St-Onge and Lucas, 1993). The main Povungnituk-Chukotat Group contact was also considered a regional thrust. b) Revised interpretation based on the current study, with considerably fewer thrusts (c.f. Mungall 2007). Rectangles contain U-Pb ages (in Ma). Bold red curve schematically highlights the strong concentration of the Ni sulphide endowment at or near the basal contact of the Chukotat Group, along which komatiitic lavas (Chukotat Group) overlie greywackes and sulphidic mudstones of the Nuvilik Fm, (top of the Povungnituk Group).
Insights into timing of mineralization in the Neves-Corvo VMS deposit (Iberian Pyrite Belt)

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Abstract. Zircon geochronology in the rhyolite units related with the Neves-Corvo VMS deposit combined with chemostratigraphy-based classification indicates three different volcanic stages acting from late Famennian to Tournaisian times. The first two are space-related and with similar volcanic facies but chemically distinct; the third episode, chemically akin to the second, but with coherent volcanic facies, lasted longer until Tournaisian times. Overall felsic volcanic activity associated with the Neves-Corvo VMS deposit spanned the range of ca. 363-349 Ma within a time span of 14 Ma. The late Famennian-early Tournaisian zircon ages (ca. 363-357 Ma) of the three main rhyolites confirm the exploration potential of the main ore mineralization given by palynological data of enclosed black shales. The younger volcanic activity during mid-late Tournaisian (~350 Ma) is exclusive of Rhyolite 3 unit and is probably related to a late syn-deformation mineralizing stage. This late input of a magmatic fluid component in the Neves-Corvo system could contribute to the late anomalous Cu-enrichment.

1 Introduction

The Neves-Corvo mine is a world class VMS deposit located in the Iberian Pyrite Belt (IPB), in Portugal, with seven massive sulphide orebodies hosted in a Volcanic-Sedimentary Complex (VSC).

Copper-rich ores reserves are around 26 Mt with 2.7% Cu, 0.7% Zn, 0.2% Pb and 35 g/t Ag while Zn-rich ores are 23.5 Mt with 7.2% Zn, 0.4% Cu, 1.6% Pb and 67 g/t Ag (Lundin Mining 2016). The deposit, currently in operation for Cu, Zn and Pb, has, in some places, unusually high Cu and Sn contents (76,700 t of Sn were produced between 1990 and 2006).

The orebodies occur at the top of the lower VSC sequence, either in the felsic volcanics or in the black shales of the Neves Fm. (late Devonian, Oliveira et al. 2013), suggesting that the ore-forming hydrothermal activity occurred at a late stage of effusive/intrusive rhyolitic magmatism, and a strong genetic relationship between ore-forming process and the volcanic activity.

Insights into timing of volcanism and mineralization in the IPB can be obtained through the study of zircons present in the felsic volcanic rocks related to VMS (e.g. Barrie et al. 2002; Rosa et al. 2009; Oliveira et al. 2013).

The aim of the present work is to correlate U/Pb zircon dating results of felsic volcanics in Neves-Corvo key-horizons (Pereira et al. 2014 unpublished; Solá et al. 2015) with the high resolution chemical stratigraphy of the same felsic volcanics (Barrett 2008, unpublished; Rosa et al. 2009) in order to assess the exploration potential of each volcanic event. The obtained dataset is very promising and allowed to determine with more precision the different volcanic events which contributed to the sulphide ore formation and also to confirm the exploration potential of the main ore mineralization episode.

2 Geological setting

The Neves-Corvo/Rosário area lithostratigraphic sequence (Fig.1; Oliveira et al. 2004, 2013) includes the IPB basement, the Phyllite-Quartzite Group (PQ) whose top is Famennian in age (base unknown), followed by the VSC, of late Famennian to mid-late Visean age. The VSC comprises a lower sequence of mafic volcanic rocks, felsic rocks (mainly rhyolites), dark shales (Neves Fm.) and intercalations of black shales, carbonate nodules and volcanogenic sediments (Corvo Fm.), hosting VMS deposits on top with an upper layer of jaspers and carbonates, and an upper sequence with several shale-based formations (Graça, Grandaos, Borra de Vinho, Godinho and Brancanes Fms.) with dark, pyritic purple/green shales, volcanogenic sediments and occasional felsic volcanic rocks and intrusive basic rocks (Fig. 1). The lower and upper VSC sequences are separated by the so-called Tournaisian stratigraphic hiatus (Oliveira et al. 2004, 2013; Pereira et al. 2008). The VSC is overlain by the flysch sediments of the Mértola Fm. (upper Visean).

The Neves-Corvo stratigraphy is conditioned by a complex tectonic setting. The main structure is a SE-dipping SW-vergence Variscan antiform containing tectonic nappe package repetitions due to low-angle thrust faults (Silva et al. 1990; Oliveira et al. 2013; Inverno et al. 2015).
Stratigraphic constraints of the VSC in the IPB and particularly in the Neves-Corvo mine region are given by detailed studies of palynomorph assemblages in the VSC shale sequence (Oliveira et al. 2004, 2013; Pereira et al. 2008). These high resolution studies showed that the main ore mineralization episode in Neves-Corvo is enclosed in the uppermost Famennian black shales, spatially associated with volcanic rocks (late Strunian miospore biozone LN, 360.7±0.7-362 Ma). Late Strunian age (uppermost Famennian substage, Stree et al. 2006), therefore, becomes an important key stratigraphic horizon and an exploration guide in the IPB region considering that the same age was determined in deposits like Lousal, Caveira, Montinho and Aznalcollar (Pereira et al. 2008; Matos et al. 2011).

3 Chemical stratigraphy of rhyolites

A geochemical program carried out by Lunding Mining allowed access to an extensive database on main oxides, major and minor elements of rhyolite units in Neves-Corvo area (Barrett 2008, 2012 unpublished data). From this, an attempt of genetic classification of the main rhyolite units interpreted from the oldest (Rhyolite 0) to the youngest (Rhyolite 6), was performed based on oxide and major/minor element ratios. Rhyolites 0 to 4 occur in the lower VSC sequence while Rhyolites 5 and 6 are scarce, distal and intra-sedimentary on the upper VSC sequence and will not be considered here.

Figure 1. General geology of Neves-Corvo area, showing the ore bodies and the studied drill-holes (Ad. Oliveira et al. 2013).

Rhyolite 1 rests above PQ Fm. and below the Corvo volcanic unit located in the footwall of the massive ore mineralization episode in Neves-Corvo is enclosed in the uppermost Famennian black shales, spatially associated with volcanic rocks (late Strunian miospore biozone LN, 360.7±0.7-362 Ma). Late Strunian age (uppermost Famennian substage, Stree et al. 2006), therefore, becomes an important key stratigraphic horizon and an exploration guide in the IPB region considering that the same age was determined in deposits like Lousal, Caveira, Montinho and Aznalcollar (Pereira et al. 2008; Matos et al. 2011).

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Overall, the volcanic facies show a change from volcaniclastic transported facies, with fiamme, quartz-feldspar crystals and lithic fragments (Rhyolite 1 and 2) to massive-coherent facies (Rhyolite 3 and 4).

Rhyolite 1 rests above PQ Fm. and below the Corvo Fm. shales being Famennian in age by palynomorph dating (Oliveira et al. 2004). Rhyolite 2 forms the felsic volcanic unit located in the footwall of the massive ore lenses and related stockworks, commonly presenting intense hydrothermal alteration. This volcanic unit is located over the Corvo shales and underneath the Neves shales.

Rhyolites 1 and 2 have both transitional magmatic affinities (tholeiitic to calc-alkaline) but derived from different volcanic sources in view of the geochemical data (Barret, 2008, 2012, unpublished). Therefore, one might expect to have two volcanic episodes from two different volcanic centers acting in the same time span, relatively close spaced along distensive structures (grabens), both generating chemically distinct volcaniclastic deposits.

Rhyolite 3 occurs generally in the hanging wall of the mineralization and does not superimpose Rhyolites 1 and 2, suggesting different spatial distribution; it may locally occur immediately below massive sulfides (Rosa et al. 2008), including some stockwork veins and chlorite alteration. Rhyolite 3 locally overlies PQ Fm. directly and can be coeval with footwall Rhyolite 2 due to the presence of interbedded late Strunian Neves shales. Rhyolite 3 has chemical similarities with Rhyolite 2, but their sills and flows complex formed over a paleoridge in the depressions of which previous rhyolites (and massive sulfides) were formed.

Apparentlly, Rhyolites 1, 2 and 3 are all present in the same section only when they are out of sequence; in normal sequence at least one is absent.

Rhyolite 4 is not mineralized and not known in the Neves-Corvo mine. It is referred by Barret (2008, unpublished) in the surrounding mine east, southeast and west areas, in the same stratigraphic level as Rhyolite 3.

Palynological dating on interbedded shale layers indicates that Rhyolite 1 corresponds to a late Famennian age (Pereira et al. 2014, unpublished) while Rhyolite 2 should have formed in the latest Famennian (Strunian); Rhyolite 3 (and 4?) installation probably started still during Famennian times and lasted till Viséan.

The chemostratigraphy reveals, from the lower to upper units of the VSC lower sequence, an evolution from a tholeiitic-calc alkaline magma (Rhyolites 1 and 2) to a calc alkaline-medium alkaline (Rhyolite 3) and then to an alkaline magma (Rhyolite 4). This temporal evolution from tholeiitic to alkaline is the same observed in the mafic rocks of the bimodal sequence of VSC, where alkaline basalts are restricted to the upper part of the volcanic complex (Munhá 1983). Overall, the bimodal nature of VSC, with continental tholeites and the alkaline character of some lavas, with only minor amounts of intermediate rocks, points to a consensual genetic extensional tectonic setting of the VSC (Munhá 1983).

The distensive regime has evolved to a complex tectonic setting (transpressive regime, Silva et al. 1990) that it is locally expressed by folded low-angle thrusts with stacked lithological packages repetitions and late vertical faults. This tectonic setting can explain Rhyolite 2 and 3 duplications in the mine area. The change to a more alkaline character of magmas suggests, at the time of Rhyolite 4 formation, the rift was developing to a continental margin environment, and consequently, with less favorable conditions for the VMS formation.
4 U/Pb zircon dating results

Within a multidisciplinary joint research program (IPBVECTORS) between LNEG (Portuguese Geological Survey) and Lundin Mining, some drill-holes were selected and studied with multiple purposes, including U/Pb dating, palynological studies, volcanic facies identification and geochemical surveys.

A total of 16 rhyolite samples from 10 drill-holes (Fig. 1) were processed for zircon U/Pb laser ablation ICPMS dating, using analytical protocol of Frei and Gerdes (2009) and lab standard procedures of Mange and Maurer (1992). The samples covered Rhyolites 1, 2 and 3. Zircon ages (Table 1), are given by the concordia age of the youngest age fraction, inferred as the emplacement/crystallization age. The overall emplacement of the three main rhyolite types in Neves-Corvo deposit occurs in the range of ca. 363-349 Ma within a time span of intermittent volcanic activity of 14 Ma.

Table 1. U/Pb ages in zircons from Neves-Corvo rhyolites collected in drill-core samples

<table>
<thead>
<tr>
<th>Sample (Hole-Depth)</th>
<th>Rhyolite (Code)</th>
<th>Age (Ma)</th>
<th>Age error (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC26-368.3</td>
<td>R1</td>
<td>359.8</td>
<td>1.9</td>
</tr>
<tr>
<td>SE22A-773</td>
<td>R1</td>
<td>359.3</td>
<td>3.1</td>
</tr>
<tr>
<td>SC26-854.65</td>
<td>R1</td>
<td>358.8</td>
<td>2.1</td>
</tr>
<tr>
<td>SI02-301.5</td>
<td>R2</td>
<td>363.4</td>
<td>2.6</td>
</tr>
<tr>
<td>CA1104-1115.6</td>
<td>R2</td>
<td>361.4</td>
<td>3.2</td>
</tr>
<tr>
<td>CA1104-1073.6</td>
<td>R2</td>
<td>360.5</td>
<td>2.1</td>
</tr>
<tr>
<td>PSL48A-1-1013</td>
<td>R2</td>
<td>360.0</td>
<td>2.1</td>
</tr>
<tr>
<td>NE06A-455</td>
<td>R2</td>
<td>358.3</td>
<td>3.6</td>
</tr>
<tr>
<td>CA1104-1070.2</td>
<td>R2</td>
<td>357.5</td>
<td>3.0</td>
</tr>
<tr>
<td>SM24-610</td>
<td>R3</td>
<td>362.8</td>
<td>4.1</td>
</tr>
<tr>
<td>NF32A-972</td>
<td>R3</td>
<td>361.1</td>
<td>3.4</td>
</tr>
<tr>
<td>SU22-468</td>
<td>R3</td>
<td>356.9</td>
<td>3.5</td>
</tr>
<tr>
<td>PSN44-928</td>
<td>R3</td>
<td>352.7</td>
<td>1.9</td>
</tr>
<tr>
<td>PSN44-845.5</td>
<td>R3</td>
<td>351.5</td>
<td>3.2</td>
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</tr>
<tr>
<td>PSN44-845.9</td>
<td>R3</td>
<td>349.5</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Figure 2 shows the age for the 16 samples sorted by rhyolite type. Weighted average means have been calculated with 95% confidence and the maximum probability (75-94%) among consecutive age samples to facilitate interpretational trends. Rhyolite 1 shows stable ages around ca. 359 Ma; Rhyolite 2 can be interpreted with three age means ranging from ca. 363 to ca. 358 Ma, but not significantly different from Rhyolite 1; Rhyolite 3 shows the larger age span from ca. 362 to ca. 350 Ma. A general trend might be visible among the three rhyolites being rhyolite 1 and 2 of similar age while rhyolite 3 is younger (or has a younging trend). On the other hand, it is clearly seen that late Famennian-early Tournaisian age samples (ca. 363-357 Ma) include the three types of rhyolites while mid-late Tournaisian samples (ca. 353-349 Ma) are exclusively Rhyolite 3 type.

The U/Pb ages of Table 1 can be grouped into two sets which may reflect two different pulses/events with a small gap between them (Fig. 2; Solá et al. 2015). The older event ca. 363-357 Ma (late Famennian-early Tournaisian) confirms the exploration potential of the Neves Fm. black shales as the MS productive horizon (Oliveira et al. 2013). These black shales host Rhyolite 2. The younger pulse ca. 353-349 Ma, within middle Tournaisian ages is undetected by the fossil record of the VSC sedimentary rocks due to the absence of Tournaisian sedimentary sequences in the Neves-Corvo region (the so-called Tournaisian stratigraphic hiatus can be the result of non-preservation of the organic matter in the sediments or erosion). This later volcanic event, exclusive in Rhyolite 3 could suggest a late mineralizing stage (probably Tourainian age) and/or a syn-deformation episode (Solá et al. 2015).

Inherited zircons from the late Famennian-early Tourainian episode are present in some of the middle Tournaisian rhyolites, also with Devonian and older inheritance. Most concordant inherited ages are Devonian, suggesting that magmatic activity in the Neves-Corvo region took place roughly continuously since the Lower Devonian to Tournaisian times (~415-350 Ma).

In addition, the range of inherited U/Pb ages indicates that VS felsic volcanism derived from felsic magmas, resulting from melting of pre-existent rocks, probably derived from the fusion of PQ Fm., which is beneath the VSC, as formerly suggested by Rosa et al. (2009). Moreover, the Hf protolith model ages of VSC and PQ are consistent with this hypothesis (Rosa et al. 2009), and according to Jorge et al. (2007) the Pb in the MS ore could have been derived from the PQ sediments.

5 Conclusions and final remarks

i. In Neves-Corvo there are several felsic units within the VSC which are chemically unique, stratigraphically different but not necessarily age-distinct, in some cases...
coupled by possible tectonic repetitions.

ii. The overall felsic volcanic activity associated with Neves-Corvo VMS deposit occurs in the range of ca. 363-349 Ma, that is, within a time span of 14 Ma.

iii. Geochemistry and zircon dating strongly suggest three volcanic stages acting during late Famennian-early Tournaisian times that result in three lithostratigraphic units - Rhyolite 1 to 3. The first two are space-related but chemically distinct although with similar volcanic facies; the third, chemically similar to the second, but with different volcanic facies, lasted longer until mid-late Tournaisian times.

iv. The ca. 363-357 Ma zircon ages confirm the exploration potential of the main ore mineralization given by palynological data of Neves black shales (LN biozone, Strunian), which includes on their footwall the Rhyolite 2. This hydrothermal system was coeval with sedimentation of black shales in an anoxic environment, where paleogeographic conditions were favorable to fluid circulation and VMS deposits formation (Matos et al. 2011).

v. The younger pulse, ca. 353-349 Ma, mid-late Tournaisian, is known to date as exclusive of Rhyolite 3. This Rhyolite 3 episode started during late Famennian times too and even includes inheritance from the older pulse/event. It lasted longer but the rock is much less hydrothermally altered than Rhyolites 1 and 2, has occasional stockwork veins and it could have been emplaced into the Neves shales after the VMS mineralization was deposited.

vi. This later volcanic activity at ~350 Ma is probably related to a late mineralizing stage at the same age and/or to syn-deformation (Solá et al. 2015) associated with tectonic inversion of the basin during Variscan deformation, which disrupted the IPB stratigraphy and explains the so-called Tournaisian stratigraphic hiatus.

vii. The geochemical characteristics of the Sn and Cu mineralization in Neves-Corvo, namely the Sn and Cu enrichment and late anomalous Cu-enrichment, leading to enriched ore in bornite and in sphalerite–tetrahedrite–tennantite, imply the involvement of additional metal sources (likely magmatic) in the ore-forming system throughout time, under different thermochemical constraints (Gaspar 2002; Relvas et al. 2006).

viii. Late input of a magmatic fluid component in the Neves Corvo system has already been suggested by Pinto et al. (2005) and Jorge et al. (2007) based in ore-mineralogical and lead isotope studies, respectively.

ix. The geochronology suggests that Neves-Corvo late Famennian-early Tournaisian hydrothermal system may have been reactivated during the middle Tournaisian effusive volcanism. This explains the Cu enrichment due to mechanical and fluid-assisted tectonometamorphic remobilization processes and accounts for the formation of extremely high grade ore shoots in the deposit (Relvas et al. 2006).

x. This study highlights the significance of comprehensive, high precision U–Pb geochronology, with further data expected to help the local understanding of Neves-Corvo and IPB geology. Critical geological time periods such as the late Famennian-early Tournaisian and mid-late Tournaisian are presently important exploration guide horizons.

Acknowledgements

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LA-ICP-MS Rb-Sr dating of LCT rare-element pegmatites and associated rocks of Leinster, Ireland

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Abstract. High technology metals such as lithium and tantalum are commonly hosted in pegmatites, leading to renewed interest in understanding their origin. Obtaining accurate and precise results from pegmatites can be challenging. We have applied a newly developed laser ablation Rb-Sr dating method using reaction gases in a quadrupole ICP-MS to spodumene pegmatites and country rocks, late Caledonian granodiorite and Ordovician schist, in southeast Ireland. Rb-Sr isochron ages and initial $^{87}Sr/^{86}Sr$ ratios obtained are: around 413 Ma and 0.7109 ± 49 to 0.8348 ± 82 for lithium pegmatites; around 413 Ma and 0.7054 ± 50 to 0.7102 ± 28 for barren pegmatites; 420.6 ± 8.4 Ma and 0.7068 ± 28 for granodiorite; 406.5 ± 5.8 and 0.7160 ± 58 for schist. The method is sufficiently accurate and precise to date pegmatites. Ages obtained are consistent with the emplacement age of the Leinster Granite. Age constraints from schist within a pegmatite exomorphic halo are shown to be a good tool to determine pegmatite age. Highly variable initial $^{87}Sr/^{86}Sr$ ratios in spodumene pegmatites emplaced near schists show evidence for country rock contamination.

1 Introduction

Rare-element granitic pegmatites are well known as significant sources of various commodities, including the increasingly important high-technology metals (e.g. Li and Ta). As the range of use of such resources grows, the interest in understanding the mechanisms and timing of formation of these unusual rocks also increases.

Pegmatite age constraints are important to better understand petrogenetic processes involved in the formation of ore minerals that they host, but their geochemical complexity often brings challenges to obtaining precise and accurate ages (McCauley and Bradley 2014). The Rb-Sr isochron method is, in theory, adequate to date pegmatites as they commonly have high Rb minerals. In addition, initial $^{87}Sr/^{86}Sr$ ratios may yield valuable source indications and other petrogenetic constraints. A recently developed in situ Rb-Sr dating technique (Zack and Hogmalm 2016; Hogmalm et al. 2017) overcomes the main problems usually associated with the method, using data acquired with high spatial resolution, resulting in accurate and precise ages. We present the results of this technique applied to LCT (Li,Cs,Ta) rare-element pegmatites, currently being actively explored for Li, and their country rocks in south Leinster, Ireland.

2 Geological setting and background

The Leinster pegmatite belt (Fig. 1) is a system of meter-scale dykes oriented NE-SW that occur along the eastern margin of the Tullow Lowlands pluton, the largest of the S-type two-mica granitic plutons of the late Caledonian Leinster Granite batholith. Pegmatite dykes are associated with the East Carlow Deformation Zone (ECDZ, McArdle and Kennedy 1985) and intrude the Leinster Granite, minor associated granitic intrusions and Ordovician metasedimentary rocks of the Ribband Group (Graham and Stillman 2009). Mineralized pegmatites are spodumene-bearing (lithium pyroxene, LiAlSi$_2$O$_6$) and occur spatially associated with barren pegmatites.

Ages of emplacement for the different rock types of the Leinster Granite range from approximately 405 to 418 Ma according to U-Pb ages in monazite and zircon (O’Connor et al. 1989; Fristchle 2016). A published Rb-Sr isochron age using whole-rock samples of lithium pegmatite yields 402.3 ± 7.5 Ma (data from O’Connor et al. 1991 using the recommended $^{87}$Rb decay constant of Villa et al. 2015). Taken with imprecise but similar initial $^{87}Sr/^{86}Sr$ ratios for granitic rocks and pegmatites (O’Connor et al. 1991; Mohr 1991), the Li-rich pegmatitic fluids were tentatively explained as residual melts from extreme fractional crystallization of Leinster Granite magma (Whitworth and Rankin 1989; O’Connor et al. 1991; Whitworth 1992), but an origin by direct anatexsis of metasediments has been considered another possibility based on results of geochemical modelling (Barros and Menuge 2016).

3 Methodology

Around 200 m of drill core samples that crosscut pegmatites and country rocks in two localities, Aclare and Moylisha (Fig. 1), were petrographically analysed. Representative samples were selected for Rb-Sr isotope analysis in the Microgeochemistry Laboratory at the University of Gothenburg, using an Agilent 8800QQQ with combined ESI 213NWR (TwoVol2) laser ablation system. Rb and Sr were separated using reaction gases (e.g. O$_2$, SF$_6$ and N$_2$O) in a reaction cell between the two
ICP-MS quadrupoles, allowing measurements before and after reactions, according to the routine developed by Zack and Hogmalm (2016) and Hogmalm et al. (2017). Glass standards NIST SRM 610, 612 and BCR-2G and nanoparticulate pressed powder tablets of phlogopite Mica-Mg and muscovite Högsbo-Ms were used for calibration and analysed systematically between samples. After data acquisition, the software Glitter was used for signal revision and to generate count rates for the masses of interest. Isotope ratios were calculated using transformation factors obtained from the standards for both low Rb and moderate Sr (610, 612 and BCR-2G) and high Rb and low Sr (Mica-Mg) phases and drift corrections applied when needed. Isotope ratios were then used to obtain isochron ages with Isoplot (Ludwig 2008), using the decay constant of Villa et al. (2015).

4 Results

4.1 Characterization

Pegmatite dykes are 3 to 20 metres wide and can be divided into border zone (≤30 cm thick), intermediate zone (1-10 m) and central zone (1-2 m), all spodumene-bearing. The primary mineral assemblage is: spodumene, quartz, muscovite, K-feldspar and minor spessartine and apatite. Albitization is common and characterized by areas dominated by saccharoidal albite with a wide range of accessory minerals, including muscovite, quartz, beryl, cassiterite, columbite-tantalite, sphalerite, apatite and lithiophilite-triplihilde, occurring in pegmatite dykes only and often associated with alteration of spodumene to fine-grained green mica. Pegmatites with similar mineralogy, but spodumene-free, commonly crosscut granodiorite in some localities (e.g. Moylisha).

Spodumene pegmatites are emplaced in granitic rocks of the Tullow Lowlands pluton in Moylisha and in the contact zone between the pluton and hanging wall schist in Aclare. Two types of granitic rocks occur in the areas studied: porphyritic granodiorite, composed of quartz, labradorite, microcline, biotite and less than 5% muscovite; and foliated granodiorite, with rarer microcline and higher amounts of biotite and muscovite. These two rock types are also common in other plutons of the batholith. The schist is mainly composed of chlorite, muscovite, plagioclase and quartz, with accessory ilmenite, arsenopyrite, andalusite, garnet and staurolite, indicating low pressure amphibolite facies contact metamorphism in the aureole of the Tullow Lowlands Pluton. Tourmalinization is common in both country rocks in the immediate contact zone with lithium pegmatites.

4.2 Rb-Sr dating

Results obtained, 2σ errors and related isochron statistical analysis are presented on Table 1.

Table 1. Summary of results obtained in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position</th>
<th>Zone (*)</th>
<th>Age Ma</th>
<th>Initial 87Sr/86Sr</th>
<th>MSWD</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li pegmatite</td>
<td>Dyke 1</td>
<td>UB</td>
<td>406.8 ± 2.3</td>
<td>0.7221 ± 35</td>
<td>0.57</td>
<td>20</td>
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<tr>
<td>Li pegmatite</td>
<td>Dyke 1</td>
<td>LB</td>
<td>436.7 ± 4.2</td>
<td>0.7058 ± 49</td>
<td>1.00</td>
<td>10</td>
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<tr>
<td>Li pegmatite</td>
<td>Dyke 2</td>
<td>UB</td>
<td>412.0 ± 3.6</td>
<td>0.7654 ± 70</td>
<td>2.10</td>
<td>7</td>
</tr>
<tr>
<td>Li pegmatite</td>
<td>Dyke 2</td>
<td>LB</td>
<td>431.8 ± 3.2</td>
<td>0.7102 ± 28</td>
<td>1.11</td>
<td>19</td>
</tr>
<tr>
<td>Li pegmatite</td>
<td>Dyke 3</td>
<td>C</td>
<td>424 ± 11</td>
<td>0.7054 ± 70</td>
<td>2.10</td>
<td>7</td>
</tr>
<tr>
<td>Li pegmatite</td>
<td>Dyke 4</td>
<td>C</td>
<td>413.2 ± 2.6</td>
<td>0.7102 ± 28</td>
<td>1.11</td>
<td>19</td>
</tr>
<tr>
<td>Li pegmatite</td>
<td>Dyke 5</td>
<td>UB</td>
<td>412.6 ± 3.7</td>
<td>0.7629 ± 83</td>
<td>0.60</td>
<td>7</td>
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<tr>
<td>Li pegmatite</td>
<td>Dyke 5</td>
<td>LB</td>
<td>404.0 ± 5.6</td>
<td>0.7381 ± 65</td>
<td>0.75</td>
<td>15</td>
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<tr>
<td>Li pegmatite</td>
<td>Dyke 6</td>
<td>UB</td>
<td>429.5 ± 28</td>
<td>0.7963 ± 56</td>
<td>1.70</td>
<td>19</td>
</tr>
<tr>
<td>Li pegmatite</td>
<td>Dyke 6</td>
<td>LB</td>
<td>431.5 ± 25</td>
<td>0.7068 ± 56</td>
<td>0.60</td>
<td>7</td>
</tr>
<tr>
<td>Li pegmatite</td>
<td>Dyke 7</td>
<td>C</td>
<td>416.3 ± 2.5</td>
<td>0.7400 ± 51</td>
<td>1.00</td>
<td>10</td>
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<tr>
<td>Li pegmatite</td>
<td>Dyke 7</td>
<td>LB</td>
<td>420.6 ± 3.0</td>
<td>0.7102 ± 49</td>
<td>1.00</td>
<td>11</td>
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<tr>
<td>Granodiorite</td>
<td>FG</td>
<td>354.2 ± 6.4</td>
<td>0.7054 ± 75</td>
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<tr>
<td>Granodiorite</td>
<td>FG</td>
<td>384.2 ± 8.1</td>
<td>0.7054 ± 75</td>
<td>1.00</td>
<td>14</td>
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</tr>
<tr>
<td>Granodiorite</td>
<td>FG</td>
<td>407 ± 22</td>
<td>0.7054 ± 75</td>
<td>1.00</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

n = number of data points. (*) For pegmatites: UB = upper border, LB = lower border, I = intermediate zone, C = central zone. For country rocks: FG = foliated granite, H = within pegmatite halo, T = tourmalinized.

To calculate Rb-Sr isochron ages for spodumene pegmatites, primary muscovite, K-feldspar and apatite that are interpreted as contemporaneous to spodumene, as well as saccharoidal albite and associated fine-grained muscovite, were analysed. All isochrons were constructed from minerals extracted from small hand samples. Ages obtained vary from 404.4 ± 5.6 to 424 ± 11 Ma for spodumene and barren pegmatites. For analyses with n = 7 to 20, MSWD between 0.25 and 2 is considered acceptable. Initial 87Sr/86Sr ratios are 0.7054 ± 70 and 0.7102 ± 28 for barren pegmatites and between 0.7109 ± 49 and 0.8348 ± 82 for spodumene pegmatites. Figure 2 presents the variation obtained for samples of dyke 6.

Isochron ages for granodiorite (part of the Leinster Granite) and schist (part of the Ribband Group) were obtained by analysis of muscovite, plagioclase, K-feldspar and tourmaline, the last occurring only in contact zones with pegmatite. Ages / initial 87Sr/86Sr ratios obtained are: 420.6 ± 8.4 Ma / 0.7068 ± 28 for granodiorite over 4 m away from the contact with spodumene pegmatite; 384.2 ±
8.1 Ma / 0.7022 ± 69 and 407 ± 22 Ma / 0.7134 ± 75 for granodiorite and 406.5 ± 5.8 Ma / 0.7160 ± 58 for schist, the last three within the halo of a spodumene pegmatite. Some of these isochrons are presented in Figure 3.

5 Discussion

Figure 4 presents a summary of ages obtained in the study. Pegmatite ages suggest emplacement around 413 Ma, with maximum and minimum ages of 420 and 400 Ma considering errors, in agreement with the late Caledonian emplacement of the Leinster Granite. The older foliated granodiorite Rb-Sr age of around 420 Ma is similar to a U-Pb age of 417.4 ± 1.7 Ma obtained by Fritschle (2016) from Northern Pluton foliated granite. Granodiorite samples within the pegmatite exomorphic halo yield a somewhat younger age, but as this rock and pegmatites have been emplaced within a short time period, this can be interpreted as added Rb in granodiorite from pegmatite and consequent increase in the $^{87}\text{Rb}/^{86}\text{Sr}$ ratios in high Rb phases such as muscovite, resulting in a significant decrease in the isochron’s slope and consequently an apparently younger age. This effect can be observed even in granodiorite further from the contact (Fig. 3A), where high Rb muscovite yields an age around 20 Ma younger than low Rb muscovite. This also indicates that the geochemical halo might be much wider than observable through mineralogical changes.

The Rb effect is also present in schist (Fig. 3B), with an age noticeably younger than that accepted (Ordovician). The well fitted isochron suggests that added radiogenic Rb and schist-hosted Sr have been effectively re-homogenized at the scale sampled; the isochron age dates pegmatite emplacement. Dating reset country rocks is therefore a potential tool to constrain or confirm pegmatite emplacement ages, especially where getting precise results from pegmatites is challenging.

As Sr contents in granodiorite and schist are significantly higher than in pegmatites, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained for the country rocks in this study are interpreted as good approximations to the initial ratio of the granodiorite and to the average ratio of the schist metasediments at the time of pegmatite intrusion. Values obtained for granodiorite are similar to the range of model initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at 405 Ma obtained by Mohr (1991) for whole-rock samples of the Leinster Granite’s Northern pluton, between 0.7046 and 0.7106. Similar initial ratios for granodiorite and barren pegmatite indicate a possible common source, but highly variable and generally much higher initial ratios in lithium pegmatites suggest that an additional component more enriched in Rb was involved. The variation observed within dykes in Aclare (e.g. dykes 6 and 7) might result from significant contamination, with radiogenic Sr progressively added from schist to pegmatites in the contact zone, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increasing towards the late crystallized core of the dykes (Fig. 5). Sr isotope ratios in Moylisha samples are lower, likely because these pegmatites are not emplaced near schist.
Saccharoidal albite and associated fine-grained muscovite are satisfactorily fitted in all spodumene pegmatite isochrons, pointing to the same age and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as adjacent pegmatitic minerals. Hence, the albitization process can be inferred to have resulted from Na-rich fluids generated from the crystallizing pegmatites.

![Figure 4](image1.png)

**Figure 4.** Age results obtained for the rocks in Leinster. Age range for lithium mineralization within errors is highlighted in grey and granodiorite and schist samples adjacent to the contact with spodumene pegmatite are circled.

![Figure 5](image2.png)

**Figure 5.** Isotope exchange in contact zone between schist and spodumene pegmatite, with Rb loss and Sr gain in pegmatite and progressive increase of $^{87}\text{Sr}$ and hence initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio towards the core.

6 Conclusions

LA-ICP-MS Rb-Sr dating is an adequate and useful method to date rare-element pegmatites, as they commonly have as primary minerals high-Rb and low-Sr muscovite and low-Rb and high-Sr plagioclase and/or tourmaline. Resulting ages and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have greater precision than previous attempts. This method also provides satisfactory ages for other muscovite-bearing granitic rocks. Additionally, dating of sufficiently older immediate country rocks is shown to be a reasonable alternative to constrain or confirm pegmatite emplacement ages.

Mineralized and barren pegmatites in Leinster are contemporaneous, emplaced at around 413 Ma and crosscutting granodiorite, crystallized at around 420 Ma in both localities, and Ordovician schist in Aclare. The spatial resolution of the method allowed measurements in different zones of various dykes with great textural control, which would be hard to achieve using other methods due to the high heterogeneity of pegmatites. Minerals in the albitized portions point to the same age and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of pegmatitic minerals, suggesting in situ formation as the final stage of pegmatite crystallization. Variation in initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within dykes suggests significant contamination from non-granitic country rocks.

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References


Lu-Hf chronometry and geothermometry of garnet from the gold-bearing sillimanite-garnet-biotite schist at the Borden gold deposit, Chapleau, Ontario

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Abstract. Located at the southern margin of the Kapuskasing Structural Zone, the Borden gold deposit hosts low-grade gold mineralization within upper amphibolite to granulite facies garnet-biotite gneisses (±sillimanite). We here present garnet geothermometry and Lu-Hf geochronology of the gold-hosting rock lithologies to constrain the geological history of the deposit. Garnet-biotite geothermometry yields temperatures ranging from 475°C to 933°C ±50°C. The \(^{176}\text{Lu}_{-176}\text{Hf}\) isotopic internal isochron of garnet fractions and corresponding whole-rock splits (with and without dissolved zircons) from a gneissic unit yields a precise internal isochron age at 2629.0 ± 4.3 Ma (with an initial \(^{176}\text{Hf}/^{177}\text{Hf}\) = 0.281210 ±0.000010 and MSWD = 0.66). The Hf isotopic composition of this gneiss has an initial \(\varepsilon_{\text{Hf}}\) = +4.1 which indicates that the protolith was derived from a long-term depleted (high Lu/Hf) mantle reservoir. Our new results suggest that peak granulite facies metamorphism associated with garnet growth, which pre-dates the gold mineralization, took place ~2629 Ma. This age is consistent with the youngest age population of zircons from the paragneisses which were previously dated in the area. The Lu-Hf chronology of garnet provides thus a better time constraint on the time of peak metamorphism at Borden.

1 Introduction

The Superior Province is one of the oldest cratons in the world. It is hypothesized to have been assembled by the end of the Archean through the accretion of terranes now represented by narrow subprovinces (Corfu and Davis 1992; Moser et al. 2008). The Abitibi and Wawa Subprovinces are interpreted to be the last terranes accreted between 2750-2670 Ma (Corfu and Davis 1992) during northward subduction during the Kenoran Orogeny (Moser et al. 2008).

The Borden gold deposit occurs in the Archean Superior province of the Canadian Shield. It is located within an unconventional setting within the southern margin of the Kapuskasing Structural Zone, a structurally controlled region of granulite and upper amphibolite facies metamorphic rocks. Owing to the high-grade of metamorphism, very little historical exploration was undertaken in the Borden area. In 2010, Probe Mines discovered the multi-million ounce Borden gold deposit within the Borden Lake Belt, an east-striking lithological assemblage, consisting of metasedimentary, felsic and mafic gneisses. An assortment of lithologies, each exhibiting structural and textural variations, are host to gold in various concentrations. There are a few occurrences of visible gold in core but more gold is identified in microstructural analysis. Gold-hosting lithologies on the Borden property are garnet-biotite gneiss (±sillimanite), amphibolite (±garnet), biotite-quartz-feldspathic gneiss and deformed quartz veins. Gold is commonly identified at contacts between unfoliated granulite-facies lithons and surrounding retrograde amphibolite, indicating the significance of retrograde metamorphism to the gold mineralization. Gold mineralization appears to be contemporaneous with retrograde metamorphism of granulite facies lithologies to amphibolite facies and with ductile deformation of the retrograde amphibolite facies units.

Developing a more precise understanding of the petrological and chronological constraints in gold-hosting rocks is critical to establish the metamorphic history and timing of mineralization in ore deposits and their extent. Many traditional systems (U-Pb in zircons, Rb-Sr in amphiboles, K-Ar in feldspar or micas) are not ideal for dating metamorphic rocks or the mineralization itself as dated minerals may have crystallized in the presence of different fluids or pre-date the mineralization itself, or may be disturbed by later geological processes. The U-Pb ages of zircons are often igneous or may be partially reset by metamorphic events (Hoskin and Schaltegger 2003). The Re-Os system is useful to date sulphide assemblages, but only if Re is present in concentrations high enough for precise age determination. One of the most successful geochronologic application of the Lu-Hf system \(^{176}\text{Lu}^{176}\text{Hf}\) with a half-life of ~37.1 Ga) has been garner geochronology (Vervoort 2015). Owing to the high partition coefficient of Lu into garnet compared to Hf, \(^{176}\text{Lu}^{176}\text{Hf}\) internal isochron ages can be obtained with a precision of 0.2-0.5% for Archean ages using garnet separates and corresponding whole-rock compositions. Moreover, the Lu-Hf closure temperature in garnet appear to be in the range of ~700–750 °C for garnets 1 mm in diameter and larger (Smit et al. 2013), making it an ideal tool to date high metamorphic grade garnet-bearing schists.

We present here results of geothermometry and \(^{176}\text{Lu}^{176}\text{Hf}\) geochronology of garnet which bring new
constraints on the conditions and timing of formation of gold mineralization at the Borden gold deposit.

2 Geological context

The Borden property is located within the Borden Lake Belt (BLB). The BLB is a 5 km by 25 km east-striking lithological assemblage, consisting of paragneiss (metapelites and metaconglomerate), orthogneiss (metavolcanic rock), felsic and mafic gneisses, all of which display high-grade metamorphism from upper-amphibolite to granulite facies. The Borden zone is defined by lithological, structural, density and seismic velocity changes reflecting the transition from granulite to amphibolite facies (Percival 1986; Moser 1994). A gradual transition from granulite to amphibolite facies metamorphism occurs through the Wawa Gneiss Domain of the Saganash Lake Fault to the northwest (Bursnall et al. 1994).

Published zircon ages from a metagranulite matrix yield a maximum age for metagranulite deposition at the Borden Belt of: 2671 ±12 Ma (Moser et al. 2008) and 2667±2 Ma (Krogh 1993). Garnet formation was assumed to have been at 2660 Ma, based on the age of the oldest metamorphic zircon in retrograde mafic granulite (Moser 1994). Detrital zircon dating by Moser et al. (2008) utilizes unrecrystallized zircon cores constraining a lower age bracket of 2659 ± 8 Ma for burial of Borden Lake metasediments in the lower crust. Moser and others (2008) conclude that protracted radial growth of zircon, rather than short-lived in situ recrystallization, aids in the prediction that growth would have occurred around detrital cores for as much as 80 m.y., during which apparent Ti in zircon temperatures vary between 660 and 706°C. Metamorphic growth events appear to have been most frequent at ~2620 Ma, when temperatures were above 650°C, and the events coincided with boudinage in the lower crust and crustal-scale fluid flow along brittle structural breaks at higher levels (Krogh 1993). Evidence for late Archean (~2630 Ma) fault activity exists along the Ivanhoe Lake fault zone (Krogh and Moser 1994).

The Wawa Gneissic Domain preserves the structural transition between upper and lower crustal levels of the Abitibi-Wawa Orogen. In Moser’s (1994) tectonic model, during the early history of the Abitibi-Wawa Orogen (2700-2680 Ma) the tectonic and deformation sequence began with northward subduction. Subsequent folding and thrusting of Timiskaming-age sediments and continued north-south shortening resulted in burial of the Borden Lake Belt to mid-crustal depths at 2660-2670 Ma (Moser 1994). A final episode of compression, loosely bracketed between 2637 and 2580 Ma, was directed parallel to the length of the orogen, causing folding in the Kapuskasing exhumation, reactivation of major faults in the Abitibi and Michipicoten greenstone belts, and, possibly, reverse faulting in the vicinity of the Ivanhoe Lake deformation zone (Moser 1994).

3 Methods and results

We conducted petrographic observations of the garnet-biotite schists, garnet-biotite geothermometry and garnet dating to constrain the metamorphic and structural evolution relative to the timing of gold mineralization.

3.1 Petrography of garnet-biotite schist (±sillimanite)

The garnet-biotite schist (such as sample FD 01340 selected for Lu-Hf chronometry) is commonly associated with economic gold mineralization on the Borden property. Outcrop-scale occurrences are moderately to strongly foliated garnet-biotite schist with variable modal abundances of garnet and sillimanite.

Garnet porphyroblasts vary in size and modal abundance. Garnet is anhedral to subhedral, fine- to very coarse-grained and appears red in colour. Biotite commonly forms a complete or partial corona around the garnet crystals with some occurrences of biotite forming asymmetric tails. The garnet presumably grew as porphyroblasts, although within the strongly foliated garnet-biotite schist unit, the garnet is often observed to be subhedral to anhedral. The diminution of the crystal shape, abundant internal fractures and setting within a strongly foliated groundmass suggest that deformation occurred during and after garnet growth. The strong foliation of surrounding groundmass is deflected around the garnet, suggesting that the competent garnet behaved as a porphyroclast during subsequent ductile deformation.

3.2 Garnet compositions and geothermometry

Garnet and biotite compositions were analysed using a scanning electron microscope (SEM) at Lakehead University for the purpose of garnet-biotite geothermometry. Garnet grains were individually characterized to end-member compositions from elemental data and the results identified them as dominantly almandine (60 to 70%), with moderate components of pyrope (15%), spessartine (15%) and minor components of andradite (<5%) and grossular (<3%). The specific mineral formula for Borden garnet was determined to be Fe2Mg0.5Mn0.4Ca0.1Al2(SiO4)3.

The garnet-biotite geothermometer developed by Ferry and Spear (1978) was used to determine metamorphic temperatures for garnet-biotite schist samples from the Borden gold deposit’s Discovery Outcrop.

Garnet compositions adjacent to biotite inclusions typically yielded metamorphic temperatures ranging from 416°C to 611°C ±50°C. Garnet rim to groundmass biotite generally yielded higher metamorphic temperatures ranging from 472°C to 933°C ±50°C. Overall, calculations based on Borden property garnet-biotite geothermometry yield a metamorphic temperature range of 411°C to 933°C ±50°C (see Fig. 1 for sample FD 01340).
3.1 \textsuperscript{176}Lu-\textsuperscript{176}Hf dating of garnet

Garnet separates from the garnet-biotite schist unit on the Discovery Outcrop were prepared for \textsuperscript{176}Lu-\textsuperscript{176}Hf geochronology at the University of Western Ontario. A fine, homogenized whole-rock powder was produced in a stainless steel mill. The remaining materials were crushed and sieved into three-grain fractions. Garnet grains were concentrated from the 125-250 micron fraction using a Frantz magnetic separator followed by heavy liquid density separation (methylene iodide, density approximately 3.2 g/cm\textsuperscript{3}) prior to further purification by hand picking.

Three splits of whole-rock (WR) powder of sample FD 01340 between 0.15 to 0.65 g were dissolved following two methods. First, WR1 was dissolved using Parr bomb vessel dissolution at 155°C (methods described in Bouvier et al., 2008) to ensure that all refractory minerals, including zircons, were fully dissolved. Second, a hot plate dissolution method at 120°C and atmospheric pressure was utilized to avoid dissolving refractory minerals, which may not be at isotopic disequilibrium.

Garnet fractions were prepared according to the methods described in Zirakparvar et al. (2010). About 0.10 to 0.15 g of grains were first acid washed in 1M hydrochloric acid (HCl) at room temperature before acid digestion. Mixed \textsuperscript{149}Sm-\textsuperscript{150}Nd and \textsuperscript{176}Lu-\textsuperscript{180}Hf spikes were finally added to the sample solutions for isotopic dilution. Detailed protocol for Hf-REE separation and purification is described in Bouvier et al. (2008). Total analytical blanks were 20 pg for Hf and 5 pg for Lu, which are negligible.

Purified fractions of Hf and Lu with Yb (used to correct the instrumental mass bias on \textsuperscript{175}Lu/\textsuperscript{176}Lu) were analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) at Laboratoire Magmas et Volcans, Clermont Université (France). The average \textsuperscript{176}Hf/\textsuperscript{177}Hf ratios and two standard deviation (2SD) for the JMC 475 Hf isotopic standards measured in static mode during analytical sessions were respectively 0.282160 ± 0.000009 (2SD, 10 ppb Hf) and 0.282154 ± 0.000008 (2SD, 20 ppb Hf) using an Aridus II nebulizer with a Neptune Plus MC-ICP-MS. The Lu fractions of the samples were collected with part of the Yb and thus analyzed together to correct for interference and instrumental mass bias using the method described in Vervoort et al. (2004). External reproducibility on isotopic ratios used for age calculations are ±0.000010 for \textsuperscript{176}Hf/\textsuperscript{177}Hf and ±0.5% for Lu/Hf based on repeated measurements of BCR-2 standards using the same isotopic dilution method as described in Bouvier and Boyet (2016).

The Lu-Hf isotopic analyses of garnet and whole-rock fractions yield a precise internal isochron age at 2629.0 ±4.3 Ma (with an initial \textsuperscript{176}Hf/\textsuperscript{177}Hf = 0.281210 ±0.000010 and MSWD = 0.66) from five data points (Fig. 2). This age is within error of the Lu-Hf isochron age of 2630.4 ±4.7 Ma (with an initial \textsuperscript{176}Hf/\textsuperscript{177}Hf =0.281204 ±0.000013 and MSWD = 0.16) when the whole rock dissolved with zircons is not included in the age calculation. The initial Hf isotopic composition of this schist corresponds to \varepsilon_{Hf} =+4.1 (epsilon unit is the deviation in parts per 10,000 relative to Chondrite Uniform Reservoir of Bouvier et al. (2008) at 2629 Ma).

4 Discussion

The garnet-biotite schist is the unit most commonly associated with gold mineralization. The stable mineral assemblage of coarse sillimanite with K-feldspar, quartz and a complete lack of muscovite represents the peak conditions of granulite facies metamorphism. The presence of fibrolite and coarse sillimanite suggests secondary growth of sillimanite during amphibolite facies retrograde metamorphism.

Garnet-biotite geothermometry based on Borden property garnet has yielded a metamorphic temperature range up to 933°C ±50°C. An overall increase in metamorphic temperature from core to rim of individual
garnet grains indicates growth during prograde metamorphism to granulite facies. Lower temperature at the outer margin of some grains may document the retrograde metamorphism to amphibolite facies.

The garnet-biotite schist had been initially interpreted as a metasedimentary unit due to the abundance of aluminous minerals. The initial Hf isotopic composition of the garnet-biotite schist from Discovery Outcrop indicates that the protolith of this rock was derived from a long-term depleted (high Lu/Hf) mantle reservoir. This evidence suggests that the garnet-biotite schist unit may have been a hydrothermally altered mafic igneous rock.

The Lu-Hf chronometry results suggest that peak granulite facies metamorphism associated with garnet growth took place at 2629 ±4.3 Ma. This age corresponds to the younger end of the period suggested by earlier estimates of the age of granulite facies metamorphism using U-Pb dates of zircons.

Retrograde metamorphism of these lithologies was critical to the structural control of mineralization at this deposit. Lenses of relict granulite facies rock were more competent than surrounding retrograde amphibolite facies lithologies, producing the requisite conditions for localized brittle deformation and mineralization during dominantly ductile shear-zone deformation. Thus, mineralization is suspected to form after ~2629 Ma.

5 Conclusions

Garnet-biotite geothermometry based on Borden garnet-biotite schist has yielded a metamorphic temperature range up to 933°C ±50°C. Unzoned garnet from the Discovery Outcrop yields lower temperatures at the core and higher temperatures at the rim of each grain. This indicates that garnet equilibration was reached during peak metamorphism and garnet growth took place during prograde metamorphism to the granulite facies. Abundance of aluminous minerals and the Hf radiogenic isotopic signature (εHf=+4.1) suggests a hydrothermally altered mafic igneous rock.

Research on the property to date provides evidence for gold mineralization in association with brittle-ductile heterogeneous strain and rheological competency contrasts between minerals on the microstructural scale as well as lithologies on the deposit scale.

Our new Lu-Hf geochronological results on garnet at 2629 ±4.3 Ma are consistent with the youngest population of zircon U-Pb ages measured in the paragneiss within the Borden Lake Belt area (Krogh, 1993). Gold mineralization appears later during retrograde metamorphism of granulite facies lithologies to amphibolite facies, and with ductile deformation of the retrograde amphibolite facies units after ~2629 Ma.

Acknowledgements

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U-Pb and $^{40}$Ar/$^{39}$Ar chronology of hydrothermal zircon, garnet, rutile and muscovite, Big Bell gold deposit, Yilgarn Craton, Western Australia

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**Abstract.** The Hemlo-type Big Bell deposit (75 t Au) occurs in a narrow mafic-ultramafic greenstone belt bounded to the southeast by granodiorite-tonalite (2740-2700 Ma) and to the northwest by granite batholiths (2625 Ma). The steeply dipping greenstones are intruded parallel to bedding by granodiorite porphyry, both lineated and metamorphosed at 670±50°C during emplacement of the southeast border pluton at 2700±7 Ma. The calcic-potassic Big Bell alteration zone, centred on amphibolite-granodiorite dyke contacts, contains two scheelite-bearing ore bodies: almandine-cummingtonite-hornblende skarn (1-3 g/t Au, 1700 g/t As) dated at 2662±5 Ma (almandine U-Pb), and the muscovite-microcline gneiss of the Main Lode (3-5 g/t Au, 580 g/t Sb). Garnet-cordierite-biotite schist borders the lode and the skarn. Fe-Mg thermometry constrains P-T conditions during mineralization to 540-600°C and 300-400 MPa. The northwest granite and late Sn-Ta-Nb granite-pegmatite dykes intruded at 2625-2610 Ma. They are associated with auriferous andradite-diopside and barren epidote skarn veins. Zircons intergrown with andradite are dated at 2612±7 and 2609±10 Ma. Granite-pegmatite magmatic and hydrothermal activity did not cause recrystallization in the Main Lode but the thermal anomaly (about 450°C) reset rutile and muscovite in the microcline gneiss to 2614±4 Ma and 2603±8 Ma, respectively.

**1 Introduction**

The Big Bell gold deposit is located at 27°20’ south latitude and 117°40’ east longitude in the northwest part of the Archean Yilgarn Craton, Western Australia. Past production (1937-2003) amounts to 31 million metric tons at 2.8 g/t gold. The Main Lode consists of pyrite- and stibnite-rich muscovite-microcline gneiss and is unique amongst the gold deposits in the craton (Mueller and Groves 1991). The genesis of Hemlo-type deposits is controversial. Models for Big Bell invoke either wall-rock replacement at greenschist-facies conditions prior to high-grade metamorphism and partial melting in the lode (e.g. Phillips and Powell 2009) or post-metamorphic replacement (Wilkins 1993). We review the radiometric ages published since the first study (Mueller et al. 1996), and present new chronologic data on hydrothermal zircon in skarn and on rutile and muscovite in the Main Lode. The ages are quoted at the 95% confidence level, and are interpreted in the light of recent P-T constraints (Mueller and McNaughton 2017).

**2 Geologic setting**

The Big Bell deposit is located in a wedge-shaped spur of the Meekatharra greenstone belt, about 1.5 km wide at the mine, which widens to the northeast and is bounded by granitoid batholiths. The minimum age of the greenstones is defined by the Polelle Group felsic volcanic rocks preserved in synclines and dated at 2806±4 Ma northeast of Cue. At Cue, a tonalite pluton 2758±4 Ma old cuts across the Fingall meta-gabbrro sill setting a limit for regional folding and low-grade metamorphism (Fig. 1).

**Figure 1.** Geological map of the Big Bell-Cue mining district, Meekatharra greenstone belt, Western Australia, the zircon U-Pb ages are referenced in Mueller and McNaughton (2017).

At Big Bell, the greenstones consist of meta-komatiite, intercalated magnesian and tholeiitic amphibolite (plagioclase An30-60), and thin interflow beds of graphic chert. The succession strikes N30°E, dips 75-80° southeast, and is foliated parallel to the compositional layering. Numerous dykes of lineated granodiorite porphyry are emplaced into the foliated ultramafic-mafic
Figure 2. Geological map of the Big Bell mine area, Yilgarn Craton, showing the Big Bell gold ore bodies in the contact-bound calcic-potassic alteration zone. Coordinates are mine grid.

3 Skarn and gneiss ore bodies

The amphibolites and linedite granodiorite porphyries of Big Bell are overprinted by a 300 m wide zone of calcic-potassic alteration bound to the northwest contact of the main dyke (Fig. 2). The zone grades outward into spaced garnet-biotite bands and boudinaged veins of diopside-hornblende skarn in porphyry and amphibolite. The inner zone is composed of sulfide- and magnetite-bearing mafic schist/gneiss (0.65-1.38 wt.% TiO₂) and lesser skarn replacing amphibolite, and of sulfide-poor felsic gneiss (0.31-0.46 % TiO₂) replacing granodiorite porphyry. Major constituents in mafic metasomatic gneiss are almandine + cordierite + biotite. Felsic gneiss retains a remnant quartz-eye texture, and is altered to biotite + muscovite + calcic plagioclase ± andalusite ± sillimanite. The inner zone contains two gold ore bodies: reduced Au-As skarn, and the Au-Sb microcline gneiss of the Main Lode, both separated by 40 m-thick felsic gneiss (Fig. 2).

3.1 Reduced Au-As skarn

The ore skarn (1-3 g/t Au) in the hanging wall of the Main Lode is 1-12 m thick, and consists of almandine, cummingtonite, hornblende, minor Ti-magnetite (5-10%), and biotite (Fig. 3). Zoned loellingite-arsenopyrite, pyrrhotite, and scheelite are disseminated (0.5-2%). Loellingite-arsenopyrite aggregates enclose euhedra of almandine, electronite, and native bismuth. The skarn is located at the footwall contact of thick almandine-cordierite-biotite schist and gneiss (0.1-0.5 g/t Au). Fe-Mg exchange thermometry constrains the temperature during
gneiss-skarn formation to 540-600°C and the pressure to 300-400 MPa (Mueller and McNaughton 2017).

![Diagram of minerals](image)

**Figure 3.** Reduced Au-As skarn, bands of almandine (alm) + biotite (bt) + Ti-magnetite (mag) in a matrix of cummingtonite + hornblende, enclosed in pyrrhotite-loellingite-arsenopyrite (po-loel-asp) aggregates, drill core PD-19, 565.4 m. Skarn almandine gave a concordant U-Pb age of 2662±5 Ma.

### 3.2 Au-Sb gneiss of the Main Lode

The Main Lode gneiss is enclosed in an envelope of low-grade (1-2 g/t Au) cordierite-garnet-biotite schist mineralized with magnetite, arsenopyrite, pyrrhotite, and pyrite (Fig. 2). The schist formed at a temperature of 608±50°C (Mueller and McNaughton 2017). The Main Lode gneiss is up to 40 m thick and persists 1.5 km down dip. The average composition is 45 vol.% quartz, 30% K-feldspar (microcline + orthoclase), 4% muscovite, 2% biotite, 2-3% plagioclase (An05-30), and minor andalusite, sillimanite, calcite, tourmaline, and W-Sb rutile. The gneiss contains 5-10% pyrite, minor pyrrhotite, arsenopyrite, molybdenite and scheelite, and late-stage sphalerite, tetraedrite-tennantite, stibnite, aurostibite, and Au-Ag-Hg alloy. Scheelite is enriched to 0.1 wt.% in zones up to 6 m thick (Big Bell Mines staff 1953). Sericite partly replaces andalusite and K-feldspar.

### 3.3 Age of gold ore at Big Bell

Fractions of almandine garnet from the Au-As skarn provide a concordant U-Pb age of 2662±5 Ma, which is insensitive to the common lead correction due to high 206/204 Pb ratios (330-432; Mueller et al. 1996). The garnet contains 1-micron inclusions of zircon, identified by energy-dispersive X-ray analysis. Almandine has a high closure temperature (>800°C) to U-Pb diffusion, which also applies to exsolved zircon (Mezger 1990).

Minerals separated from the Main Lode provide contradictory ages. Molybdenite gave a single Re-Os model age of 2635±13 Ma (Stein and Markey 2001). The 40Ar/39Ar analyses of muscovite (1-10 mm) in three lode samples showed that thermal disturbance affected all but one. This muscovite, separated from a stibnite-sphalerite-gold vein, yielded a plateau of 90% of the 39Ar released and an age of 2603±8 Ma (MSWD=1.17) using Fish Canyon sanidine as standard and the K-Ar decay constants of Renne et al. (2010). Rutile (0.3-0.5 mm) separated from microcline gneiss and analysed using the SHRIMP ion microprobe, gave a precise concordant U-Pb age of 2614±4 Ma (MSWD=1.12, n=22). The closure temperature for lead diffusion in rutile is estimated at 420-490°C (Mezger 1990; Kooijman et al. 2010), and for argon diffusion in muscovite at 425±70°C at slow to moderate rates of cooling (Scibior et al. 2015).

## 4 Post-ore granite and pegmatite

Voluminous biotite granite emplaced 300 m northwest of the Big Bell deposit is dated at 2627±8 Ma (Fig. 2). Amphibolite xenoliths in this pluton record the lowest hornblende-plagioclase temperature (628±50°C) measured indicating it lacks a crystalline aureole in the older high-grade rocks. The granite is crosscut by garnet-muscovite pegmatite and by albite granite dykes, which also crosscut the steeply dipping metamorphic rocks (Fig. 2) and the Main Lode 800 m below surface. Near-concordant zircons provide a minimum 207Pb/206Pb age of 2608±6 Ma for pegmatite emplacement. Some dykes are mineralized with accessory magnetite, pyrrhotite, and chalcopyrite, and many contain elevated Li, Sn, Ta and Nb.

## 5 Granite-related oxidized skarns

Oxidized calcic skarns bound to the contacts of granodiorite orthogneiss and forming foliation-parallel bands and veins 2-40 cm thick, replace amphibolite and meta-komatiite southeast and northwest of the open pit. They are absent within the inner alteration zone of the Big Bell deposit. The most common type is zoned andradite-diopside skarn (Fig. 4a) mineralized with accessory scheelite, molybdenite, pyrite, pyrrhotite, chalcopyrite and sphalerite. The andradite zone is barren (<0.1 g/t Au) but pyrite-rich diopside zones contain up to 1.5 g/t gold. Oxidized contact skarn was mined from shafts in the weathered zone, for example at Mary Belle (Fig. 2). The second type consists of epidote-albite-calcite veins with actinolite-chlorite selvages. Massive magnetite-epidote skarn, containing interstitial biotite, chlorite, chalcopyrite and bornite, occurs close to the northwest granite.

### 5.1 Zircon U-Pb age of oxidized skarn

Hydrothermal zircons (0.1-0.5 mm) of low to moderate uranium (10-534 ppm) and low thorium content (1-37 ppm) were separated from two andradite-diopside veins in amphibolite intersected by drill holes northwest and southeast of the open pit (Fig. 2). The 2-10 cm wide andradite cores of these veins yielded 25-50 zircons each, quantities impossible to derive from the host rock. The low Th/U ratios (0.05-0.08) also set the hydrothermal zircons apart from their igneous counterparts in the local intrusions.
Figure 4. Andradite-diopside replacement skarn in amphibolite dated by hydrothermal zircon U-Pb ages at 2612±7 to 2609±10 Ma. a Growth-zoned, cm-sized andradite crystals (ad) in contact with diopside (di), drill core BBD-32A, 687.8 m. b Cathodoluminescence image of zircon 8, inner oscillatory and sector zones (SHRIMP spots 1 and 4: 41-47 ppm U) are embayed by the luminescent rim and crossed by veinlets of uranium-poor zircon (Spot 2: 3 ppm U), drill hole PD-19A, 785.0 m. (Th/U=0.58-0.78). The zircons display prominent sector and oscillatory zones in cores partly replaced by rims and veinlets of luminescent but uranium-free zircon (Fig. 4b). The SHRIMP analyses from both veins are grouped into single populations providing concordant U-Pb ages of 2612±7 Ma and 2609±10 Ma, respectively.

6 Sequence of events at Big Bell

(1) Emplacement of granodiorite porphyry dykes parallel to foliation in the steeply dipping greenstone succession at 2737±4 Ma.

(2) Emplacement of the co-genetic main granodiorite-tonalite pluton of the southeast batholith at 2700±7 Ma, and contemporaneous aureole metamorphism reaching a peak temperature of 670±50°C.

(3) Calcic-potassic alteration and Au-W mineralization at 2662±5 Ma bound to the amphibolite-granodiorite contacts of the main porphyry dyke complex. Arsenic-rich gold skarn forms early at fluid temperatures of 540-600°C, and the antimony-rich muscovite-microcline Main Lode forms late. Pressure estimates of 300-400 MPa indicate mineralization at 11-14 km crustal depth.

(4) Emplacement of the northwest biotite granite batholith at 2627±8 Ma, followed by the intrusion of rare-metal (Sn-Ta-Nb) albite granite and garnet-bearing pegmatite dykes prior to 2608±6 Ma.

(5) The border granite does not cause recrystallization of the older high-grade rocks. Thermal resetting (at 425±70°C) of rutile and muscovite in the Main Lode takes place at 2614±4 to 2603±8 Ma.

(6) Contemporaneous with rare-metal granite-pegmatite emplacement, oxidized andradite-diopside and epidote replacement skarns form at the periphery of the gold deposit, some containing sub-economic Au-W-Cu grades. Skarn zircon ages (2612±7 and 2609±10 Ma) confirm the presence of a second hydrothermal system 50 Ma younger than the main one.

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Recent advances in Re-Os geochronology of Co-, As-, and Cu-sulphide and sulpharsenide minerals

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Abstract. New Re-Os data for sulpharsenide (arsenopyrite, löllingite, and cobaltite) minerals yield reproducible Re-Os isotope data and provide reliable ages through isochron regression at a precision of 5.5% or lower. Our data on arsenopyrite-löllingite complement earlier studies and show that these minerals are particularly suitable to date hydrothermal gold mineralisation and give insights into the thermal evolution of metamorphosed ore deposits (e.g., early Mesoproterozoic evolution of the Broken Hill Zn-Pb-Ag deposit, Australia). Various types of cobaltite mineralisation in the Idaho cobalt belt (ICB), USA are distinguished on the basis of their petrography and major and trace elements geochemistry. The Re-Os data of these cobaltite types record the evolution of the ICB from middle Mesoproterozoic mineralisation at ca. 1349 Ma through to two stages of deformation and metamorphism during the subsequent Grenvillian (ca. 1120 Ma) and Cordilleran (ca. 110 Ma) orogenies. In addition to these new studies of sulpharsenide minerals, new Re-Os data of Cu-sulphide minerals suggest that bornite might be the most suitable Cu-sulphide mineral for Re-Os geochronology.

1 The Re-Os geochronometer – a tool to directly date sulphide and sulpharsenide mineralisation in the ore deposit environment

Sulphide and sulpharsenide minerals contain chalcophile and siderophile (e.g., Fe, Ni, Co, Cu) elements. Two minor siderophile elements, rhenium (Re) and osmium (Os), may be concentrated in crustal sulphide and sulpharsenide minerals, allowing dating by the long-lived $^{187}$Re-$^{187}$Os isotope system with a half-life of 41.6 Ga ($\lambda$$^{187}$Re = 1.666 ± 0.005 x 10$^{-11}$ a$^{-1}$, Smoliar et al. 1996, Selby et al. 2007). In the last 15–20 years, there has been significant development of the Re-Os chronometer in a variety of sulphide and sulpharsenide minerals to determine precise ages of ore deposits (e.g., Selby and Creaser 2001, Stein et al. 2000, 2001, Davies et al. 2010, Morelli et al. 2010, Ootes et al. 2011, Santtilan et al. 2017a, Santtilan et al. 2017b).

The robust Re-Os chronometer in molybdenite (10s – 1,000s ppm Re) was developed over the last two decades. Given that the Os budget in molybdenite is almost exclusively contributed by the time-integrated radioactive decay of the measured $^{187}$Re to $^{187}$Os (>99% of the total Os budget), the chronometer is systematically utilised to produce multi-grain mineralisation model ages at a resolution of 0.5% (2$\sigma$) or better in the dating of porphyry-related and epithermal type ore deposits (e.g., Selby and Creaser 2001, Stein et al. 2001, Chiaradia et al. 2009, Chiaradia et al. 2013, Spencer et al. 2015).

In contrast to molybdenite, the Os budget of pyrite typically comprises $^{187}$Os produced through the decay of $^{187}$Re but often “common Os” (e.g., $^{192}$Os, $^{187}$Os, $^{198}$Os) originally incorporated with Re (up to 100s ppb Re) at the time of pyrite formation and prior to the onset of decay of $^{187}$Re. Hence, the Os isotopic composition of pyrite is not always consistent with the model age approach, but can still yield precise and accurate isochron regression ages in $^{187}$Os/$^{188}$Os-$^{187}$Re/$^{188}$Os space with a resolution of 1.5% (2$\sigma$) or better for a coeval and cogenetic pyrite sample suite. Remarkable examples of pyrite dating exist for magmatic, intrusion-related and sediment-hosted mineral deposits (e.g., Stein et al. 2001, Ootes et al. 2011, Hnatyshin et al. 2015).

In recent years, investigation of Re-Os systematics of Cu-sulphides (e.g., bornite, chalcopyrite, chalcocite; Selby et al. 2009, Alderton et al. 2016) has been initiated given the economic importance of sediment-hosted Cu mineralisation. Similarly, the Re-Os isotopic system in arsenopyrite and löllingite has been used to develop isochron ages to constrain the timing of gold mineralisation in hydrothermal gold deposits (Mikulski et al. 2005, Davies et al. 2010, Morelli et al. 2010).

Here we present new advances in the Re-Os systematics of arsenopyrite-löllingite (FeAsS-FeAs2) that bring new insights into the metamorphic evolution of the Broken Hill Pb-Zn-Ag district in Australia (Saintilan et al. 2017a). We also investigate the Re-Os systematics of cobaltite (CoAsS) from Co-Cu-Au deposits hosted by metasedimentary rocks of the Idaho cobalt belt (ICB) in east-central Idaho, USA (Saintilan et al. 2017b). In addition, Cu-sulphides (bornite, chalcocite and
chalcopyrite) were studied from the non-
metamorphosed sandstone-hosted Cu-Ag Spar Lake
deposit a few hundred kilometres to the north of the ICB.

2 Re-Os systematics of arsenopyrite-
löllingite (FeAsS-FeAs₂) and cobaltite
(CoAsS) in metamorphosed hydrothermal
ore deposits

2.1 Insights into the metamorphic evolution
of the Broken Hill block using arsenopyrite-
löllingite Re-Os geochronology and
thermometry.

Saintilan et al. (2017a) studied the Re-Os systematics of
Re- and Os-rich arsenopyrite and löllingite aggregates (100
to 500 ppb Re and 60 to 400 ppt Os) that are interstitial to
spessartine garnet and disseminated in granulite-facies
garnetite in the neighbourhood of the supergiant Pb-Zn-Ag
Broken Hill deposit, southern Curnamona Province, New
South Wales, Australia.

Figure 1. ¹⁸⁷Os/¹⁸⁸Os vs. ¹⁸⁷Re/¹⁸⁸Re data points (n = 13)
for arsenopyrite (dark blue) and arsenopyrite ± löllingite
(sky blue) from the Broken Hill Pb-Zn-Ag deposit, Australia
with 2σ absolute error ellipses (from Saintilan et al. 2017a).

Analyses of arsenopyrite and arsenopyrite ± löllingite
define a Model 1 isochron with an age of 1574 ± 38 Ma
(Fig. 1, 2σ, n = 13, mean square weighted deviation
MSWD = 1.4, initial ¹⁸⁷Os/¹⁸⁸Os ratio of 0.666 ± 0.006). This age indicates that cooling from peak metamorphism
of ~800°C at 1602 Ma (monazite thermochronology,
McFarlane and Frost 2009) to at least 550°C (first
temperature of stability of arsenopyrite; Pokrovski et al.
2002; Tomkins et al. 2006) at ca. 1574 Ma occurred at a
rate of ~9°C Myr⁻¹, which is similar to the rate of cooling
(~10°C Myr⁻¹) determined for previously published
SHRIMP U-Pb ages from successive monazite generations
(McFarlane and Frost 2009). These results are consistent
with the late phase of retrograde metamorphism that was
initiated between ca. 1590 and 1575 Ma.

2.2 Re-Os systematics and geochemistry of
cobaltite in the Idaho cobalt belt: Evidence
for middle Mesoproterozoic sediment-hosted
Co-Cu sulphide mineralisation with
Grenvillian and Cretaceous remobilisation

Saintilan et al. (2017b) focused on cobaltite in mineral
deposits metamorphosed at the greenschist to amphibolite
facies in the Idaho Cobalt Belt of the Belt-Purcell Basin,
USA. These authors were able to understand the complex
Re-Os isotopic system in cobaltite. A minimum aliquot
size of 200 mg was empirically constrained to obtain
reproducible data from cobaltite with Re and Os contents
of ca. 2–3 ppb and 50–60 ppt, respectively. Using the
1/¹⁹²Os ratio as a measure of “common” Os and by
corollary initial Os concentration in cobaltite, it was
concluded that the absence of a linear relationship between
1/¹⁹²Os and ¹⁸⁷Os/¹⁸⁸Os meant that post-mineralisation
fluids did not overprint the primary Re-Os systematics of
fine-grained cobaltite at the Haynes-Stellite deposit.
Hence, it was identified that a proto-ore of fine-grained
cobaltite formed at 1349 ± 76 Ma in the middle
Mesoproterozoic (Fig. 2a, Model 1 Re-Os isochron age,
2σ, n = 4, MSWD = 2.1, initial ¹⁸⁷Os/¹⁸⁸Os ratio of 4.7 ±
2.2) prior to Mesoproterozoic Grenvillian deformation (ca.
1190–1006 Ma) and Cretaceous greenschist-facies
metamorphism (ca. 110–83 Ma). The initial ¹⁸⁷Os/¹⁸⁸Os
ratio of isochron regression reflects a likely source of Os
(and by inference the source of metals) as being Archean
and Paleoproterozoic Laurentian basement rocks. In
contrast, Ni-rich fine-grained cobaltite in the Idaho zone of
the Blackbird deposit records possible Grenvillian
metamorphic overprint at ca. 1132 Ma (Fig. 2b, Model 3
isochron age, n = 7, MSWD = 9.3, initial ¹⁸⁷Os/¹⁸⁸Os ratio
of 9.0 ± 2.9). Finally, the severely disturbed Re-Os
systematics of coarse-grained massive cobaltite
metamorphosed to the amphibolite facies in the Chicago
zone of the Blackbird deposit did not yield any age
information. This disturbance of the Re-Os systematics
in cobaltite of likely Mesoproterozoic origin is proposed to be
related to greenschist-facies metamorphism during the
Cretaceous Cordilleran orogeny. Based on thermal
conditions of 400–520°C for Cretaceous metamorphism in
the garnet zone located less than 100 m to the north-east of
the Chicago zone (Eiseman 1988), our case study suggests
a maximum closure temperature for the Re-Os isotopic
system in cobaltite at ca. 400°C.
3 Re-Os systematics of Cu-sulphides (bornite, chalcopyrite, chalcocite) in sediment-hosted epigenetic mineralisation

Sulphide mineralisation in the sediment-hosted Cu-Ag Spar Lake ore deposit, which was metamorphosed to the biotite isograd of greenschist facies during burial metamorphism (Hayes et al. 2012), comprise three main Cu-sulphide species (bornite, chalcopyrite and chalcocite). The new Re-Os systematics of these minerals all exhibit high $^{187}\text{Re}/^{188}\text{Os}$ (~250–3800) and highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions (~20–200). The Re-Os systematics of chalcocite and chalcopyrite do not yield any accurate age information. In contrast, the Re-Os systematics of bornite identifies Cretaceous resetting at ca. 75 Ma of the Re-Os isotopic system in bornite that probably formed originally in the Mesoproterozoic.

4 Perspectives and conclusions

The application of the Re-Os geochronometer to sulpharsenide minerals yields reproducible data and geochronological information at a precision of 2.4% or better for arsenopyrite-löllingite, and 5.6% for cobaltite (Davies et al. 2010, Morelli et al. 2010, Saintilan et al. 2017a, 2017b). Further, our preliminary results for Cu-sulphides suggest that the Re-Os isotopic system in a Mesoproterozoic bornite proto-ore was reset during the Cordilleran orogeny in Cretaceous time. The Re-Os systematics of chalcopyrite and chalcocite were disturbed post-mineralisation, most probably also during Cretaceous dynamothermal events. Bornite might be the most robust Cu-sulphide mineral for Re-Os geochronology (as previously pointed out by Selby et al. 2009) for reasons that remain to be ascertained.

These findings provide guidelines for the development of Re-Os geochronology of critical sulphide or sulpharsenide minerals in major sediment-hosted deposits with long-standing controversy regarding their age (e.g., Central African Copper Belt).

Acknowledgements

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References


Abstract. Cassiterite is the dominant ore mineral in most tin deposits and an associated mineral in some tungsten and VMS deposits. It has a detectable U content and it generally remains stable and is not easily affected by late hydrothermal events. Thus, the U–Pb age of cassiterite may help constrain the timing of tin mineralization. Both isotope dilution thermal ionization mass spectrometer (ID-TIMS) and laser ablation multi-collector inductively coupled plasma mass spectrometer (LA-MC-ICP-MS) have been applied to cassiterite U–Pb dating. Here we show that cassiterite U–Pb dating results using LA-ICP-MS are comparable to those using LA-MC-ICP-MS. Herein, three cassiterite samples are analyzed by in-situ LA-ICP-MS method. Dating of two cassiterite samples from Rutongo Nb-Ta-Sn and Gatumba Ta-Sn rare metal deposits in Central Africa gives U–Pb ages of 957 ± 21 Ma and 998 ± 10 Ma, respectively, which agree well with the zircon U–Pb age of the parental G4 granite and represent the timing of rare metal mineralization event. One cassiterite collected from the Piaotang W-Sn deposit in the Nanling Range of South China gives an precise timing constraint on mineralization (159.5 ± 1.5 Ma), which is also consistent with the published zircon U–Pb age of parental granite and 40Ar–39Ar age of cassiterite.

1 Introduction

Precise and accurate isotopic dating is crucial for constraining the timing and genesis of mineral deposits. However, it is often difficult to obtain the accurate and precise ages of ore minerals directly due to the lack of suitable minerals for conventional radiometric dating. Modern dating techniques including U–Pb, 40Ar–39Ar, Re–Os and Sm–Nd isotope systems, have been used to constrain the temporal relationship between igneous intrusion and associated hydrothermal mineralization. Cassiterite (SnO2) is a common ore mineral in rare metal granites/pegmatites and tin deposits, and is also an associated mineral in some tungsten and VMS deposits. It belongs to the rutile group (M4+O2), which in principle should have high U and low common Pb contents in its crystal structure. Cassiterite U–Pb ages directly date tin mineralization (Gulson and Jones 1993; Liu et al. 2007; Yuan et al. 2008).

Cassiterite usually has common Pb contents much higher than those of zircon. Moreover, the U content of cassiterite is generally at low ppm levels, which is lower than that of zircon, rutile, apatite, etc, with higher common Pb proportion. As a result, published ID-TIMS cassiterite U–Pb age displays uncertainties considerably larger than those of zircon U–Pb ages. In particular, cassiterite formed during hydrothermal processes may contain mineral/fluid inclusions with non-equilibrium common Pb that is detrimental to precise isotope dating (Clayton and Rojkovic 1999).

In recent years, in-situ LA-ICP-MS U–Pb dating of cassiterite yields 206Pb/207Pb versus 238U/207Pb “isochron” ages (Chen et al. 2014; Gao et al. 2014; Yuan et al. 2011; Zhang et al. 2014; Zhang et al. 2015) seemingly comparable to ID-TIMS results. Nevertheless, some of the samples do not yield reasonable isochron ages, which makes this method unpopular. In this study, we try to evaluate and optimize in-situ cassiterite U–Pb dating method using LA-ICP-MS. Our results show that the Tera-Wasserburg U–Pb lower intercept age is better than 206Pb/207Pb versus 238U/207Pb “isochron” age for those cassiterites with high common Pb, because the former is controlled mainly by 238U/206Pb ratios of data points with low common Pb contents. It is also suggested that cassiterite U–Pb dating results using LA-ICP-MS (with quadrupole mass spectrometer) are comparable to those of LA-MC-ICP-MS.

2 Sample preparation and analytical method

2.1 Sampling preparation

Three cassiterite samples are used in this study. Cassiterite sample PT-1 is a large crystal (3 cm × 4 cm) collected from one cassiterite-quartz vein of the Piaotang W-Sn deposit in the Nanling Range of south China. Two cassiterite samples RT-1 (10 cm × 5 cm) and GT-1 (Sn
concentrates) were sampled from the Rutong Nb-Ta-Sn and Gatumba Ta-Sn rare metal deposits in Rwanda of Central Africa, respectively.

Tin concentrates were crushed into 40-60 mesh, and cassiterite grains were separated using conventional magnetic and heavy liquid separation techniques. Cassiterite grains were then handpicked under a binocular microscope. The large cassiterite crystals of sample RT-1 and PT-1 were cut into two pieces. Cassiterite grains were mounted in epoxy, and then polished down to near half sections to expose internal structures. Cassiterite samples were checked carefully under the light optical microscope, electron microprobe (EMP) and cathodoluminescence equipped with scanning electron microscope (SEM-CL) to observe mineral/fluid inclusions and cracks.

2.1 LA-ICP-MS cassiterite U-Pb dating

U–Pb isotopic and trace elemental analysis of cassiterite used a LA-ICP-MS system at the CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The system consists of an Agilent 7900 ICP-MS coupled with a Resonetics RESolution S-155 laser. This laser ablation system is large (155 mm x 105 mm) and can load 20 epoxy resin mounts at each turn. About 99% ablated material is washed out in less than 1.5 s due to its two-volume laser-ablation cell. A squid smoothing device was used to reduce statistical error induced by laser-ablation pulses and to improve the data quality (Li et al. 2012). Helium gas carrying the ablated sample aerosol is mixed with argon carrier gas and nitrogen as additional di-atomic gas to enhance sensitivity, and finally flows into the ICP-MS. Prior to analysis, the system was optimized using NIST SRM610 ablated with 29 µm spot size and 5 mm/s scan speed to achieve maximum signal intensity and low oxidation rate. The spot size is adjustable (4–200 µm) and the laser pulse frequency is 1–20 Hz (Li et al. 2016).

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 were used as external elemental and isotopic calibration standards, respectively. AY-4 was collected from the Anyuan skarn-type tin deposit of the Furong tin ore field in the middle Nanling Range. This cassiterite sample has been well studied using ID-TIMS with a U–Pb age of 158.2 ± 0.4 Ma (Yuan et al. 2011). It also has relatively low common lead. NIST SRM 610 was analyzed twice for every ten analyses of the tested sample; AY-4 was analyzed twice for every five analyses of the tested sample. Each spot analysis incorporated a background acquisition of approximately 20 s followed by 40 s sample data acquisition. Isotopes were measured in time-resolved mode. For U–Pb dating and trace elemental analysis, dwell times for each mass scan are 15 ms for 204Pb, 206Pb, 208Pb, 238U, 235U, 25 ms for 207Pb, and 8 ms for other elements. 118Sn is used as an internal standard for calibrating the trace elements of cassiterite. Raw data reduction was performed off-line by ICPMSDataCal software. Isoplot 4.0 was used to calculate the U–Pb ages and draw concordia diagrams. Data errors for isotopic ratios in the following samples are 1 σ and the errors of their weighted mean 206Pb/238U ages are 2 σ (Li et al. 2016).

3 Case study

3.1 Rutongo and Gatumba rare metal deposits in Central Africa

The Mesoproterozoic Kibara orogen in Central Africa hosts different granite-related rare metal deposits, such as cassiterite, columbite-tantalite, wolframite, beryl and spodumene. The primary deposits of these minerals comprise pegmatites and quartz veins which are related to the youngest and most evolved G4-granite generation in northern Kibara orogen (Dewaele et al. 2010). The zircon SHRIMP U–Pb age of the Kigali granite (G4-granite) is 986 ± 10 Ma (Tack et al. 2010).
The Rutongo area in western Rwanda is located to the northern Kibara orogen and characterized by cassiterite-quartz veins dominantly occurring in quartzites. These ore veins are associated with intense alteration of silification, tourmalization, sericitization and muscovitization. Cassiterite coexists with muscovite in fractures in and along the margins of the quartz veins (Dewaele et al. 2010).

The Gatumba mining district is close to the Rutongo area and hosts Neoproterozoic pegmatite intrusions with a prominent Ta-Sn mineralization. The mineral assemblage of the pegmatites is dominated by quartz, alkali feldspar, muscovite, tourmaline, columbite, tantalite and cassiterite. Typical accessory minerals are amblygonite, spodumene, beryl and Li-phosphate minerals.

LA-ICP-MS U–Pb dating gives a Tera-Wasserburg intercept age of 957 ± 21 Ma (2 σ, n = 49, MSWD = 1.4) for the Rutongo cassiterite crystal (Figure 1) and a lower concordia intercept age of 998 ± 10 Ma (2 σ, n = 36, MSWD = 0.36) for the Gatumba cassiterite concentrate (Figure 2). Both ages are consistent with the published in-situ zircon U–Pb age (986 ± 10 Ma) of the parental Kigali granite and in-situ columbite-tantaleite U–Pb ages of the pegmatites (975 ± 8 Ma to 966 ± 9 Ma; Dewaele et al. 2011) within errors. These new cassiterite U–Pb ages represent the timing of tin mineralization in the Rutongo area and Ta-Sn mineralization in the Gatumba mining district, respectively, and indicate that the U–Pb isotopes of cassiterites in these two deposits have not been overprinted by the Pan-Africa orogeny (600 Ma to 500 Ma).

### 3.2 Piaotang W-Sn deposit in the Nanling Range, South China

The Nanling Range in South China covers a total area of 200,000 km². In this region, the basement which is composed of a metamorphosed Neo-proterozoic to Ordovician flysch-volcanic series and non-metamorphosed Late Devonian to Early Triassic sedimentary rocks is intensively folded and deformed (Wang and Shu 2012). The granitoids formed from multiple cycles of tectonomagmatism. They are commonly associated with W-Sn rare metal mineralization that defines the Nanling metallogenic belt as one of the 19 important metallogenic target areas in China. Previous studies indicate that the W and Sn mineralization in the Nanling Range and in its vicinity occurred from the Neoproterozoic, through the Paleozoic to the Mesozoic (Hu and Zhou 2012; Mao et al. 2013). Over this long time span, the Jurassic and Cretaceous periods are of high economic interest.

The Piaotang W–Sn deposit is located 12 km northeast of Dayu County, in the southern Jiangxi Province of the eastern Nanling Range. Small-scale mining of alluvial and primary tungsten mineralization started in 1919, but detailed industrial exploration was only carried out by geological survey teams in 1958 to 1966. Intensive drilling work identified a hidden granitic pluton and a major wolframite-quartz vein system. Industrial mining started in 1971 with an annual production of about 700 t WO₃. The deposit has total metal reserves of 92,000 t WO₃ (0.154% WO₃ ore grade) and 63,000 t Sn (0.115% Sn ore grade), respectively, with by-product Cu, Zn and Ag (Mao et al. 2013). The ore minerals of Piaotang deposit comprise cassiterite and wolframite, with some molybdenite, bismuthinite, chalcocite, galena and sphalerite (Zhang et al. 2010).

![Figure 3. U–Pb concordia plot and weighted mean age diagram for cassiterite from the Piaotang W–Sn deposit.](image)

Sample PT-01, the brown cassiterite pod, was collected from a stage III quartz vein in metamorphosed sandstone at the 338 m mining level. The wall-rock alteration around the quartz vein is weak. Forty analytical spots were measured on two cassiterite grains from the Piaotang W–Sn deposit. Due to their low U and Pb contents, U–Pb dating of zone II cassiterite (core) failed. Zone I cassiterite (rim) has very low Th but measurable U contents. The composition of 31 ablated spots on the two cassiterite grains varies from 9.2–28.3 ppm ²³⁸U, 0.13–0.24 ppm ²⁰⁶Pb and 0.94–2.81 ppm ²⁰⁸Pb, respectively. The weighted mean ²⁰⁶Pb/²³⁸U age is 159.5 ± 1.5 Ma (2 σ, MSWD = 0.4) (Figure 3). It agrees well with the zircon U–Pb age of igneous zircon, as well as the previously published fluid inclusions ⁴⁰Ar–³⁹Ar age of cassiterite (159.1 ± 0.9 Ma, Bai et al. 2013). Therefore, we conclude that the timing of W–Sn mineralization in the Piaotang deposit is defined at 159.5 ± 1.5 Ma.

### 4 Conclusion

Cassiterite is a common ore mineral of tin deposits which can be dated by LA-ICP-MS. Tera-Wasserburg U–Pb intercept age is the best way to eliminate common Pb effects. Dating of two cassiterite samples from the Rutong Nb-Ta-Sn and Gatumba Ta-Sn rare metal deposits in Central Africa gives U–Pb ages of 957 ± 21 Ma (Tera-Wasserburg age) and 998 ± 10 Ma, respectively. These two ages agree well with the zircon U–Pb age of the parental G4 granite, which indicates the U–Pb system in these two Rwandan cassiterite samples appears to be unaffected by Pan-African metamorphism and could represent the timing of rare metal mineralization. One cassiterite collected from the Piaotang W–Sn deposit in the Nanling Range of South China gives an excellent timing constraint on mineralization (159.5 ± 1.5 Ma), which is also in consistent with the published zircon U–Pb age of the parental granite and ⁴⁰Ar–³⁹Ar age of cassiterite.
Acknowledgements

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References


U-Pb geochronology of the Aksug porphyry Cu deposit, Eastern Tuva, Russia

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Abstract. Aksug, located in Altai-Sayan Fold Belt within Early Paleozoic Khamsara batholith is a large porphyry Cu deposit with 3.3 Mt metal copper, its formation is confined to accretion-collision events related to the interaction of Siberian continent with Paleo-Asian ocean. New geochronologic data from the Aksug deposit yield a Middle-Late Cambrian crystallization U–Pb age of 500.4±5.9 and 499.2±6.3 Ma for zircons from granodiorite porphyries that host the Cu mineralization, and 504.1±5.2 Ma for precursor barren quartz diorite. The ages of ore-bearing porphyries disagree with previous 40Ar/39Ar age determinations, being significantly older. New SHRIMP zircon and published Re-Os molybdenite ages highlight the importance of Cambrian metallogenic event within the Altai-Sayan area.

1 Introduction

The Aksug (Ak-Sug, Aksugskoye) porphyry Cu deposit in the northeastern part of Tuva republic, Russia was discovered during regional geological surveys in 1952. The mining district remains relatively poorly studied, as the region is difficult to access by conventional means. In particular, geochronological information is scarce and controversial. Here, we present new zircon U–Pb data that allow to constrain the timing of formation of the Aksug porphyry Cu deposit.

2 Geological outline

The Aksug deposit occurs within the Altai-Sayan area in the north-eastern part of Central-Asian Orogenic Belt (CAOB). The Altai–Sayan Fold Belt (ASFB) occupies the southwest frame of the Siberian Craton and comprise the large fragment of the CAOB. It forms a subduction-related accretionary orogen with juvenile crust of Vendian–Early Paleozoic age. The juvenile continental crust was formed during the Late Precambrian–Early Paleozoic evolution of island-arc systems in an open ocean or bordering a marginal basin. Terrains of island arc genesis, formed during convergence in the Paleouasian ocean, compose the main structure of the Early Caledonian ASFB. Extensive granitoid magmatism took place as the result of multiple subduction–accretion events in Early Paleozoic. Subduction-related gabbroids and granitoids (tonalite–granodiorite) occurred during the formation of the juvenile arc-continentel crust and the syn- and post-collisional granitoids formed during and after subduction–accretion of island-arcs to Siberian continent.

Late Vendian – Early Cambrian lithologic complexes in the Khamsara zone are fragments of immature late Neoproterozoic to Cambrian island arc terrane (Berzin and Kungurtsev 1996) named differently in literature: Tannu-Ola–Khamsara, Tuva–Mongolian, Kuznetsk–Tannu-Ola and Kuznetsk–Khamsara. The collision of the terrane with the Siberian continent in the Late Cambrian–Early Ordovician (Berzin and Kungurtsev 1996) was accompanied by the emplacement of granitoid batholiths of diverse compositions varying from gabbro to leucogranites. Plutos during the accretion-collisional stage are composed mainly of intermediate subalkaline rocks (predominantly diorites and tonalities).

The Aksug pluton and associated porphyry Cu mineralization are located within the giant Khamsara granitoid batholith (4500 km²) in the northeastern part of Tuva republic, Russia (Fig. 1). Two magmatic suites were emplaced during the evolution of the Aksug Cu porphyry system: plutonic suite and ore-bearing porphyry suite (Fig. 2). The plutonic suite involves the formation of large diorite-tonalite-plagiogranite pluton with minor gabbroic rocks. The pluton has been built by stocks and dikes of sodic, calc-alkaline quartz diorite, tonalite and granodiorite porphyries (the Aksug porphyry series). Low-grade molybdenite-pyrite-chalcopyrite mineralization is related to stage I granodiorite porphyries. Emplacement of a second generation of granodiorite porphyries (stage II) superimposed high-grade chalcopyrite-bornite-molybdenite ore onto the low-grade proto-ore.
Zircons were extracted from three rock samples using standard magnetic separation techniques. The zircons were handpicked under a microscope, mounted in epoxy resin and polished. Measurements of U, Th and Pb were conducted using the SHRIMP-II high-resolution secondary-ion mass spectrometer at the Center of Isotopic Research of the Karpinsky All-Russian Geological Research Institute (VSEGEI), St. Petersburg (Russia). Analytical procedures are similar to those described by (Williams 1998; Larionov et al. 2004). The TEMORA (Black et al. 2003) and 91500 (Wiedenbeck et al. 1995) zircons were used as standards. The data were processed using the procedure of Williams (1998) and references therein and by using the SQUID and ISOPLOT/Ex software of Ludwig (1999, 2000). Cathodoluminescent images were obtained on a CamScan MX2500S scanning electron microscope. The errors in ages listed in Table 1 are cited as 1σ, uncertainties in calculated concordia ages are reported at the 2σ level.

3 Analytical methods

Zircons were extracted from three rock samples using standard magnetic separation techniques. The zircons were handpicked under a microscope, mounted in epoxy resin and polished. Measurements of U, Th and Pb were conducted using the SHRIMP-II high-resolution secondary-ion mass spectrometer at the Center of Isotopic Research of the Karpinsky All-Russian Geological Research Institute (VSEGEI), St. Petersburg (Russia). Analytical procedures are similar to those described by (Williams 1998; Larionov et al. 2004). The TEMORA (Black et al. 2003) and 91500 (Wiedenbeck et al. 1995) zircons were used as standards. The data were processed using the procedure of Williams (1998) and references therein and by using the SQUID and ISOPLOT/Ex software of Ludwig (1999, 2000). Cathodoluminescent images were obtained on a CamScan MX2500S scanning electron microscope. The errors in ages listed in Table 1 are cited as 1σ, uncertainties in calculated concordia ages are reported at the 2σ level.

Table 1. SHRIMP U–Pb isotopic data for zircon from the Aksug intrusions

<table>
<thead>
<tr>
<th>Spot</th>
<th>206Pb/238U (Ma)</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>206Pb/238U</th>
<th>206Pb/238U</th>
<th>RHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-0494-1</td>
<td>3.2</td>
<td>107</td>
<td>29</td>
<td>0.28</td>
<td>4.22</td>
<td>50±11</td>
</tr>
<tr>
<td>S-0494-1</td>
<td>0.74</td>
<td>60</td>
<td>11</td>
<td>0.18</td>
<td>11.7</td>
<td>496±3.9</td>
</tr>
<tr>
<td>S-0494-2</td>
<td>0.33</td>
<td>109</td>
<td>15</td>
<td>0.14</td>
<td>7.65</td>
<td>50±11</td>
</tr>
<tr>
<td>S-0494-3</td>
<td>0.10</td>
<td>291</td>
<td>149</td>
<td>0.53</td>
<td>20.9</td>
<td>515±3.9</td>
</tr>
<tr>
<td>S-0494-5</td>
<td>0.57</td>
<td>90</td>
<td>16</td>
<td>0.18</td>
<td>6.24</td>
<td>49±11</td>
</tr>
<tr>
<td>S-0494-9</td>
<td>0.45</td>
<td>122</td>
<td>27</td>
<td>0.23</td>
<td>8.53</td>
<td>50±11</td>
</tr>
</tbody>
</table>

Note. Errors are 1-sigma. Pbc and Pb* indicate the common and radiogenic portions, respectively. Error in standard calibration was 0.6% (not included in above errors but required when comparing data from different mounts). (1) Common Pb corrected using measured 206Pb. RHO - error correlation coefficient between 206Pb/238U and 206Pb/238U.

Figure 2. Simplified geological map of the Aksug deposit. 1- Lower Cambrian volcano-sedimentary suite; Plutonic series: 2- gabbro, 3- diorite, 4- pyroxen-hornblende quartz diorite, 5- hornblende quartz diorite, 6- tonalite; Porphyry series: 7- porphyry tonalite, 8- granodiorite porphyry I, 9- granodiorite porphyry II; the granite-aplite series: 10- dikes of granodiorite, granite, aplite; 11- the Lower Devonian volcano-sedimentary series, 12- recent sediments, 13- faults, 14- sample locations.
4 Sample description

Three samples were collected from the Aksug deposit. The sampling locations are shown in figure 2. The sample S-0494G (quartz diorite) was collected from prospect pit №7, the samples S-0491A (granodiorite porphyry I) and S-0494 (granodiorite porphyry II) were collected from drill holes 23 and 13, respectively.

5 U-Pb dating

Nearly all zircon crystals analysed are euhedral prismatic or angular-shaped transparent light pink grains or fragments of such grains. Cathodoluminescent images show well-preserved primary oscillatory growth zones, typical of magmatic zircons without older cores and overgrowth rims (Fig. 3 A-C). The Th/U ratios from diorite sample S-0494G and granodioritic porphyry samples S-0491A and S-0494 have ranges from 0.18 to 0.40, from 0.16 to 0.49 and from 0.14 to 0.51, respectively, which is consistent with their igneous origin. The results of the zircon U-Pb dating of samples from the Aksug deposit are listed in Table 1 and are shown in a concordia diagram in figure 3 (D-F).

Ten analyses of ten zircons from quartz diorite (S-0494G) yielded a concordia age of 504.1±5.2 Ma (MSWD of concordance = 0.37). Ten analyses of nine zircons from granodiorite porphyry I (S-0491A) yielded a concordia age of 500.4±5.9 Ma (MSWD of concordance = 0.073). Ten analyses of ten zircons from granodiorite porphyry II (S-0494) yielded a concordia age of 499.2±6.3 Ma (MSWD of concordance = 0.0059).

6 Discussion

Previous geochronological studies of the Aksug deposit were reported as Late Cambrian - Middle Ordovician ages (497-462 Ma) for plutonic series (gabbro, diorite, quartz diorite) and Early Devonian age (~404 Ma) for ore-bearing granodiorite porphyry on the basis of 40Ar/39Ar determinations (Sotnikov et al. 2003). However, molybdenite Re–Os dating yielded a large discrepancy in Re–Os versus 40Ar/39Ar ages (Berzina et al. 2003). Re–Os ages of molybdenite from Aksug (511 ± 2 Ma) from one sample and replicates of 516 ± 2 and 518 ± 2 Ma from another sample are all significantly older than the 40Ar/39Ar ages for ore-bearing porphyries and even the precursor plutonic rocks that host ore-bearing porphyries. The new Re-Os ages of molybdenite from Aksug (517.3 ± 3 and 517.4 ± 3) reported recently by Pollard et al. (2017) are similar to the older ages obtained by Berzina et al. (2003). New high-resolution SHRIMP U–Pb zircon ages, obtained from the Aksug rocks, provide further constraints on the time of formation of the deposit.

Quartz diorite from barren plutonic suite of Aksug has a SHRIMP zircon age of 504.1 ± 5.2 Ma, which is relatively close to the 40Ar/39Ar age of 497 ± 1 Ma for diorite reported by Sotnikov et al. (2003). SHRIMP zircon dating of the ore-bearing porphyry suite yielded ages of 500.4 ± 5.9 and 499.2 ± 6.3 Ma for granodioritic porphyries of stage I and II, respectively. These ages disagree with the previous 40Ar/39Ar age for the porphyry series by being significantly older. The new U–Pb data presented herein provide evidence that Cambrian magmatic event is responsible for the porphyry intrusion...
and Cu–Mo mineralization at Aksug. The previously reported Early Devonian $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Sotnikov et al. 2003) do not reflect ages of primary crystallization of the Aksug porphyry intrusions. The $^{40}\text{Ar}/^{39}\text{Ar}$ ages probably reflect the later magmatic overprint.

However, the molybdenite Re–Os ages (Berzina et al. 2003, Pollard et al. 2017) are several million years older than the one for newly dated hosting porphyry intrusions. This suggests either: 1) that U–Pb zircon dates are slightly younger than their true ages as a result of Pb-loss and/or inappropriate common Pb correction and/or 2) that the Re-Os ages are biased by analytical problems or by complex system behaviour in molybdenite. The current data set does not allow us to rule out the reason of discrepancy between U-Pb and Re-Os ages. Nevertheless, in spite of some discrepancies between previously reported Re-Os and the new U–Pb ages, they provide an evidence that the deposit was formed in the Cambrian period, not in the Early Devonian as previously thought.

The U–Pb zircon ages of the Aksug rocks are consistent with those recently reported for the rocks in the Kyzyk-Chadr porphyry Cu–Mo deposit, located ~200 km SW from the Aksug within Ozhin batholith and occurring in a similar geotectonic setting (Gusev et al. 2014). The U–Pb SHRIMP zircon ages for Kyzyk-Chadr barren granite that was intruded by porphyry is 508 ± 7 Ma, and for the ore-bearing quartz diorite porphyry and the granodiorite porphyry is 507 ± 2 and 490 ± 4 Ma, respectively.

The new results are in good agreement with the age of numerous Late-Vendian – Early Paleozoic granitoid intrusions comprising large Kaa-Khem and Tannu-Ola batholiths (Fig. 1) in eastern Tuva (Rudnev et al. 2015). According to Rudnev et al. (2015), an extensive volume of granitoids was emplaced during Vend–Early Cambrian (~562–518 Ma) in an island-arc environment. More intense magmatic activity occurred during accretion-collision stage (~500–450 Ma).

The new results indicate that the large plutonic and small ore-related porphyry Aksug intrusions were emplaced during a much shorter interval and without significant time gap between them than previously thought (Sotnikov et al. 2003). Available geochronological and isotopic data show that the magmas related to porphyritic Cu(Mo) (Sotnikov et al. 2003, Available geochemical and isotopic data show that the magmas related to porphyritic Cu(Mo) (Sotnikov et al. 2003) are several million years older than the one for newly dated hosting porphyry intrusions. This suggests either: 1) that U–Pb zircon dates are slightly younger than their true ages as a result of Pb-loss and/or inappropriate common Pb correction and/or 2) that the Re-Os ages are biased by analytical problems or by complex system behaviour in molybdenite. The current data set does not allow us to rule out the reason of discrepancy between U-Pb and Re-Os ages. Nevertheless, in spite of some discrepancies between previously reported Re-Os and the new U–Pb ages, they provide an evidence that the deposit was formed in the Cambrian period, not in the Early Devonian as previously thought.

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The new results indicate that the large plutonic and small ore-related porphyry Aksug intrusions were emplaced during a much shorter interval and without significant time gap between them than previously thought (Sotnikov et al. 2003). Available geochronological and isotopic data show that the magmas related to porphyritic Cu(Mo) mineralization at Aksug were mainly derived from mantle depleted metasomatized mantle was possibly involved in the generation of their precursor magma.

7 Conclusion

Zircon U–Pb SHRIMP dating yielded ages of 500.4 ± 5.9 and 499.2 ± 6.3 Ma for ore-related granodiorite porphyries and 504.1 ± 5.2 Ma for barren precursor quartz diorite, hosting porphyry intrusions. These new U-Pb ages and reported Re-Os molybdenite ages (Berzina et al. 2003, Pollard et al. 2017) further confirm an important and extensive magmatic-metallogenic event in Altai-Sayan area during the Cambrian.

Acknowledgements

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Towards a high resolution U-Pb temporal framework for the Oslo Graben

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Abstract. The Oslo Graben is a highly magmatic rift structure that evolved between about 310 and 260 Ma. The evolution was characterized by several steps. It started with rifting and deposition of clastic sediments, followed by alkalic mafic and ultramafic basalts and some microsyenites at around 300 Ma. Emplacement of the large Larvik larvikite complex took place between 298 and 290 Ma, contemporaneously with the early phases of rhomb porphyry extrusions, the latter lasting until about 280 Ma. Large volcanic complexes formed around 286-280 Ma in the Vestfold region and at 276-272 Ma further north, broadly in conjunction with emplacement of large granitic batholiths. Magmatism was concluded by the emplacement of the youngest dykes and granites at 262-259 Ma.

1 Introduction

The Oslo Graben represents a long-lived, magma-rich rift structure developed in Precambrian crust of the Baltic Shield in the period between the late Carboniferous and the end of the Permian. In the past it has yielded important mineral resources, especially Zn, Pb, Cu, Bi and Fe from skarn deposits (and magmatic Mo), and it remains an active source of the unique larvikite ornamental stone. Moreover, it has long been accepted that the hydrothermal activity related to the rift magmatism was involved in the development of the Kongsberg silver deposits.

Extensive mapping throughout the past century and Rb-Sr geochronology, mainly between 1970 and 1990 have established a broad chronological framework for the development of the Oslo Graben (Sundvoll and Larsen 1990; Sundvoll et al. 1990). In our subsequent studies we employ ID-TIMS U-Pb, and also Ar-Ar geochronology to resolve in more detail the chronology of the rift and also to verify some proposed correlations.

2 Geological setting

The development of the Oslo Graben has been divided in six stages (Larsen et al. 2008): (1) a proto-rift stage with deposition of mainly continental sediments and local intrusions of syenitic sills; (2) initial rift stage with the first basaltic volcanism; (3) rift climax, with rhomb porphyry fissure volcanoes; (4) mature rift, with central volcanoes and caldera collapse; (5) syenitic to alkali granitic batholiths; (6) late small granitic plutons.

Figure 1. Geological map of the Oslo Graben area (from Larsen et al. 2008). Abbreviations: Brum = Brumunddal, Krok = Krokskogen, Oy = Øyangen, He = Heggelia, Ni = Nittedal, Bæ = Bærum, Gl = Glitrevann, Dr = Drammen, Sa = Sande, Hi = Hillestad and Ra = Rammes.
3  Summary of the U-Pb geochronology

A comprehensive U-Pb geochronological program is being carried out to constrain in more detail the chronology of the main development stages of the belt.

The earliest period of rift-related sedimentation cannot be dated directly, but the youngest detrital zircon grain in these sediments indicates a maximum depositional age of 319 Ma (Dahlgren and Corfu 2001), consistent with the Moscovian age (ca. 310 Ma) of fossils in local marine limestones (Olaussen 1981).

A representative sample of the syenitic (maaïsite) sills, representing the earliest magmatic activity of the area, yields a zircon U-Pb age of 300 Ma. These were essentially coeval with mafic to ultramafic alkalic volcanic units formed during initial rifting, yielding ages of 300-299 Ma largely based on U-Pb in perovskite (Corfu and Dahlgren 2008).

This early magmatism was followed by emplacement of the Larvik plutonic complex, comprising nested, circular bodies emplaced progressively from east to west and then to the northwest between 298 and 290 Ma (Dahlgren et al., 1996). This event corresponds to the time of eruption of the earliest rhomb porphyry lavas in the Krokskogen area. Flows of the latter sequence erupted periodically until about 280 Ma, as supported also by Ar-Ar feldspar dating.

Massive volcanic and subvolcanic activity followed in the Krokskogen area between 278 and 272 Ma, significantly later than the corresponding volcanism in the Vestfold area, which occurred between 286 and 280 Ma. Larvikites to granites of the Siljan and Skrim plutonic complex formed at 282-277 Ma (Pedersen et al., 1995).

The age of the large granitoid batholiths is currently being investigated by other groups, but preliminary ages suggest that they evolved largely in connection with development of the large volcanic complexes. Correlating this event in greater detail will be a task of future research. The youngest plutonic activity was marked by the local emplacement of syenitic dykes, one dated at 262 Ma, and emplacement of a granitic pluton at 259 Ma, both in Oslo.

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References

U-Pb geochronology of the igneous rocks associated to the Rio Tinto VMS deposit

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Abstract. Rio Tinto in the Iberian Pyrite Belt (IPB) is the largest volcanogenic massive sulfide concentration on Earth. Its geology is composed of several igneous lithotypes associated with the Volcanic Sedimentary Complex (VSC) of Late Devonian-Early Carboniferous age.

In this work, we present new SHRIMP U-Pb zircon dating of the rocks hosting the ore, including: 1) volcaniclastic felsic rocks of the Zarandas area; 2) the hydrothermally altered felsic rocks hosting the stockwork; 3) equivalent felsic coherent rocks but lacking hydrothermal alteration from Zarandas; and, 4) a late rhyolite cryptodome that crosscuts the mineralized Rio Tinto rocks, 5) a granodiorite and 6) a tonalite, the last two in the village of Gerena. The obtained ages establish the relationship between these lithotypes and provide clues on the formation of this world class deposit.

1 Introduction

The Iberian Pyrite Belt (IPB) is one of the most outstanding VMS provinces in the world, with more than 1600 Mt of massive sulfides originally in place and around 250Mt of stockwork ore. Rio Tinto is one of the eight giant deposits that belong to IPB and accounts for 510 Mt of the province's total ore (Tornos 2006). Previous studies have dealt with the volcanic rocks associated with the mineralization, but the geochronological knowledge of the evolution of the magmatism related to the mineralization in this deposit is still low. This work seeks to establish the geological evolution of the Rio Tinto region based on zircon geochronology of selected samples of the different lithologic facies described by Conde (2016) and Rosa (1992) aiming to better understand the genesis of the Rio Tinto district, one of the most important volcanic-hosted massive sulphide district in the world.

The samples dated in this study were collected in the Rio Tinto mine, in the Zarandas area, south of the mine, where equivalent rocks but lacking hydrothermal alteration are found and in the village of Gerena (Fig. 1). The samples from the Rio Tinto mine are a massive rhyodacite underlying the massive sulfides (sample RT-05) in the Atalaya open pit, and a late rhyolite cryptodome (sample RT-02) that crosscuts equivalent hydrothermally altered rocks hosting the stockwork in Filón Norte-Cerro Colorado. The two Zarandas lithotypes studied are a

Figure 1. a Location of Rio Tinto, Zarandas and Gerena in the Iberian Pyrite Belt, b in detail, the Rio Tinto Mine with the samples locations and c the coarse-grained granodiorite (GR-01) and the fine-grained tonalite (GR-02) sampled.

volcaniclastic felsic rock (sample ZN-01) that is intruded by a fine-grained coherent rhyodacite (sample ZN-02). The two lithotypes of the Gerena Massif studied were a fine-
grained tonalite (sample GR-02) that occurs as numerous enclaves in the middle of a coarse-grained granodiorite (sample GR-01).

Analyses were performed in the Laboratory of High Resolution Geochronology of the Institute of Geosciences of the University of São Paulo (GeoLab-IGc-USP) following the analytical procedures presented by Sato et al. (2014).

2 Geological setting

The Iberian Pyrite Belt (IPB) was form within a set of pull-apart basins, related to the oblique collision of the South Portuguese plate with the Ossa Morena Zone (Tornos et al. 2005), in the southern part of the Iberian Variscan orogenic belt. The transtensional opening of this first order basins led to the suture of this collision is defined by the oceanic Pulo de Lobo terrane, Acebucher-Beja ophiolite and by the South Iberian shearzone. This collision and the syn-volcanic activity triggered circulation of hydrothermal fluids, which led to formation of syngenetic massive sulfide (VMS) deposits. The magmatism observed in the region is bi-modal, predominantly felsic. The felsic and mafic rocks evolved in different ways and are not related to fractional crystallization. The basic rocks are associated to a decompression of the upper mantle related to the transtensional tectonics and the felsic rocks with crustal melting at low pressures, which implies a high heat flow generated by crustal thinning, magma underplating and/or significant emplacement of primary magmas within the crust (Mitjavila et al., 1997).

The IPB is the northernmost unit of the South Portuguese Zone and consists in a 250km long and 25 to 75km wide belt dominated by volcanic and sedimentary rocks. The regional geology is relatively simple and has been described in detail by Tornos (2006).

In a simplified scheme, the IPB is formed by a volcanosedimentary sequence that includes from bottom to top: 1) the Phyllite-Quartzite (PQ) Group, a monotonous detrital sequence of alternating mudstone and sandstone deposited in a shallow marine continental shelf and of late Devonian age; 2) the Volcanic Sedimentary (VS) Complex, which includes a heterogeneous mafic-felsic volcanic sequence interbedded with mudstone and sandstone deposited in a shallow marine continental shelf and of late Devonian age; 3) the Flysch Group, formed by felsic rocks with crustal melting at low pressures, which implies a high heat flow generated by crustal thinning, magma underplating and/or significant emplacement of primary magmas within the crust (Mitjavila et al., 1997).

At Rio Tinto district, the whole sequence crops out. The PQ Group can be found in the adjacent areas on the north and the south of the Rio Tinto synclinal. Conformably above it, in the thick VSC have been described four major units (Tornos 2006; Mellado et al. 2006; Conde 2016). (1) The footwall (Mafic-Siliciclastic Unit), comprises mafic rocks (sills and lava) interbedded with dark shale and mafic volcaniclastic rocks. Above it, thin the (2) Lower Sedimentary Unit made up of dark shale and a characteristic layer of polymictic conglomerate, which includes fragments of shale, felsic rocks, and locally, pyrite rich nodules of likey hydrothermal replacive origin. This sedimentary unit is usually tectonically overlain by (3) the thick Felsic Unit. This is an heterogeneous a thick volcanic sequence that includes felsic domes and sills of dacitic-rhyodacitic composition, with associated breccias (autobreccias and hyaloclastite), interbedded with pumice-, crystal- and vitriclast-rich sandstone and minor shale. Late intrusive rhyolite crosscuts the hydrothermal altered rhyodacite and the related stockwork. Both the mafic and felsic rocks show a pervasive hydrothermal alteration and host a large stockwork that includes large lenses of replacive massive sulphides. The uppermost felsic rocks underlie an exhalative, shale-hosted, mineralization that is rooted in the stockwork zone (Tornos 2006; Conde 2016). Tectonically, the Felsic Unit is capped by Upper Sedimentary Unit comprising dark shale, green and red siltstone and chemical sediments (chert). The sequence in the Zarandas area is similar but lacks of hydrothermal alteration and mineralization.

Plutonic rocks are uncommon in the IPB and are confined to the northern part. Despite showing unclear relationships with the VS Complex, U/Pb ages obtained in the Campofrío pluton (354 ± 5 Myr, Dunning et al. 2002, 346 ± 1 Myr, Barrie et al. 2002) show that at least some of them correspond to the subvolcanic roots of the VS Complex.

The plutonic rocks of the Gerena Massif are bimodal and thus could be related to the VSC magmatism. They show a process of mingling between two distinct rock types: i) a fine granular tonalite and ii) a medium grained granodiorite.

3 Results and discussion

The U-Pb zircon concordia ages obtained in this work are shown in Figure 2 and allow us to establish an evolutionary model of the magmatic activity occurring in the Rio Tinto region. The volcaniclastic sandstone of Zarandas (ZN-01) represents, with an concordia age of 358 ± 2.1 Myr, the onset of the felsic volcanism in the area. This volcaniclastic sandstone presents fragments of pumice, which indicates a small transport distance, possibly less than a few km (Rosa et al., 2010) and implies that the volcanism is local. Rocks of this age are known in several areas and VMS deposits of the Portuguese IPB - from the west to east, Carreira, Azinheira de Barros, Lagoa Salgada, Aljustrel, Albernoa and Serra Branca (Barrie et al. 2002; Rosa et al. 2009).

Both the dome complexes of Zarandas and Cerro Colorado have indistinguishable ages close to 350 Myr (ZN-02: 350 ± 2.4 Myr; RT-05 is 348 ± 2.5 Myr), which are compatible with the TIMS ages obtained by Valenzuela et al. (2011) for the footwall rhyolite of San Dionisio ore body of Rio Tinto and a regional altered rhyolite from Rio Tintos region.
Figure 2. a U-Pb Concordia ages obtained for the sample ZN-01 and b concordia age obtained for the sample ZN-02. c and d concordia ages obtained in the two populations of zircons analyzed in sample RT-02. e Concordia age obtained for the sample RT-05. f Concordia ages obtained for the sample GR-01. g Two populations of zircon present in the sample GR-02 and h the concordia age obtain for the younger zircon population in GR-02. All ages were calculated using the Isoplot version 4.0 program (Ludwig 2009).
Late rhyolite postdating mineralization and hydrothermal alteration (RT-02) shows two populations of zircons with ages of 339 ±2.6 and 351 ±2.7 Myr. The first one younger probably records the age of emplacement while the older likely reflects inheritance from the previous units via assimilation, which has also been observed in the nearby Aljustrel deposit (Rosa et al. 2009).

These U-Pb ages suggest that the felsic magmatism at Rio Tinto lasted for at least 19 Myr (358 ± 2.1 Myr - 339 ± 2.6 Myr), which increases significantly the duration of the magmatism at Rio Tinto of Valenzuela et al. (2011) (351.5 ± 0.4 Myr - 345.7 ± 0.6 Myr). This igneous activity is also of longer duration than the period of 7 Myr and 9 Myr of igneous activity observed by Rosa et al (2009) in Aljustrel and Serra Branca respectively. This long time span shows that VSC volcanism occurred intermittently over an extended period -greater than that already described for IPB- and mineralization is an episodic event within the duration of the volcanic/magmatic activity – and this episodic event occurred in the age of 350 Ma.

The coarse-grained granodiorite (GR-01) at Gerena has an concordia age of 349 ±2.4 Myr and confirms that the intrusive rocks here are age-correlated with the dome complexes at Rio Tinto and, thus, these plutonic rocks are the roots of the VS Complex. The related tonalite (GR-02) hosts two distinct zircon populations. A first population has Rhyacian ages (upper intercept age of 2195 ±7.4 Myr) and records a Pb loss event in the Ediacaran times (587 ±29 Myr). This age shows that the tonalite is sourced in the Paleoproterozoic, as also documented for the volcanic rocks of the VSC magmatism in Rosa et al. (2009). The second zircon population yields an concordia age of 348 ±1.9 Myr, which also correlates with the 350 Myr magmatic event.

In summary, the obtained data show that the felsic magmatism at the Rio Tinto region started at 358 Myr and lasted at least until 339 Myr. The mineralization is likely to be formed in relationship with a 350 Myr magmatic event that produced large felsic dome complexes and the rocks of the Gerena Massif are probably the roots of the VSC at 350 Myr.

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References


Multi-isotope dating to constrain gold mineralization in the Xiadian deposit, Jiaodong peninsula

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Abstract. The Xiadian gold deposit, located in the Zhaoyuan–Laizhou belt, Jiaodong peninsula, is characterized by disseminated and stockwork ores enclosed by hydrothermally altered wallrocks. The exact age and the genesis of the gold deposit remain controversial. The wallrock Linglong granite represents the earliest magmatic event at Xiadian, and yielded a zircon LA–ICPMS U–Pb age of 159.5±0.9 Ma (2σ, MSWD=0.63). Subsequent geologic events were recorded by minor amounts of quartz–pyrite–molybdenite veins which yield a weight average Re–Os molybdenite model age of 125.9±0.8 Ma (2σ, MSWD=0.23) by molybdenite Re–Os method. The formation of such veins was close to the emplacement of adjacent Guojialing granodiorite (126–130 Ma), and thus may be considered as a product of post-magmatic hydrothermal activity. Gold mineralization took place at 120.0±1.4 Ma (2σ, MSWD=0.59), determined by LA–ICPMS U–Pb dating on hydrothermal monazite from quartz–polymetallic sulfide veins. Prior to and post mineralization, voluminous hydrothermally altered porphyric diorite and fresh quartz diorite porphyry dykes were emplaced, which yielded U–Pb ages of 121.3±1.4 Ma (2σ, MSWD=0.28) and 115.8±1.9 Ma (2σ, MSWD=0.71), respectively. Based on these geochronological data, the genesis of the Xiadian deposit might be related to the craton destruction and lithosphere thinning in the eastern North China Craton.

1 Introduction

Jiaodong gold province, with an area of approximately 3500 km², is located within the southeastern margin of the North China Craton and is the largest gold producing region in China with reserves of >3000 t gold (Goldfarb and Santosh, 2014). The Zhaoyuan–Laizhou gold belt, situated in the northwestern Jiaodong peninsula (Fig. 1), hosts several giant gold deposits, like Sanshandao, Jiaojia, Xincheng, Linglong, and Dayingezhuang, accounting for over 80% of the Jiaodong gold reserves. The Xiadian gold deposit, located in the southern part of this belt, is characterized by disseminated and stockwork–style pyrite–sericite–quartz alteration and related ores controlled by the Zhaoyuan–Pingdu fault.

Previous geochronological studies by Rb–Sr, K–Ar and 40Ar–39Ar dating of alteration minerals, U–Pb dating of hydrothermal zircon, as well as 40Ar–39Ar and Rb–Sr dating on quartz and pyrite, indicated that gold mineralization in the Jiaodong gold province is clustered at 120±5 Ma (Fan et al., 2016). Although mineralization and alteration types at the Xiadian deposit resemble those of other gold deposits in Jiaodong, its mineralization timing has been controversial. Yang et al. (2016) reported zircon fission track (ZFT) ages for the Xiadian gold deposit, and suggested that the timing of mineralization was close to 130 Ma, and that the mineralization was controlled by the Linglong metamorphic core complex. However, the closure temperature of ZFT (240±50 ºC) is lower than the temperature of gold mineralization (ranging from 140 to 380ºC, concentrated at 240-300 ºC) at Xiadian (Xu et al., 2013). In addition, the complex hydrothermal activity would cause a broad range of ZFT ages. So the age of gold mineralization and the associated geological event remain equivocal. In this report, we present LA–ICPMS zircon U–Pb ages for the wallrock Linglong granite, as well as pre–ore and post–ore porphyry dykes. Moreover, we represent high-precision monazite U–Pb ages and molybdenite Re–Os ages for hydrothermal fluid alteration events at Xiadian.

2 Regional and ore deposit geology

The Jiaodong peninsula occupies the easternmost edge of the Eastern Block of the North China Craton and is geologically divided into the southeastern Ludong terrane and the northwestern Jiaobei terrane by the Mishan fault. The Ludong terrane petrologically belongs to the northern margin of the South China Block, which records a subduction history associated with a Triassic collisional event.

The Jiaobei terrane petrologically belongs to the northern margin of the South China Block, which records a subduction history associated with a Triassic collisional event.

The Jiaobei terrane is principally defined by the Archean Jiaodong Group and the Paleoproterozoic Fenzishan and Jingshan Groups. Mesozoic magmatic rocks are widely...
exposed in the Jiaobei terrane and two main periods of magmatism are recognized, Jurassic and Early Cretaceous. The Jurassic magmatic activity is represented by the crustally-derived Linglong, Luanjiahe, and Kunyushan granitoids, emplaced at 160–150 Ma (Yang et al., 2012). In the Early Cretaceous, extensive magmatism took place through strong crust-mantle interaction, including formation of widespread granitoids (130–126 Ma and 113–110 Ma), mafic to felsic volcanic rocks in the Jiaolai Basin (130–110 Ma), and numerous mafic dikes (124–122 Ma) with less commonly at 110 to 102 Ma (Yang et al., 2012; Cai et al., 2013). The Mesozoic granitoids are hosts for most gold deposits.

Gold deposits in the peninsula can be divided into three mineralized belts from west to east, which include Zhaoyuan-Laizhou, Penglai-Qixia, and Muping-Rushan (Fig. 1). Gold deposits have been classified as the Linglong-type and the Jiaojia-type, both of which are essentially fault controlled. The Linglong-type mineralization is characterized by massive auriferous quartz veins hosted in subsidiary second- or third-order faults cutting Mesozoic granitoids, whereas the Jiaojia-type mineralization consists of disseminated- and stockwork-style ores located in regional faults, which are enveloped by broad alteration halos.

The Xiadian gold deposit, with a reserve of >200 tons of Au (Yang et al., 2016), is structurally controlled by the southern part of the NE-treading Zhaoyuan–Pingdu fault (Fig. 1). The deposit is mainly hosted in the fault wall of the fault, as well as the contacts between Jiaodong Group and Linglong granite, forming five discontinuous lenticular orebodies. Some pre-ore and post-ore dykes are also present. The pre-ore porphyritic diorite dykes are cut by quartz–sulfide veins and display quartz and pyrite alteration. The post-ore quartz diorite porphyry dykes are devoid of mineralization and alteration.

A quartz–pyrite–molybdenite vein, cutting pegmatite hosted in the silicified Linglong granite, was found in the 39ZK6 borehole at downhole depths between -738m and -741m. The vein is commonly 5–8 mm wide and shows no crosscutting relationship with the gold-rich orebodies. Petrographic and scanning electron microscopy (SEM) observations revealed that molybdenite in the vein is intergrown with pyrite and quartz (Fig. 2a, 2b). Wallrocks exhibit strong silicification, sericitization, pyrite-sericite-quartz alteration and carbonate alteration. The pyrite–sericite–quartz alteration is accompanied by gold mineralization. Silicification occurred before, during and after gold mineralization.

Field and optical microscopy investigations indicate four hydrothermal stages at Xiadian, i.e. (I) quartz–pyrite, (II) quartz-sericite–pyrite, (III) quartz-polymetallic sulphide and (IV) quartz–calcite–pyrite stages. Accessory monazite, zircon, apatite, rutile, and thorite (enclosed in monazite) were identified in thin sections. The monazite is typically light yellow in transmitted light, forming euhedral to anhedral crystals of variable size (10–300 μm). Small monazites are often enclosed by pyrite and quartz (Fig. 2c). Large monazite grains commonly host pyrite and sericite (Fig. 2d, e). Quartz, thorite and rutile are additional mineral inclusions in the monazite. All these features indicate that the monazite was formed during the Stage III hydrothermal mineralization event and associated fluid infiltration into the Linglong granite, resulting in the gold–bearing veins and related minerals (Fig. 4f).

3 Geochronologic results

Sixteen spots on zircon were analyzed for the Linglong granite, yielding concordant $^{206}\text{Pb}/^{238}\text{U}$ ages with a weighted mean of 159.5±0.9 Ma (2σ, MSWD=0.63). The weighted $^{206}\text{Pb}/^{238}\text{U}$ age is interpreted as the crystallization age of the granite. Fifteen grains were selected from the pre-ore dyke for analysis. Four spots yield concordant $^{206}\text{Pb}/^{238}\text{U}$ age with a weighted mean of 121.3±1.4 Ma (2σ, MSWD=0.28), representing the age of the intrusion of the pre-ore dyke. The other zircon analyses are discordant with $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 145.6±13.1 Ma (2σ) to 2080.7±53.2 Ma (2σ) which may not be of magmatic origin as they are dark under CL or with uneven rims. Twenty–one spots on zircon were analysed for the post–ore dyke, yielding concordant $^{206}\text{Pb}/^{238}\text{U}$ ages with a weighted mean of 115.8±1.9 Ma (2σ, MSWD=0.71). The weighted $^{206}\text{Pb}/^{238}\text{U}$ ages are interpreted as the crystallization age of the zircons and approximate emplacement of the pre–ore dyke. Molybdenite have Re contents ranging from 7.8 to 107.1 ppm, and common Os contents from 30 to 50 ppb. A well-fitting $^{187}\text{Re}$ vs $^{187}\text{Os}$
isochron produces an age of 124.8±2.1 Ma (2σ, MSWD=0.10). The model ages are calculated with the decay constant of λ_{187Re}=1.666×10^{-11} yr^{-1} with an uncertainty of 0.017×10^{-11} (1%). Calculated Re-Os molybdenite model ages range from 125.0 to 126.4 Ma, yielding a weight average Re-Os molybdenite model age of 125.9±0.80 Ma (2σ, MSWD=0.23) (Fig. 3), which is in good agreement with the five-point $^{187}\text{Re}$ vs. $^{187}\text{Os}$ isochron age, reflecting that the molybdenite formed at ca. 126 Ma.

The in-situ U–Pb dating of 27 spots on monazite grains from two polished thin sections are analysed. The U–Pb data cluster on the Tera–Wasserburg concordia diagram, and give a lower intercept age of 120.2±2.0 Ma (MSWD=0.78) (Fig. 4). The initial $^{207}\text{Pb}/^{206}\text{Pb}$ data is 0.8827±0.02. The $^{207}\text{Pb}$-corrected weighted $^{206}\text{Pb}/^{238}\text{U}$ age is 120.0±1.4 Ma (n=27, MSWD=0.59) which is in agreement with the lower intercept age.

4 Discussion

The obtained LA–ICPMS zircon U–Pb dating age of 159.5±0.9 Ma for the Linglong granite at Xiadian agrees well with the previous zircon U–Pb ages ~160 Ma in the Zhaoyuan–Laizhou belt (Yang et al., 2012). The exposed Linglong granite at Xiadian coincided with the regional Late Jurassic magmatic event. Geodynamic processes for formation of the Late Jurassic Linglong granite at Jiaodong are considered to have been related to large-scale extension of the lithosphere coupled with upwelling of the asthenosphere (Yang et al., 2012). During the Early Cretaceous, asthenospheric upwelling caused intense interaction between crust and mantle, with corresponding multi-stage magma mixing and emplacement of the Guojialing granodiorite at ~130 Ma marking the end of the Jiaodong extensional event (Jiang et al., 2016; Mills et al., 2015). Guojialing granodiorite, though not observed in the Xiadian gold deposit, was intercepted in a drill hole in the nearby Dayingezhuang gold deposit at a depth of ~1483 m. At Xiadian, evidence for the presence of the Early Cretaceous hydrothermal activity is represented by the quartz–pyrite–molybdenite veins. Well defined, high-precision, and accurate isochron ages for five molybdenite samples indicated that molybdenite mineralization occurred at ca. 126 Ma, closely followed by the intrusion of the Guojialing granodiorite. Since there are no other hydrothermal events during that time at Jiaodong, it is postulated that the molybdenite originated from differentiation of the Guojialing granodiorite.

The zircon U-Pb dating indicates that the age of the dykes in the Jiaodong peninsula range from 127 to 87 Ma (Cai et al., 2013). Geochronological results shows that the U–Pb ages of the pre-ore diorite dykes and post-ore quartz diorite dykes at Xiadian are 121.3±1.4 Ma and 115.8±1.9 Ma, respectively. These ages overlap the intrusion of the regional Early Cretaceous dykes (Fig. 5). Liu et al. (2004) showed that the emplacement of the dykes has been correlated to the Cretaceous crustal extension in the Jiaodong peninsula. The U–Pb ages of the pre–ore and post–ore dykes can constrain the gold mineralization age at Xiadian between 121 Ma and 116 Ma.

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Previous geochronological studies of gold mineralization in the Jiaodong peninsula employed the indirect method on alteration minerals and quartz, for example, Rb-Sr, K-Ar and $^{40}$Ar/$^{39}$Ar dating on sericite/muscovite and $^{40}$Ar/$^{39}$Ar on quartz, and U-Pb dating on hydrothermal zircon, or direct method Rb-Sr dating on sulphide. Those results indicated that gold mineralization in the Jiaodong district occurred between 125 and 114 Ma. However, no direct and in-situ dating results have been reported yet. As monazite has a robust isotopic system (U-Th-Pb) with high closure temperatures, it is an ideal mineral for dating hydrothermal deposits. The monazite closely associated with pyrite, quartz and sericite in quartz-polymetallic sulphide veins at Xiadian indicates that it was formed during the Stage III hydrothermal mineralization event. Monazite U-Pb dating in this study provides the first direct in-situ age for the gold mineralization at Jiaodong, and also vigorously constrains the gold mineralization in the Jiaodong peninsula at ca. 120 Ma (Fig. 5).

During the period of gold mineralization at ~120 Ma, the eastern North China Craton (NCC) witnessed craton destruction or decratonization (Zhu et al. 2012), regional tectonic inversion and significant lithosphere thinning, strong crust–mantle interaction and asthenospheric upwelling (Zhai et al., 2003). Zhu et al. (2015) have well demonstrated possible relations between genesis of gold deposits and craton destruction in the NCC, and classified those deposits into decratonic gold deposits. The Xiadian gold deposit should be one case related to the craton destruction based on above geochronological data.

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References
Geochronological constraints on Late Devonian volcanic-hosted massive sulfide deposit stratigraphy at Myra Falls, British Columbia, Canada

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Abstract. The Myra Falls volcanic-hosted massive sulfide (VHMS) camp is one of western Canada’s most productive polymetallic mines. Mineralization occurs at two stratigraphic ore horizons in volcanic strata of the mid-Paleozoic Sicker Group. Previous geochronology studies at Myra Falls have yielded relatively imprecise age results. To investigate the crystallization history of the felsic volcanic host rocks we have employed a combination of LA-ICP-MS and CA-ID-TIMS U-Pb zircon analysis of samples from the subsurface H-W ore horizon on sample of coherent rhyolite. These new results combined with available data from the H-W ore horizon indicate felsic volcanism occurred between 366 ±4 Ma and 357.9 ±2.5 Ma. High precision CA-ID-TIMS and LA-ICP-MS U-Pb zircon results indicate that coherent rhyolite host rocks of the Ridge East Zone crystallized at 362.46 ±0.57 Ma, 362.32 ±0.74 Ma and 357.9 ±2.5 Ma.

1 Introduction

Myra Falls is an underground polymetallic mine located on central Vancouver Island in Strathcona Provincial Park, 90 km southwest of Campbell River, BC, Canada (Fig. 1). It is one of western Canada’s most productive VHMS mining camps exceeding 30 Mt of ore production as of April 2013 at 5.5% zinc, 1.6% copper, 0.6% lead, 2.0 g/t gold and 54 g/t silver (per. comm. Rick Sawyer).

Host rocks are Late Devonian to Early Mississippian submarine felsic volcanic and marine sedimentary rocks of the Myra Formation (Juras 1987). Over eleven massive sulfide orebodies have been discovered and mined since 1966. Massive sulfide mineralization form lens- to pod-shaped geometries that are spatially- and temporally-related to two cycles of felsic volcanism, which, define two camp-scale stratigraphic ore horizons (Juras 1987; Robinson et al. 1996). The near surface Lynx-Myra-Price (L-M-P) and subsurface Harold-Wright (H-W) ore horizons are separated by up to 500 m of stratigraphy.

Though the overall stratigraphy of the Myra Formation is well documented (e.g. Juras 1987; Robinson et al. 1996; Sinclair 2000; Chong 2004; Jones et al. 2006), important geochronological questions remain. Here, we present new U-Pb zircon ages from coherent rhyolite within the Myra Formation to better constrain the temporal relationship between the H-W ore horizon and their host rocks.

Figure 1. a. Location map of Myra Falls and Cowichan Lake uplift and associated VHMS deposits (after Yorath et al. 1999). b. Map of Myra Falls showing two camp-scale ore horizons, L-M-P (grey) and H-W (red) (after Jones et al. 2006). c. Composite cross section of Myra Falls (after Jones et al. 2006). The west block area (WBA) is located between the Ridge Zone East (RZE) and the Ridge Zone West (RZW).

2 Geologic background

Within the Cowichan Lake uplift, the Sicker Group is subdivided into four formations: (1) Late Devonian Duck; (2) Late Devonian Nitinat; (3) Late Devonian and VHMS-bearing McLaughlin Ridge; and (4) Early Mississippian Fourth Lake. The Sicker Group stratigraphy located within the Butt Lake uplift is subdivided into four formations: (1) Late Devonian Price; (2) Late Devonian and VHMS-bearing Myra; (3) Early Mississippian Thelwood; and (4) Middle Mississippian to Pennsylvanian Flower Ridge (Fig. 2) (Muller 1980, Juras 1987, Yorath et al. 1999).
Figure 2. Sicker Group chronostratigraphy showing temporal relations between units in Cowichan Lake and Buttle Lake areas. Chronology and lithofacies data are from Juras (1987), Massey and Friday (1987), Yorath et al. (1999), Sinclair (2000), and Ruks (2015). 9: Juras (1987). Alphanumeric symbols explained in figure 3.

The Price Formation consists of pyroxene-feldspar phryic and amygdaloidal basaltic-andesitic lavas and breccia (Juras 1987). It forms the stratigraphic footwall to the HW orebody and has a minimum thickness of 300 m (e.g. Jones et al. 2006). The transition from mafic to felsic volcano-sedimentary rocks marks the contact with the overlying Myra Formation.

The Myra Formation is a ≥500 m thick sequence of rhyolitic, andesitic, and basaltic volcanic and marine sedimentary rocks and is subdivided into seven lithofacies by Sinclair (2000)(Fig. 2). The HW Rhyolite, which is the basal unit of the Myra Formation, consists of rhyolitic lava flows and domes, volcaniclastic rocks, and argillite. The Hanging Wall Andesite is a discontinuous unit overlying the HW Rhyolite and it consists of andesitic lavas and bedded feldspar crystal-rich volcaniclastic rocks. The Lower Mixed Volcaniclastic unit consists of andesitic-rich volcaniclastic deposits, is laterally continuous through the camp, and overlies the Hanging Wall Andesite. The L-M-P Horizon consists of massive to thickly bedded, quartz-feldspar, crystal-rich, rhyolitic volcaniclastic rocks and is overlain by mafic to intermediate composition bedded mudstone, sandstone, and breccia volcaniclastic rocks of the Upper Mixed Volcaniclastic unit. The Upper Rhyolite unit consists of quartz-feldspar, crystal-rich, volcaniclastic rhyolite, argillite, chert and jasper and is overlain by the Upper Mafic unit. This unit is a 200 m thick sequence of basaltic volcaniclastic with lesser lavas and forms the top of the Myra Formation.

The Battle and HW orebodies are massive sulfide deposits hosted beneath the coherent rhyolite, within the HW Rhyolite, and located near the contact with the underlying Price Formation (Barrett and Sherlock 1996; Robinson et al. 1996; Sinclair 2000). The Ridge and Marshall Zones are hosted in the HW Rhyolite, but at different stratigraphic levels and within different volcanic facies. The Ridge Zone is subdivided into East and West Zones. Both of these sub-zones are hosted in felsic volcaniclastic stratiigraphy. However, the East Zone is located ~50 m above the Price Formation contact with coherent rhyolite within and above mineralization. The West Zone lacks coherent rhyolite and mineralization is up to 100 m above the Price Formation contact (Chong 2004). The Marshall Zone massive sulfide deposit occurs 100-150 m above the Price Formation contact and is hosted in coherent rhyolite and the associated breccia (company report Barrett and MacLean 2000). Massive sulfide ore at the Price Mine is hosted within felsic volcanic stratiigraphy of the L-M-P ore horizon, ~700 m above the HW orebody.

3 Previous geochronology

Numerous authors have used U-Pb zircon geochronology to decipher temporal relationships between lithostratigraphic units and sulfide mineralization at Myra Falls (Fig. 3). The first attempt to constrain crystallization ages at Myra Falls was by Juras (1987) who reported a U-Pb zircon age of 370 ±18/-6 Ma (5 zircon fractions) and identified a Late Devonian age for the Myra Formation.

Additional attempts to date the felsic volcanic stratigraphy at Myra Falls focused on the HW Rhyolite above the HW orebody. Minimum Pb-Pb ages of ~370 Ma (2 zircon grains) and 366 ±4 Ma (5 zircon fractions) from coherent rhyolite samples were reported by Brandon et al. (1986) and Parrish and McNicoll (1992), respectively. Barrett and Sherlock (1996) reported an age of 365 ±4 Ma (weighted mean age of 5 fractions) for a felsic volcanic sample. These authors produced age results consistent with a Late Devonian to Early Mississippian age for the lower Myra Formation; however, the samples were restricted to the HW Rhyolite above the HW orebody and have relatively large errors.

The most recent age constraint of the Myra Formation is of a coherent rhyolite of the HW Rhyolite located beneath the Marshall Zone. The sample is hydrothermally altered and mineralized, forms the immediate footwall to the Marshall Zone, and yielded an LA-ICP-MS U-Pb zircon age of 361.5 ±2.5 Ma (Ruks 2015).

4 LA-ICP-MS and CA-ID-TIMS methods

To investigate the crystallization history of felsic stratigraphy of the Myra Falls VHMS camp we utilized two U-Pb zircon dating. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the University of Tasmania (UTas), Australia and chemical abrasion, isotopic dilution thermal ionization mass spectrometry (CA-ID-TIMS) at the University of British Columbia, Vancouver, Canada (UBC).
Three coherent rhyolite samples (UPB02, UPB05, UPB08), were collected for U-Pb zircon dating by LA-ICP-MS. Sample preparation involved crushing 200-400 g of drill core or underground mine exposure sample in a Cr-steel ring mill to a grain size <400 µm. Non-magnetic heavy minerals were separated using a gold pan and a Fe-B-Nd hand magnet. For pyrite-rich samples, the heavy mineral concentrate was roasted in an oven at ~350°C for ~2 hours and the subsequent pyrite was removed with a hand magnet. Zircons were then hand picked from the heavy mineral concentrate under a petrographic microscope. The selected crystals were mounted into a 2.5 cm diameter epoxy mould. The mount was polished using a clean polishing lap after a 12-hr drying period and then washed with distilled water in an ultrasonic bath. Analyses were performed on an Agilent 7900 quadrupole ICP-MS with a 193 nm Coherent Ar-F excimer laser and Resonetic S155 ablation cell at the UTas. Data collection and reduction were completed using the methods described in Halpin et al. (2014).

Two samples (UPB02 and UPB05) of coherent rhyolite were investigated for CA-ID-TIMS U-Pb zircon dating at the Pacific Centre for Isotopic and Geochemical Research (PCIGR) facility at UBC. Zircons, from 0.5-1 kg drill core or underground mine exposure samples, were separated using conventional crushing, grinding, wet shaking table, heavy liquid, and magnetic separation methods at UBC. Five zircons were selected from UPB05. Sample UPB02 was prepared at the UTas, by the methods described above, and five zircons were picked for analysis. Data collection and reduction was completed using the methods described in Mattinson (2005) and Scoates and Friedman (2008).

5 Results

Zircons analysed ranged in size from 10-60 µm. Morphologies varied from euhedral, to subhedral with weakly resorbed margins, to broken euhedral fragments. Igneous zoning occurred in all zircon grains and no inherited cores were present. For LA-ICP-MS analysis the diameter of the beam size varied from 9-29 µm.

5.1 LA-ICP-MS results

Sample UPB02 is a hydrothermally altered and mineralized quartz-phryic rhyolite. Twenty zircons were analysed with a beam size of 19 and 29 µm. Four analyses were discarded due to lead loss. The sample yielded a lower intercept age of 364.2 ±3.3 Ma (MSWD = 0.61; 16 zircon analyses).

Sample UPB08 is a quartz-feldspar phryic rhyolite with pervasive sericite alteration and minor, disseminated, and fine-grained pyrite. Twenty-seven zircon grains were analysed with a beam size of 19 µm. In general, the zircons were greater than 30 µm in size. Four analysed zircons showed evidence of lead-loss and were discarded. The sample yielded a model solution lower intercept age of 357.9 ±2.5 Ma (MSWD = 1.2; 95% conf.; 23 zircon analyses).

Sample UPB05 is a quartz-feldspar phryic rhyolite with pervasive sericite alteration and minor, disseminated, and fine-grained pyrite. Seven zircons, ~20 µm in size were analysed. Due to the small grain size, a beam diameter of 9 µm was used and each grain was analysed twice. No systematic variations were identified between the two measurements. However, greater errors due to the smaller beam size were encountered. The sample yielded a model solution lower intercept age of 353.8 ±8.2 Ma (MSWD = 0.47; 95% conf.; 7 zircons; 14 analyses).

5.2 CA-ID-TIMS results

Five zircons were analysed from sample UPB02, two were rejected as a result of lead loss. The sample yielded a concordant age of 362.32 ±0.74 Ma (MSWD = 0.07, 3 zircon analyses). Five zircons were analysed from sample UPB05, one was rejected due to lead loss. The sample yielded a concordant age of 362.46 ±0.57 Ma (MSWD = 0.71, 4 zircon analyses).

6 Discussion and conclusion

New age determinations from this study with available U-Pb age constraints for the Myra and McLaughlin Ridge Formations are shown in figure 3. Previous age constraints of coherent rhyolite from the H-W ore horizon suggested two phases of volcanism that overlap in error at ~365 Ma and at ~361.5 Ma (Parrish and McNicoll 1992; Barrett and Sherlock 1992; A: UPB02 (TIMS); B: UPB05 (TIMS); C: UPB08 (LA-ICP-MS)).

New zircon U-Pb age results confirm this and suggest the possibility of a third, younger phase of felsic volcanism in the H-W ore horizon. The oldest, crystallization age comes from coherent rhyolite immediately above the HW orebody at 365 ±4 Ma (Parrish and McNicoll 1992). A
sample of strongly altered and mineralized coherent rhyolite from the Marshall Zone produced a crystallization age of 361.5 ±2.5 Ma (Ruks 2015). This constrains the timing of VHMS mineralization in the Marshall Zone to be post 361.5 Ma (Ruks 2015).

Samples UPB02 and UPB05 represent strongly altered and moderately mineralized coherent rhyolites located in the Ridge North East orebody at the same stratigraphic level as coherent rhyolite of the Battle orebody. The CA-ID-TIMS results from these samples indicated crystallization ages of 362.32 ±0.74 Ma and 362.46 ±0.57 Ma (Fig. 3). These results overlap with the upper errors of the HW orebody and the lower errors of the Marshall Zone age results. The age results of the HW orebody samples likely represent the first phase of a three-phased volcanic system, however the large errors of these results do not preclude the possibility that coherent rhyolite of the HW, Ridge Zone East and Marshal Zone crystallized at the same time.

A weakly altered sample located at the top of the coherent rhyolite body in the Ridge Zone East yielded a crystallization age of 357.9 ±2.5 Ma. This result does not overlap in error with the older results and is highly suggestive that there were at least two stages (if not three) of felsic volcanism in the H-W ore horizon at Myra Falls.

Juras (1987) reported an age of 370 †18/−6 Ma for a sample of Upper Rhyolite, but described the sample as volcaniclastic with >50% of the zircons representing fragments (Fig. 2). An attempt to resolve the crystallization age of rhyolite in the Price Mine stratigraphy was made in this study, but was unsuccessful due to challenges in separating appropriate zircons for analysis.

Ruks (2015) identified multiple phases of Late Devonian to Early Mississippian felsic volcanism associated with VHMS mineralization in the Cowichan Lake area. These age results range from 363.0 ±6.7 Ma to 353.1 ±3.4 Ma. Felsic host rocks of the Lara and Lenora VHMS occurrences (samples 2-4, Fig. 3) overlap in age with host rocks of the H-W ore horizon at Myra Falls. The age of felsic host rocks to the Jane VHMS occurrence (sample 1, Fig. 3) does not coincide with any of the age results for the H-W ore horizon. It is possible, that the age of the Jane VHMS occurrence is analogous to the stratigraphically younger deposits of the L-M-P ore horizon at Myra Falls. The compilation of U-Pb zircon age results of felsic volcanic rocks of the Sicker Group on Southern Vancouver Island indicate that volcanism was long-lived from 366 ±4 Ma (Parrish and McNicoll 1992) to 353.1 ±3.4 Ma (Ruks 2015), with multiple VHMS mineralization events occurring throughout its depositional history.

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Geochemistry and U-Pb monazite geochronology of uraniferous greisen veins in the high heat production Mt. Douglas Granite, NB Canada: implications for post-magmatic hydrothermal activity

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Abstract. Medium- to fine-grained porphyritic high heat production (HHP) peraluminous leucogranites of the units Dmd2 and Dmd3 of the Late Devonian Mount Douglas body, southwestern New Brunswick, Canada, are associated with mineralized greisen and sheeted veins. Gamma-Ray Spectrometry survey, microscopic observation, SEM-BSE imaging, and laser ablation Q-ICP-MS measurement of the related veins demonstrate the locally uraniferous nature of the Mount Douglas’s greisen veins. U- and Th-bearing minerals, such as monazite, zircon, xenotime, thorite, bastnaesite, and uraninite occur in these veins, but also other sulfide and oxide minerals, such as wolframite (≤143 ppm U; ≤83 ppm Th), hematite and martite (up to 41 ppm U and 6 ppm Th) display significant anomalies of U and Th. A mineralization age derived from U-Pb geochronology of monazite grains taken from greisen veins yielded a range of 358.2±2.4 to 360.9±6.6 Ma, which is around 10 Ma younger than the crystallization age of the Mount Douglas granite (~370 Ma), showing post-magmatic hydrothermal activity within the pluton. This is consistent with previous investigations showing the pluton lies within an area of present HHP. The HHP nature of this pluton may be the reason for post magmatic hydrothermal activity producing uraniferous greisen veins 10 Myr younger than the intrusion.

1 Introduction

Fractional crystallization, as one of the most important processes in the Late Devonian Mount Douglas Granite (leucogranite) (~370 Ma), led the pluton to evolve to three different units, i.e., Dmd1, Dmd2, and Dmd3 (McLeod 1990), and to produce endogenic Sn, W, and Mo occurrences (Fig. 1). The ore deposits are typically associated with greisen and sheeted veining of only units Dmd2 and Dmd3 rather than Dmd1, the least fractionated phase of the Mount Douglas system. Our preliminary observations of the greisen veins recognized the uraniferous nature for some parts of these plutons, particularly Dmd2 and Dmd3. The uraniferous nature of the complex has been reported by former studies, such as Chandra (1981), Hassan (1984), and Hassan and Hale (1987); their investigations following up on airborne radiometric (Airborne Gamma-Ray Spectrometer survey) anomalies in New Brunswick demonstrated a high potential of U-enrichment in the eastern part of the Saint George Batholith, where the Mount Douglas body is located. For this study, geochemical and geochronological features of the related greisen veins have been considered to better understand the uraniferous nature of the suite and the timing of the vein formation.

2 Analytical Procedures

To determine the geochemistry and economic potential of the Mount Douglas suite, new studies were performed using in situ laser ablation quadrupole inductively coupled plasma-mass spectrometry (LA Q-ICP-MS) guided by backscattered electron (BSE) imaging using a JEOL6400 scanning electron microscope (SEM) at the University of New Brunswick Microscopy and Microanalysis Facility. Measurements were performed on target minerals, including wolframite, sphalerite, pyrite, arsenopyrite, magnetite, uraninite, galena, and chalcopyrite taken from greisen and sheeted veins, however for this study, focus will be placed only on U- and Th-rich minerals.

U-Pb crystallization ages of hydrothermal monazite grains were determined using in situ laser ablation Q-ICP-MS supported by SEM-BSE imaging. This method has been applied to monazite-bearing greisen veins that were sampled throughout the pluton. Standard polished thin sections (thickness of 30 μm) were prepared and the monazite grains were analysed using a Resonetics S-155-LR 193 nm ArF Excimer laser ablation (LA) system coupled to an Agilent 7700x quadrupole inductively coupled plasma-mass spectrometer (ICP-MS) (see McFarlane and Luo 2012; McFarlane 2015; and Azadbakht et al. 2016 for details of the method).

3 Greisen veins

The most differentiated units of the Mount Douglas granite, Dmd2 and Dmd3, are spatially and temporally associated with mineralized greisens and sheeted veins. A typical assemblage of greisen minerals, including sericitized pseudomorphed K-feldspar and plagioclase, quartz, fluorite, chlorite with minor muscovite, are accompanied by complex hydrothermal paragenesis of oxide and sulfide minerals (Fig. 2). The associated oxide and sulfide minerals commonly are pyrite, arsenopyrite, hematite, martite, cassiterite, and galena, but also Ta-rich wolframite, In-Cd-rich sphalerite, chalcopryite, native bismuth, and rare uraninite. Radiating fibrous and needle-shaped to tabular thick crystal of hematite and martite co-precipitated in clots with sulphide minerals, such as sphalerite and pyrite, and
locally with hydrothermal monazite, xenotime, zircon, and uraninite. The fine to medium anhedral sphalerite grains (up to 0.6 mm in length) and tabular wolframite (0.5 mm in length) are homogeneous and contrast-adjusted BSE images do not reveal any internal zoning, which can be attributed to a relatively uniform composition of the mineralizing fluid.

4 Geochemistry of the uraniferous greisen veins

Locally, some greisen veins are uraniferous and exhibit considerable U-, Th-, and REE-bearing minerals. Common U- and Th-bearing minerals occurring in these veins are monazite, zircon, xenotime, thorite, bastnaesite, and uraninite that are accompanied by other sulfide and oxide minerals that have notably high concentration of these elements. These anomalous assemblages are more evident in oxide minerals (Table 1), including wolframite (≤ 143 ppm U; ≤ 83 ppm Th), hematite and martite, in which radiating fibrous to platelet-shaped hematite reaches up to 41 ppm U and 6 ppm Th. Current studies manifested uranium incorporation into hematite lattice as uranyl in a process that the U⁶⁺ can incorporate into a distorted, octahedrally coordinated site replacing Fe³⁺ (Marshall et al., 2014). Some sulfides, such as galena, show high values of these elements as well (up to 0.29 wt.% U and 0.14 wt.% Th).

5 Geochronology of the greisen veins

Some locally uraniferous greisen veins are associated with U- and Th-bearing minerals, in which oxide and sulfide minerals co-precipitated in clots with hydrothermal monazite, zircon, xenotime, Th-silicates, bastnaesite, and rare uraninite (Fig. 2c, d). These type of veins provide an ideal setting to determine mineralization age of the Mount Douglas’s greisen, in which monazite has been considered for geochronological study. Only those monazite grains large enough to accommodate a 17 µm diameter crater are measurable using laser ablation. Mineralization age derived from in situ laser ablation ICP-MS U-Pb hydrothermal monazite taken from earthy-red greisen veins yielded a range of 358.2 ± 2.4 to 360.9 ± 6.6 Ma (Fig. 3), which is around 10 Myr younger than the crystallization age obtained for the Mount Douglas granite (~370 Ma, Mohammadi et al., 2016) using U-Pb monazite and zircon geochronology.

6 Concluding remarks

Uraniferous nature of the Mount Douglas suite has been demonstrated by Gamma-Ray spectrometry measurements including down to the micro-scale using LA-Q-ICP-MS of the associated minerals. Besides, U-, Th-, and REE-bearing minerals, such as monazite, zircon, xenotime, thorite, bastnaesite, and uraninite that are associated with the greisen veins, some other oxide and sulfide minerals, such as wolframite, hematite, martite, and galena display significant anomalies of U and Th. This anomaly is in agreement with previous airborne radiometric surveys in New Brunswick. The anomaly that is generated by higher U and Th in this body is mainly associated with the most highly differentiated, youngest phases, units Dmd2 and Dmd3 exhibiting ≤ 71 ppm Th and ≤ 22 ppm U (Table 1). U-Pb mineralization age derived from hydrothermal monazite coexisting with sulfide and oxide minerals in the associated greisen veins gave a range of 358.2 ± 2.4 to 360.9 ± 6.6 Ma. The obtained mineralization age is ~10 Myr younger than the crystallization age of the suite (~370 Ma), revealing post-magmatic hydrothermal activity within the Mount Douglas pluton. Former investigations on this body display that the pluton lies within an area of present high heat production (HHP), where there is a high heat flow (70 mW/m²) produced by a 1.4-3.3 km radiogenic layer. Redistribution of U and Th by groundwater movement through fractures is probably caused by this heat flow anomaly. Post magmatic hydrothermal activity of the pluton that produces uraniferous greisen veins 10 Myr younger than the intrusion probably is associated with the HHP nature of this pluton.

Acknowledgements

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Figure 1. a) Regional geological setting of the Saint George Batholith, southwestern New Brunswick, Canada and the location of the Mount Douglas leucogranite (modified after Thorne et al. 2013). Mineral occurrences associated with the Mount Douglas Granite, based on the Metallogenic Map of New Brunswick, NR-7 (2002) are shown in black diamond. b) Location of one of the greisen-vein associated of the unit as a representative mineralized unit (sample 86#, unit Dmd3), southwestern Disappointment Lake. c) Field observation of the Mount Douglas leucogranite: greisen and sheeted veins that are associated with medium- to fine-grained porphyritic granite of subunit Dmd3. d) Associated minerals of the greisen vein including oxide and sulfide minerals.

Table 1. Geochemical result of LA-ICP-MS analyses of U- and Th-rich oxide and sulfide minerals taken from the greisen veins of the Mount Douglas granite. The whole rock data are from McLeod (1990).

<table>
<thead>
<tr>
<th>Material</th>
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<th>Average</th>
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<th>Average</th>
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<td></td>
<td></td>
<td>Th (ppm)</td>
<td></td>
</tr>
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<td>18-60</td>
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</tr>
<tr>
<td>Dmd3</td>
<td>5-22</td>
<td>13</td>
<td>30-71</td>
<td>51</td>
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</table>
Figure 2. a) Photomicrograph of a representative greisen vein of the Mount Douglas granite (XPL image) with typical assemblages of greisen minerals, including highly sericitized K-feldspar, quartz, fluorite, and oxide/sulfide minerals that formed along a vein (dark colour). b) SEM-BSE image of the vein in figure “a” with assemblage of oxide and sulfide minerals that mostly are pyrite, arsenopyrite, sphalerite, wolframite, and fluorite. c) Coexisting of hydrothermal monazite with zircon and radiating fibrous hematite in a greisen vein that has been used for U-Pb geochronology (sample 263-7B, Figure 3). d) Co-participate of hydrothermal monazite grains with pyrite along a vein in a greisen sheeted vein that have been analysed for U-Pb geochronology.

Figure 3. A representative U-Pb concordia plot for laser ablation ICP-MS analyses of hydrothermal monazite grains taken from greisen veins (sample 263-7B, Figure 2c). Concordia age = 359.2 ± 3.0 Ma; data point error ellipses are 2σ; MSWD of concordance = 0.0021; probability of concordance = 0.96. The blue ellipse is weighted-mean error ellipse.
Grenvillian age for the sediment-hosted Cu-Ag mineralization at Seal Lake, Labrador, Canada

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Abstract. The sediment-hosted stratiform Cu-Ag mineralization in the Mesoproterozoic (1270-1225 Ma) Seal Lake Group consists of sulfide assemblages present in two intimately associated mineralization styles: finely disseminated sulfides and a variety of sulfide-bearing quartz-carbonate veins, veinlets, and metamorphic sweats. Mineralization is controlled by structure and redox boundaries between rock packages, and displays a positive correlation with the intensity of deformation and metamorphism. Intensely folded and sheared greenish black shale and slate characteristically contain a paragenesis of chalcocite-digenite-bornite with subordinate chalcopyrite, whereas reddish siliciclastics and hematitized basalt flows and diabase/gabbro sills carry native Cu. The mineralization has been historically compared with the Keweenawan district of the Lake Superior region. Molybdenite intergrown with bornite from the Seal Lake Main showing yields a Re-Os model age of 1084.0 ± 5.1 Ma, which represents the timing of the sediment-hosted Cu-Ag mineralization and of Grenvillian deformation and metamorphism during Rodinia assembly (1100-900 Ma).

1 Introduction

The absence of suitable minerals for reliably determining the absolute age of sediment-hosted stratiform Cu mineralization has historically complicated definition of a genetic model and assignment of the deposit type to specific metallogenic events. Syngenetic, diagenetic, and epigenetic proposals populate the literature, with a current view favoring mineralization in multiple events spanning the several hundred million years from early diagenesis in a rift environment to epigenesis during and after basin inversion (Hitzman et al. 2010). Recent work has used precise dates for ore-related, paragenetically-constrained molybdenite (Re-Os) and titanite (U-Pb) to confirm a synorogenic and synmetamorphic timing of the Cu mineralization in several sediment-hosted Cu deposits and prospects (Perelló et al. 2015; 2016; Sillitoe et al. 2015; 2017). This paper reports a Re-Os model age on molybdenite associated with bornite and chalcocite from the sediment-hosted stratiform Cu-Ag mineralization at Seal Lake (Fig. 1).

2 Geological context

Since identification of Cu mineralization during the mid-1940s over 250 Cu showings have been catalogued in the Seal Lake region. The prospects and occurrences are hosted by igneous and siliciclastic rocks of the Mesoproterozoic Seal Lake Group of Labrador’s Central Mineral Belt (Brummer and Mann 1961; Wilton 1996) and the style of the sediment-hosted Cu-Ag mineralization has been compared with the classic Keweenawan province of the Lake Superior region and the White Pine deposit in particular (Gandhi and Brown 1975; Brown 1981).

The Seal Lake Group (Brummer and Mann 1961; Baragar 1981) is a thick sequence of subaerial to shallow marine siliciclastic rocks and basalt flows exposed along a large (120 km long; 45 km wide), east-trending synclinal structure. The Group straddles the Grenville Front near the junction of the Churchill, Nain, and Grenville tectonic provinces (Gower et al. 1980; Fig. 1) and unconformably overlies Archean (>2500 Ma) gneisses, Mesoproterozoic (~1650 Ma) volcanic and sedimentary rocks, Mesoproterozoic (~1450 Ma) anorthosite, and Mesoproterozoic (~1330 Ma) felsic volcanic rocks. The southern boundary of the Group is a thrust contact with Paleoproterozoic granitoids of the Trans-Labrador batholith (Brummer and Mann 1961; van Nostrand 2009; Fig. 1). Such north-directed brittle and ductile thrusts are interpreted to be responsible for the intense, large-scale, fold-thrust-style deformation and tectonic stacking of the Group’s formations as well as the metamorphic effects, including mylonite formation, observed in rocks of the southern limb of the syncline (Brummer and Mann 1961; van Nostrand 2009; van Nostrand and Macfarlane 2011). The Group comprises six formations of which the middle and upper units (Salmon Lake and Adeline Island Formations, respectively) contain the majority of the native metal, oxide, and sulfide Cu occurrences. The siliciclastic rocks of all formations comprise purple-red...
and maroon arkosic sandstone, siltstone, and subordinate conglomerate interbedded with green, gray, and black siltstone and shale. Local chert and calcareous rocks are present in the upper units, implying a general subaerial to shallow-marine transition from the lowest to highest stratigraphic levels (Brummer and Mann 1961). The Upper Red Quartzite Formation (Fig. 1), however, indicates basin culmination. Quartzite, phyllite, slate, quartz-sericite schist, and chlorite schist represent the metamorphic equivalents of these rocks in areas where deformation and metamorphism are more intense, as in the southern exposures. The original 10,500-m thickness estimate for the Group (Brummer and Mann 1961) is probably exaggerated by stratigraphic repetition caused by folding and thrusting (Gandhi and Brown 1975), and by inflation due to abundant diabase/gabbro sill intrusions (Naskaupi Sills) – with individual bodies of up to 250 m thick – in its lower and middle parts (Baragar 1981; Wilton 1989b; Romer et al. 1995; van Nostrand and MacFarlane 2011). Basalt flows of the Salmon Lake Formation and diabase/gabbro sills of the Group display tholeiitic compositions and were likely derived from a common magma source, with geochemical affinities with continental flood basalts. The parental magma of the sills derived its geochemical signature via fractionation and assimilation of granulitic material (Wilton 1989b).

![Simplified geology of the Seal Lake region with reference to the main tectonic provinces of Labrador. Location of Seal Lake Main and other selected occurrences shown. After Wilton (1989a) and van Nostrand and Lowe (2010)](image)

The age of the Group is constrained between ~1270 and 1225 Ma (Cadman et al. 1993; Romer et al. 1995). It accumulated in an intracratonic rift basin that formed part of a continental-scale extensional event in Laurentia and Baltica (Romer et al. 1995). The metamorphic grade varies from greenschist-facies in the south to pumppellyite facies in the north. Greenschist-facies rocks are associated with synfoliation thrusts, chlorite-epidote and tremolite-bearing assemblages in mafic flows and sills, and a muscovite-sericite association in siliciclastic rocks, in response to the gradational effects of the northward-directed Grenvillian deformation (Brummer and Mann 1961; Gowler et al. 1980; Baragar 1981; van Nostrand 2009; van Nostrand and Corcoran 2013). The absolute age of metamorphism, however, has not been determined (van Nostrand and Lowe 2010; van Nostrand and MacFarlane 2011).

### 3 Sediment-hosted Cu-Ag mineralization

Copper mineralization occurs as fine-grained, bedding- and cleavage-parallel disseminations that nucleate as irregular pods and stratiform lenses in gray to greenish shale, siltstone, and slate at redox boundaries with the reddish siliciclastics. Bedding- and foliation-parallel shear-hosted mineralization is also common. Lenticular bodies have varied dimensions, with strike-lengths ranging from a few meters to tens of meters and widths from centimeters to <5 m. Most showings are hosted by the Adeline Island Formation in proximity to the basaltic flows and diabase/gabbro sills of the Salmon Lake Formation (Fig. 1), with the latter containing ~70% of the total occurrences (Brummer and Mann 1961). Nevertheless, Cu-Ag mineralization is present in most formations of the Group. Where gray and green shale and/or slate are in contact with either lava flows or sills, Cu mineralization tends to occur at the contact or within a few meters off it. Chalcocite, digenite, bornite, and chalcopyrite dominate the occurrences and define classic assemblages of chalcocite-bornite and bornite-chalcopyrite. Chalcopyrite in association with syngenetic (framboidal, nodular) and metamorphic pyrite is also present (Gandhi and Brown 1975). Native Cu occurs in many places and, where hosted by red beds or hematitized mafic rocks, is of suspected hypogene origin. Molybdenite is present in association with Cu-bearing sulfides at several localities (Brummer and Mann 1961; Wilton 1989a) and anomalous Mo contents are relatively common, locally attaining >0.5% Mo (Wilton 1996). Supergene Cu products include malachite, azurite, cuprite, and native Cu. Despite structural complications, Cu-bearing sulfide zoning is apparent at various scales (Gandhi and Brown 1975; Wilton 1989a), with appreciable meter-scale vertical zones comprising basal hematite hosted by red bed siliciclastics, chalcocite and bornite at intermediate levels in gray and green rocks, followed by upper chalcopyrite and pyrite plus local sphalerite.

Everywhere in the region the disseminated stratiform Cu showings are accompanied by a variety of quartz-carbonate-Cu sulfide veins, veinlets, and metamorphic swarts, with attitudes ranging from bedding- and foliation-parallel to transgressive. Tectonically buckled, distorted, and boudinaged veinlets and veins are common where the effects of Grenvillian deformation and metamorphism are more intense, as in the southern part of the Seal Lake syncline. Both mineralization styles (disseminated and
veined) display the same Cu-sulfide assemblages, paragenetic sequences, and zoning, and exhibit the same Cu to Fe trend from chalcocite through digenite and bornite to chalcopyrite (Gandhi and Brown 1975). Hence, a common origin for both styles is evident (Wilton 1989a; 1996).

**Figure 2.** Schematic cross section of Seal Lake Main showing, with location of sample SL-2 (Brummer and Mann 1961). Close-up view of the contact near sample SL-2 shown in photograph. bn: bornite, cc: chalcocite, cp: chalcopyrite. See text for descriptions.

4 Molybdenite sample and age

Samples were collected during surface and core inspection of selected showings and prospects. Sample SL-2 comes from surface exposures of the Seal Lake Main showing (Figs. 1 and 2) where native Cu, chalcocite-digenite, and bornite occur in a swarm of cleavage-parallel, podiform quartz-epidote-carbonate veins at or near the contact between an upper, tabular diabase/gabbro sill and a lower, hornfelsed black slate (Fig. 2). Veins and disseminations higher up in the sill contain bornite and chalcopyrite, indicating that the normal vertical Cu-sulfide zoning postdated sill emplacement. Footwall stratigraphy comprises red slate and reddish-green amygdaloidal basalt, the former locally containing erratically mineralized quartz veins with coarse-grained clots of native Cu (Brummer and Mann 1961; Fig. 2). The showing is semicontinuous for ~300 m along the east-trending contact, with individual strike-length intervals of tens of meters averaging between 0.7 and 2% Cu over widths of ~1 m. Similar occurrences in the region typically return multigram (>200 g/t) Ag values (Gandhi and Brown 1975; Wilton 1996), particularly in bornite-bearing samples (Brummer and Mann 1961).

Sample SL-2 was collected from the sill near its footwall contact with black slate (Fig. 2). The greenschist-facies (albite, chlorite, epidote) diabase/gabbro has a porphyritic texture with subparallel plagioclase phenocrysts in a fine-grained, partly banded aggregate of albite, epidote, chlorite, pyroxene, and ilmenite-titanomagnetite. The presence of the latter assemblage is a confirmation that the sill belongs to the Ti-bearing Naskaupi Sills magmatic suite (Baragar 1981; Wilton 1989b; 1996). Copper mineralization comprises bornite, digenite, and chalcocite, both as fine-grained disseminations and veins in the sill, in association with bands of epidote and chlorite and disrupted quartz veins. Local disseminated remnants of chalcopyrite are overgrown by bornite. Molybdenite is present in crenulated and microfolded seams and intergrown with bornite and chalcocite-digenite within the chlorite-epidote bands that define the principal metamorphic foliation of the rock (Fig. 3), hence constraining its synmetamorphic timing.

**Figure 3.** Microphotographs of sample SL-2. Molybdenite (mo) in paragenetic sequence with chalcopyrite (cp), bornite (bn), and chalcocite-digenite (cc-di).

The molybdenite grains were extracted, analyzed, and dated by the Re-Os method following Selby and Creaser (2004) and Markey et al. (2007). The model age and analytical data are presented in Table 1. The age uncertainty is quoted at 2σ level and comprises all known analytical uncertainty, including that in the decay constant of $^{187}$Re. Sample SL-2 returned an age of 1084.0 ± 5.1 Ma. This age is in agreement with field relationships, given that the disseminated and vein mineralization is hosted by a Naskaupi sill and that this intrusive suite yielded U-Pb dates between 1250 and 1224 Ma (Romer et al. 1995) ~20 km to the southwest. In addition, Wilton and Selby (submitted) have also obtained Re-Os molybdenite ages of 1069.6 ± 4.7 and 1064.6 ± 5.1 Ma at the Whiskey Lake showing (Fig. 1).

**Table 1.** Analytical data for sample SL-2, Seal Lake Main

<table>
<thead>
<tr>
<th>Re ppm ±2σ</th>
<th>$^{187}$Re ppm ±2σ</th>
<th>$^{187}$Os ppb ±2σ</th>
<th>Age ±2σ</th>
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<td>5.1</td>
<td>40.2</td>
<td>0.4</td>
<td>1084.0</td>
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</table>

5 Discussion

Recent work has demonstrated the synorogenic timing of sediment-hosted Cu mineralization of various ages and scales (Perelló et al. 2015; 2016; Sillitoe et al. 2015; 2017). In accord with these studies, the Re-Os (molybdenite) model age of 1084.0 ± 5.1 Ma for Seal Lake also confirms that Cu-Ag mineralization took place in brittle and ductile rocks long after diagenesis, ~140 to 190 m.y. after active sedimentation of the Seal Lake Group ceased. Moreover, all geologic evidence at Seal Lake at regional, mesoscopic, and microscopic scales favors a synorogenic and synmetamorphic timing for both the disseminated stratiform and vein-hosted Cu mineralization (Wilton 1989a; 1996). Indeed, a positive correlation between Cu mineralization and deformation and metamorphism is readily apparent, with most prospects and showings located in the southern part of the...
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Seal Lake area where fold-thrust deformation and greenschist-facies metamorphism are more intense. In marked contrast, the exposures north of the lake, where the strata are less disturbed and the metamorphic grade only reaches zeolite facies, contain minor mineralization (Brummer and Mann 1961; Wilton 1996). Consequently, the reported molybdenite date also provides a precise age for the Grenvillian deformation and metamorphism in the region, and validates the onset of orogenic activity associated with the ca. 1090-1020 Ma Ottawa phase (Rivers 2009) in this part of the Grenville Province. Ottawa thrusting likely involved both thin-skinned folding and thick-skinned faulting, with participation of basement units from deeper levels accompanying crustal thickening of regional extent (Connelly et al. 1995; Fig. 1).

At Seal Lake, there is no evidence for a genetic link between Cu mineralization and diagenesis during basin sedimentation. Rather, the Cu-Ag mineralization formed during basin inversion as part of the assembly of the Rodinia supercontinent (1100-900 Ma; Li et al. 2008). Interestingly, the Grenvillian-age (1084-1059 Ma) sediment-hosted Cu mineralization present in basement units of the Zambian Copperbelt (Sillitoe et al. 2015) strongly suggests that the deposit type was a metallogenic complement to supercontinent construction.

Acknowledgements

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U-Pb geochronology of monazite from the Hangaslampi gold deposit in the Paleoproterozoic Kuusamo schist belt, northern Finland: implications for dating multi-stage mineralizing events

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Abstract. The Kuusamo schist belt is a fold and thrust belt, which consists of an epiclastic-volcanic sequence deposited during multiple rifting events affecting the Archean basement between 2.4 and 2.0 Ga. During Svecofennian (1.9-1.8 Ga) metamorphism and deformation, several orogenic gold deposits were formed in the belt. Among them, the Hangaslampi deposit is characterized by an Au-Co-U-Mo-REE metal association. Results of the in situ laser ablation single collector ICPMS U-Pb dating of monazite occurring in different textural settings indicate that this deposit was formed by multi-stage hydrothermal events. Monazite in the groundmass of the metavolcanic rocks yields an age of 1872 ± 4 Ma, which most likely records the age of the greenschist facies metamorphism. The hydrothermally altered metavolcanic rocks also contain a monazite population that gives an age of 1849 ± 8 Ma. The youngest population of hydrothermal monazite, giving ages of 1812 ± 10 Ma, is typically associated with late fractures and carbonate veins which cut the metavolcanic rocks. These results confirm that monazite is a robust geochronometer applicable for recognition of repeated hydrothermal events in formation of orogenic gold deposits in Precambrian terrains.

1 Introduction

The Kuusamo schist belt (KSB) is a fold and thrust belt which forms a part of the Central Lapland greenstone belt (CLGB), the most significant Paleoproterozoic orogenic gold province in northern Europe. The Geological Survey of Finland (GTK) started mineral exploration in the KSB during the 1980’s and since then more than 20 gold occurrences have been discovered in the area. Among them, the most investigated are the Juomasuo, Hangaslampi, Pohjasvaara, Meurastuksenaho, and Sivakkaharju deposits (Vanhanen 2001). The mineral resource estimates of these five gold deposits total 3.85 Mt (measured, indicated and inferred) grading 4.1 g/t Au and containing 507 200 ounces of gold (Dragon Mining 2014).

An interesting feature of gold deposits in the KSB is that concentrations of gold are locally associated with cobalt, uranium, molybdenum and rare earth elements (Vanhanen 2001), which is atypical of other orogenic gold deposits. Our current work aimed to test the hypothesis whether the peculiar element association is the result of multiple hydrothermal processes at the Hangaslampi deposit. Monazite is a rather common accessory mineral at this deposit and the high spatial resolution of the in situ LA-SC-ICPMS analytical technique allowed us to complete U-Pb age dating of individual grains according to their textural settings in the host rocks and veins.

2 Geological setting and characteristics of the Hangaslampi gold deposit

The stratigraphy of the KSB records the protracted evolution of a Paleoproterozoic basin formed by repeated rifting of the Archaean basement between 2.4 and 2.0 Ga. The basin fill consists of an approximately 2.5 km thick epiclastic-volcanic sequence with occurrences of two major horizons of greenstone formations (Fig. 1). Ore deposits in the KSB occur most typically along the boundary zones between the upper greenstone unit and sericitic schists. The lithological units were metamorphosed and folded during the Svecofennian orogeny (1.9-1.8 Ga). The metamorphic grade within the KSB decreases from amphibolite facies along the northwestern boundaries of the belt, where Svecofennian syn- to post-orogenic granitoids intruded the Archaean basement, to greenschist facies in the southern and eastern part of the belt.

The Hangaslampi gold deposit is located in the eastern part of the KSB and it is currently defined over a strike length of 270 metres to a maximum vertical extent of 90 metres from surface. It is hosted by a N-S oriented subvertical shear zone cutting the axial zone of a northerly plunging antiform comprising metamorphosed and altered intermediate and mafic volcanic rocks. The alteration appears to postdate the greenschist facies peak-metamorphism of the host rocks. The mineral resource estimates of the Hangaslampi deposit total 0.4 Mt (measured, indicated and inferred) grading 5.1 g/t Au and containing 66 100 ounces of gold (Dragon Mining 2014).
3 Methods

Observations using reflected and transmitted light polarizing microscopy were carried out on polished thin sections of drill core samples. Monazite grains were located by automated scanning of thin sections in a low-vacuum scanning electron microscope (JEOL JSM 5900 LV). Further high resolution imaging of individual grains was performed by using a high-resolution field-emission scanning electron microscope (JEOL JSM 7100F) in order to characterise internal zoning or other heterogeneities in individual grains of monazite. Quantitative analyses of monazite were completed by means of a Cameca SX100 electron microprobe. A suite of well-characterised minerals and synthetic compounds were used as standards.

U-Pb dating of monazites was performed by a Nu Plasma AttoM single collector ICPMS connected to a Photon Machine Excite laser ablation system. Large monazite crystals (n = 64) with clear petrogenetic context were targeted for analysis with a 20 micron spot size. During the analyses, in-house monazite standards A49 (1874 ± 3 Ma) and A1326 (2635 ± 2 Ma) were used. Data reduction were performed by the Glitter software (Van Achterbergh et al. 2001) and the Isoplot/Ex 3 program (Ludwig 2003).

4 Results

4.1 Geochemistry and mineralogy of the host rocks

The main rock types at the Hangaslampi deposit are mafic and intermediate metavolcanic rocks, which have undergone intensive hydrothermal alteration. Evolved, felsic metavolcanic rocks, which have been altered to sericite-quartz schists, are also occasionally found in the deposit. Samples show two distinct protolith types on the Zr/TiO$_2$-Nb/Y diagram (Pearce 1996), implying that the main rock types at Hangaslampi are metamorphosed and intensively altered basalts and andesites.

The main minerals in intermediate metavolcanic rocks are quartz, plagioclase and biotite, accompanied by variable amounts of pyrite, muscovite and chlorite, with accessory rutile, magnetite, pyrrhotite and monazite. Mafic metavolcanic rocks consist mainly of quartz, chloride and plagioclase with variable amounts of biotite, pyrite, muscovite, rutile and pyrrhotite.

The metavolcanic rocks are cut by younger fractures and carbonate veins, which are composed of dolomite, chlorite, biotite, pyrite and rutile. Gold, up to 5 μm in diameter, is most typically found as inclusions in coarse-grained pyrite hosted by sericite-quartz schist. One gold grain was observed in association with bastnäsite as an inclusion in pyrite.
Figure 2. Composition of monazites plotted on the Th/U-ratio-UO₂ diagram. Th/U-ratio has a logarithmic scale. ²⁰⁷Pb/²⁰⁶Pb ages from the same electron microprobe analysis spots are also shown on the diagram. U-Pb and microprobe data together reveal that some of the youngest monazites (~1.81 Ga) are characterized by very low Th/U-ratio. The oldest population (~1.87 Ga) of monazites is characterized by low uranium content and very high Th/U-ratio.

4.2 Textural setting, composition and U-Pb age dating of monazite

Monazite occurs in three different textural settings; 1) in the groundmass of metavolcanic rocks, 2) intergrown with biotite in strongly altered zones, and 3) in dolomite filled fractures and veins (Fig. 2).

Monazite occurring in the groundmass of the mafic metavolcanic rocks is typically associated with quartz, chlorite and muscovite and occasionally contain pyrite, pyrrhotite and chalcopyrite as inclusions. The concentrations of uranium in these monazite grains are very low (less than 0.017 wt% UO₂) and thus their Th/U ratios are very high (Fig. 2). These monazites exhibit internal, compositional zoning (Fig. 3), having Th-rich cores (1.6-3.0 wt% ThO₂) that appear distinctly brighter in backscattered electron images compared to Th-poor rims (0.1-0.2 wt% ThO₂). U-Pb data from this kind of monazite are nearly concordant. The error weighted average ²⁰⁷Pb/²⁰⁶Pb age is 1872 ± 4 Ma (MSWD = 1.5, n = 22).

In the strongly biotitized zones, which cut across the metavolcanic rocks, the monazite grains are characterized by low concentrations of uranium (0.04-0.08 wt% UO₂), whereas the concentrations of thorium are high (0.4-4.0 wt% ThO₂). These monazites are typically intergrown with biotite, rutile and pyrite. The U-Pb ages are nearly concordant, and the error weighted average ²⁰⁷Pb/²⁰⁶Pb age is 1849 ± 8 Ma (MSWD = 4.7, n = 10).

Figure 3. Back-scattered electron image of a monazite grain from groundmass of mafic metavolcanic rock, giving an age of ~1.87 Ga.

The third population of monazite in the Hangaslampi deposit is typically associated with late fractures and
dolomite veins, which cut the hydrothermally altered metavolcanic rocks. Monazite grains of this population have 0.02-0.23 wt% UO$_2$ and 0.15-1.54 wt% ThO$_2$ (Fig. 2). Monazite grains in dolomite veins are typically associated with chlorite, biotite, rutile and pyrite. Rutile commonly forms inclusions in this kind of monazite. Some of the monazite grains of the youngest population are intergrown with biotite. Most of the U-Pb data (n=16) are reversely discordant suggesting the presence of excess 206Pb in the structure of monazite (Parrish 1990). The average 207Pb/206Pb age of the concordant but slightly non-equivalent data is 1812 ± 10 Ma (MSWD = 2.4, n = 5).

5 Discussion and conclusions

The average 207Pb/206Pb age of 1872 ± 4 Ma for the oldest monazite population in the groundmass of metavolcanic rocks is interpreted to represent the time of a hydrothermal fluid flow event related to regional greenschist facies metamorphism in the eastern part of the KSB. This age group is characterized by very low uranium content.

The 207Pb/206Pb average age of 1849 ± 8 Ma for monazite from zones of strong biotite alteration together with the 1847 ± 1 Ma 207Pb/206Pb age obtained by U-Pb TIMS dating of brannerite inclusions in pyrite by Mänttäri (1995) indicate that the first stage of ore-forming processes was commenced approximately 20 million years after the peak metamorphism (1.87 Ga). No gold grains were observed in close association with monazite although this zone (drill hole KS/HL-69, between 48.5 and 49.5 m) is enriched in gold (~3 g/t Au).

Monazite grains from the late fractures and carbonate veins gives an average 207Pb/206Pb age of 1812 ± 10 Ma. The composition of monazite is highly variable but some of the grains are characterized by very low Th/U-ratio (Fig. 2). Mänttäri (1995) obtained 1822 ± 5 Ma 207Pb/206Pb age for brannerite as inclusions in pyrrhotite from the Hangaslampi deposit.

Both generations of hydrothermal monazite (1.85 Ga and 1.81 Ga) are associated with pyrite. Our observations confirmed results of Vanhanen (2001) suggesting that gold is most typically associated with different types of pyrite at the Hangaslampi deposit. Thus accumulation of gold can be connected either to the ~1.85 Ga or ~1.81 Ga hydrothermal events.

The new results indicate that the volcanic sequence at Hangaslampi experienced multiple fluid flow events, recording the age of regional metamorphism (1.87 Ga), and late stage mineralizing fluid flows at ~1.85 Ga and ~1.81 Ga, during the Svecofennian orogeny. The youngest ages indicate the connection between ore-forming events at Hangaslampi and late- to post orogenic regional hydrothermal stages, supported also by the detection of similar ages in other orogenic gold deposits in the Central Lapland greenstone belt (Mänttäri 1995; Middleton et al. 2016; Kurhila et al. 2017).

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Constrains on supergene and exotic copper mineralization in the Centinela district, Atacama Desert: New insights from a multi-disciplinary approach

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Abstract. Supergene and exotic copper mineralization, which are supergene deposit that went through lateral migration, are the result of tectonics, erosion and climate processes. However, numerous uncertainties remain regarding their formation conditions and several questions are still debated. For instance, at which stage of relief evolution cycle do they form? What is the relationship between exhumation and supergene copper mineralization? What are the erosive conditions needed during exotic copper mineralization? The occurrence of Supergene and exotic copper mineralization in the Atacama Desert suggest that this area gathers ideal conditions for mineralization and also its preservation. In order to better understand the processes involve in ore deposits, we applied a multidisciplinary approach to constrain both vertical rock displacement and erosive conditions. Both low-temperature thermochronological and sedimentological results show that in the Centinela District, in Northern Chile, the supergene and exotic mineralization occurred once the landscape was already flattened.

1 Introduction

In the Atacama Desert, numerous studies have focused on linking supergene copper mineralization and geomorphology to understand ore deposit genesis (Mortimer 1973; Clark et al. 1990; Quang et al. 2005). Nevertheless, the genesis conditions of supergene copper are still debated. Hartley and Rice (2005) proposed three principal criteria to the supergene copper mineralization: as (1) tectonically induced uplift to depress the water table, (2) a moderate precipitation rate (>100m.y-1); and finally (3) the absence of burial by subsequent sediments and preservation near surface.

In terms of geomorphologic evolution, Sillitoe (2005) proposed that low relief surfaces were not required for the formation of supergene copper mineralization. In order to contribute to discussions, we proposed a multi-disciplinary approach in the Centinela District, Atacama Desert, to quantify tectonic and erosive processes in a province where the necessary material are present to apply the corresponding methods.

First, we carried out a thermochronological study to constrain exhumation processes and define when, during the geomorphological cycle mineralization occurs (Fig. 1).

Figure 1. Steps of the geomorphologic cycle and relationship with supergene copper mineralization.
Secondly, we performed a sedimentary inventory of the gravels succession to understand the paleo-environment deposition context. Finally, we dated exotic copper mineralization using cosmogenic nuclides to estimate erosion rates variation and their impact on copper deposit genesis. This method has been applied to post 10 Ma sediments for the first time, in the Atacama Desert (Davis et al. 2014). We apply it on early Miocene to actual sediments.

2 Geological settings

The Centinela District is located in the Andean western slope, in the Precordillera morpho-structural unit at around ~23°S, 60 km south of the Calama city in Northern Chile.

The Precordillera is composed of Paleozoic and Triassic volcanic and Jurassic intrusive bodies, of Jurassic to Cretaceous volcano-sedimentary rocks and of Paleogene volcanic caldera system. Those rocks have been deformed and exhumed during the late Cretaceous back arc tectonic inversion (Mpodozis and Cornejo 2012; Mpodozis et al. 2005).

Late-Cretaceous to Eocene intrusive rock have been deformed later during the Eocene deformation phase called the “Incaic” phase in the Central Andes (Charrier et al. 2009), along the transpressive Domeyko Fault System (DFS) (Mpodozis et al. 1993; Amilibia et al. 2008; Mpodozis et Cornejo 2012). Intramountain basins like in the Centinela District associated fault systems also formed during this period. These basins host sediments eroded from the Precordillera, and exotic supergene copper mineralization.

The age of supergene copper mineralization in the Centinela district has been constrained by Ar/Ar and K/Ar dating between 25 Ma and 12 Ma (Perello et al. 2010; Riquelme et al submitted, Sillitoe and McKee et al. 1996), ending before the ~10Ma onset of hyperaridity (Rech et al. 2006; Alpers and Brimhall, 1988).

3 Methods

3.1 Sedimentological study

The study was based on facies description, clast lithology, interbedded volcanic layers and paleo-sols level identification.

The basin infill history of Centinela district was defined by a centimeter to meter scale stratigraphic column, on outcrops and on drill-cores samples, provided by Antofagasta Minerals S.A. mining company.

3.2 Low-temperature thermochronology and geochronology

We analyzed 13 granodioritic Early Paleogene and Medium Eocene samples from which we extracted 6 apatite fission track and 10 apatite (U-Th)/He ages, completed with 4 U-Pb zircon ages, before modelling the thermochronologic history of supergene Cu deposits using HeFty software (Ketcham et al. 2005).

3.3 Cosmogenic nuclides

The cosmic rays that bombard the earth atmosphere and there after the surface induce the presence of cosmogenic nuclides in target minerals. Their concentration may allow, when erosion rates are relatively low, to date burial of deposits.

We collected 9 sand samples, from 150 m deep to the surface, in the Tesoro Central open mining pits for cosmogenic radionuclide dating (Fig. 2). Sampling was focused on an exotic enriched layer of the Tesoro mining pit. We used both 10Be and 21Ne, which represent unstable and stable radionuclides, respectively to reconstruct the long-term erosion/sedimentation history.

Figure 2. Cosmogenic samples in the Tesoro open mining pit.
4 Dating results

Low-temperature thermochronological results vary from 46 Ma to 37 Ma for AFT and from 45 Ma to 22 Ma for AHe. Track lengths have also been measured. All results have been integrated in the HeFty-modeling software (Fig. 3).

Figure 3. Cooling paths from HeFty program.

All the samples dated using $^{10}\text{Be}$ and $^{21}\text{Ne}$ concentration within the Tesoro mining pit present sufficient measurable concentrations. They suggest that the maximum ages of mineralized blanket range from 10 to 14 Ma.

5 Discussion and results

The Centinela basin infill has been divided in four stratigraphic units with ages between mid-Eocene to Middle Miocene.

The middle-Eocene Esperanza gravel is coeval with porphyry copper mineralization; whereas the late-Eocene Atravesado gravel is synchronous to porphyry Cu intrusion and marks the start of rapid exhumation of the Precordillera. The erosion of porphyry copper intrusions continues during the Tesoro gravel deposit. Finally, the Arreros gravel represents the retrogradation of deposit cover while really few exhumation was happening.

We observe at least a gap of 5 Ma between the end of the main exhumation event in the Precordillera and the beginning of supergene mineralization. Our results suggest that the supergene copper mineralization occurred during a late stage of pedimentation (Figure 1) when the landscape was already flat.

Cosmogenic nuclides concentrations of samples from the exotic copper mineralized blanket suggest 10 to 12 Ma old ages. The decrease of concentration from the bottom to the surface of the enriched layer suggest that enrichment occurred before a quiescence in the sedimentation.

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Timings of fault events constraining ore-forming stages: direct age determination using Illite Age Analysis (IAA)

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Abstract. We firstly present the timings of fault events constraining ore-forming stages in the Giant Huize Zn-Pb Ore field of Yunnan Province, southwest China, using illite-age-analysis (IAA). The data show the age (118.1±0.6 Ma, 112.7±0.4 Ma, and 19.9±8.1 Ma) of authigenic 1Md/1M illites and the age (372.6±39.8 Ma, 288.7±6.2 Ma, and 263.6±6.2 Ma) of 2M1 illites. The youngest of 1Md/1M illites (19.9±8.1 Ma) is well matched with Re-Os isochron ages (20.4±3.2 Ma) of galena and sphalerite from the Fule in the Yunnan Province. The timing of the ore-formation process and the fault movement are related to tectonic events induced by Indian-Asia collision.

1 Introduction

The giant Huize Zn-Pb deposit is located along the southwestern margin of the Yangtze Platform. Many attempts have been made to date the Zn-Pb deposits using Sm-Nd, Rb-Sr, and Re-Os methods, and the orebodies yielded ages of 20.4±3.2 Ma, 201±6.2, ~228±16 Ma and 225±9.9 Ma ((Li et al. 2007; Yin et al. 2009; Liu et al. 2015; Zhang et al. 2015). They have great potential in determining the age of mineralization.

The distribution of the orebodies is mainly controlled by faults (Xiaojiang fault, Kangding-Yinliang-Shuicheng fault and Mile-Shizong-Shuicheng fault). However, there are no data for the timing of fault events, which is critical for understanding processes of formation of the Zn-Pb deposits and the geological evolution. The recently developed illite-age-analysis technique (IAA) has been successfully applied to determine the timing of multiple events in fault zones (Song et al. 2014). The dissolution-precipitation reactions follow the fault fracture zone during faulting. Newly formed 1Md/1M polytype of illite is formed at relatively low temperature, and mixed with the pre-formed 2M1 polytype illite (Grathoff and Moore 1996; Vrolijk and van der Pluijm 1999; van der Pluijm et al. 2001; Solum et al. 2005; Song et al. 2014).

Radiometric dating of near-surface faulting provides evidence for crustal evolution and regional tectonics. In this work, we provide insights into multiple ages of fault movements, which we suggest that the latest stage of Zn-Pb ore deposits were formed after India-Asia collision during 25-8 Ma (Guo et al. 2015).

2 Geological setting

The Sichuan-Yunnan-Guizhou metallogenic province (SYG) is located in the southwest Yangtze Block (Fig. 1). More than 400 epithermal Zn-Pb ore deposits and prospects have been found in this region are hosted in carbonate of lower Carboniferous (Li et al. 2007; Liu et al. 2015). The distribution of the deposits is controlled by the NE-SW-trending faults (Yin et al. 2009), and Emeishan basalt is general found in this region (Fig. 1).

Figure 1. Geotectonic map and sample location (modified from Liu, 2015). ①Nujiang fault; ②Jinshajiang-Honghe fault; ③Xianshuie Fault; ④Longmenshan Fault; ⑤Xiaoqinhe-Zhongdian Fault; ⑥Qinghe-Chenghai Fault; ⑦Anninghe-Lvzhijiang Fault; ⑧Xiaojiang Fault; ⑨Kangding-Yinliang-Shuicheng Fault; ⑩Mile-Shizong-Shuicheng Fault. 1. Emeishan basalt; 2. Direction of tectonic stress; 3. Plate junction belt; 4. Strike Fault; 5. SYG Pb-Zn metallogenic province.
3 Methods

3.1 Illite characterization and polytype quantification

Three fault clay samples (YL-5, YL-9 and YL-10) were collected with the Yulu Fault (Fig. 2). All the samples were prepared three different grain-size fractions (<0.1 μm, 0.1-0.4 μm, 0.4-1.0 μm) (Table 1) using standard gravitational settling and high-speed centrifuging techniques based on a preliminary size analysis. The suspensions (0.1 μm fraction) were flocculated by adding NaCl, and the upper clear supernatant was poured off. The different grain sizes were dialyzed and freeze-dried for X-ray diffraction (XRD) analysis, illite-polytype quantification, and K-Ar age-dating.

The XRD system (Rigaku, VariMax-007HFM) with Mo-target (λ=0.7093 Å) and imaging plate 2D-detector was utilized. The CMPR program was used for illite-polytype quantification using full-pattern-fitting with the WILDFIRE© simulated pattern. The R% value (Σ(|simulated – measured|/simulated)/n × 100) was used to determine the accuracy and iterated until R% value reached less than 10% for all fractions. The error bar was calculated by multiplying the R% value with the 2M1 illite content (Song et al. 2014).

Figure 2. Representitive field photographs showing the occurrence of the faults. a The fault between two thick-dolomite layers. b and c Small faults in the tectonic breccia.

3.2 K-Ar Dating

K-Ar dating was conducted by measuring the total K and radiogenic 40Ar at the Okayama University of Science. The analytical error of this method is within 2% on the basis of the multiple runs of two chemical standards (JG-1 granodiorite and JB-1 basalt). The minimum value that can be measured is 0.2 wt.%. Analysis of potassium and their errors follow the method reported by Nishido et al. (1984).

4 Results

Both 2M1 and 1M0/1M illite-polytypes could be recognized in most of samples, except for YL-10 (0.4-1.0 μm). Table 1 shows the illite-polytype quantification and K-Ar age-dating results.

The IAA plots for all fractions for 3 fault clay samples were characterized by 3 linear regression lines (Fig. 3). The lower intercepts at 0% 2M1 illites were 118.1±0.60 Ma, 112.7±0.4 Ma, and 19.9±8.1 Ma. The upper intercepts at 100% 2M1 illites were 372.6±39.8 Ma, 288.7±6.2 Ma, and 263.6±6.2 Ma (Fig. 3).

Figure 3. IAA plots for all size fractions of 3 samples. Error ranges are presented as shadows and the straight lines were obtained by linear regression analysis.

5 Discussions

The K-Ar ages of 1M0/1M illites indicate three times of fault activities (118.1±0.6 Ma, 112.7±0.4 Ma, and 19.9±8.1 Ma). The age of 19.9±8.1 Ma corresponds with the ore formation age of 20.4±3.2 Ma by Liu et al. (2015).

The 2M1 illites are commonly detrital in origin (Song et al. 2014) so the 2M1 illites might be derived from different bedrock sources. The age of 263.6±6.2 Ma could be related to the Emeishan basalt (~259 Ma) (Ali et al. 2005). The source of other two ages (372.6±39.8 Ma and 288.7±6.23 Ma) still should be discussed.

During the collision between India and Asia, the Sanjiang fold belt formed (Fig. 1), and the gold deposits formed around 33 Ma (Zhang et al. 2015). The continental collision caused strike-slip faulting (Fig. 1), and there might be multiple fluids which providing the source for Zn-Pb formation.
6 Conclusions

Multiple fault events are indicated by K-Ar illite dating from fault clay. These time constraints are crucial to establish the ore-forming processes of Zn-Pb deposits and their geological implications.

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Zircon U-Pb dating and Hf-O isotopes of the Archean Hongtoushan VMS Cu-Zn deposit, China

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Abstract. The Hongtoushan VMS deposit is located in the Qingyuan greenstone belt on the northern margin of NCC. We considered that there were two main stages for the formation of the Qingyuan Cu–Zn deposits: one was exhalative-hydrothermal sedimentation and another was further Cu–Zn enriched by later hydrothermal processes. The timing of the first stage occurred at 2571±6 Ma based on the magmatic zircons in the meta-mafic volcanic rocks. A large-scale hydrothermal event is documented by the recrystallized zircons in sulfide ores. The timing is tightly constrained by the hydrothermal zircon U–Pb ages of 2507±2 Ma. The 176Hf/177Hf ratios plot between depleted mantle and modern known plumes likely indicates a mantle plume setting corresponding to the ~2.6 Ga crustal growth. A modern mantle-like δ18Ozircon values of 5.5±0.1‰ (2SD) for this volcanism was well preserved in the inherited core domains, suggesting that it was most likely sourced from partial melting of juvenile crust. The weighted δ18O values of hydrothermal zircons show 5.6 ‰ to 7.0 ‰ (averaging 6.2 ‰), indicating the interaction of protoliths with surface waters at low temperature. Therefore, a submarine volcanic hydrothermal system involving mantle plumes is a preferred setting for the Neoarchean VMS Cu–Zn deposits in the Qingyuan greenstone belt.

1 Introduction

The North China Craton (NCC) is well endowed with numerous Precambrian ore deposits, providing an ideal opportunity to understand the relationship between large-scale mineralization and Precambrian evolution of this craton. The Hongtoushan deposit is the largest Archean VMS Cu–Zn deposit in China. Previous works show that the protolith of the VMS-hosting gneiss was mafic-acid volcanic rocks (Zhai et al. 1985) and the Cu-Zn mineralization time was as early as ~2.6 Ga (e.g., Zhang et al. 1984). An understanding of the geochronology and source characteristics through time would offer insight into crustal growth and the mineralization gneiss.

2 Regional and local geology

The Hongtoushan VMS Cu-Zn deposit is located in the northeastern margin of the NCC. The NCC is one of the oldest cratons in the world, consists of Archean to Paleoproterozoic metamorphic basement overlain by Mesoproterozoic to Cenozoic unmetamorphosed cover. The NCC is dominated by Neoarchean igneous rocks that were formed during two magmatic events at 2.8–2.7 Ga and 2.55–2.50 Ga (Zhai and Santosh 2011; Zhao and Cawood 2012; and references therein), representing two important episodes of crustal growth.

The Qingyuan terrane is dominated by early Archaean grey gneisses. Several Archaean greenstone belts occur along a NE-SW strike within the TTG rocks. These greenstones are generally referred to as the Qingyuan Group, which are further divided into the Jinfengling and Hongtoushan Formations. The Hongtoushan deposit has metal reserves of 0.5 Mt Cu at grades of 1.5% to 1.8% and 0.7 Mt Zn at 2.0% to 2.5%. The host rocks of the massive sulfide ores have been metamorphosed to upper amphibolite facies. The main orebodies, although intensely deformed, are stratiform and were stratigraphically controlled by the ‘rhythmic member’ in the upper part of the Hongtoushan Formation. This thin layer is composed of rhythmic interbeds of biotite plagioclase gneiss and amphibolite gneiss (Gu et al. 2007).

3 Zircon U-Pb age and O isotopes

All the samples were collected at the underground mining level of ~827 m, including host metamorphic rocks of amphibolite gneiss and biotite plagioclase gneiss and disseminated, massive, banded Cu-Zn ores. The zircons from amphibolite gneiss sample were measured by LA-ICP-MS and the rest grains were by Cameca 1280IMS; In situ zircon O isotopic analyses were conducted on zircons that were previously dated using Cameca 1280IMS.

3.1 Zircon U-Pb ages

In the amphibolite gneiss, based on the CL images and zircon U-Pb analyses, two groups of zircon are distinguished and interpreted to be all detrital origin (figure 1; Zhu et al. 2015). (1) The old group, with Th/U ratios ranging from 0.09 to 0.72, yields two imprecise age of 3106±10 Ma and 2626±29 Ma, respectively, indicating the existence of ancient supracrustal rocks in this area as old as ~2.63-3.11 Ga. (2) The magmatic zircons, with Th/U ratios ranging from 0.17 to 1.87, yield an age of 2570±2/−1 Ma, which precisely representing an earlier magmatic event. The zircons from the biotite plagioclase gneiss are igneous origin, with Th/U ratios ranging from 0.21 to 0.48, and define a weighted mean 207Pb/206Pb age of 2507±4 Ma, which precisely determine the formation age of the VMS-hosting, interbedded volcanic rocks.

In the Cu-Zn ores, most zircon grains have typical core-rim structure (Fig. 1). The core domains have Th/U ratios ranging from 0.31 to 0.69 and yield a weighted mean
207Pb/206Pb age of 2568±5 Ma (not shown). The rim domains are of hydrothermal origin, with Th/U ratios ranging from 0.01 to 0.34, and define a hydrothermal event at ca. 2507 Ma. It indicates that the Cu-Zn mineralization has a genetic relationship with later felsic volcanism.

Therefore, the ages of the Hongtoushan VMS-hosting volcanics and Cu-Zn enriched mineralization are defined at ca. 2507 Ma and the volcanism played an important role in the Hongtoushan Cu-Zn mineralization.

**Figure 1** Zircon U-Pb and O isotope analysis results

### 3.2 Hf-O isotopes

All zircons have a relative narrow range of $^{176}$Hf/$^{177}$Hf ratio (0.281349–0.281581; Zhu et al. 2017), whereas the $^{176}$Lu/$^{177}$Hf ratio is relatively small and concentrated for the volcanic zircon ranging from 0.0002 to 0.0005 compared with the large and scattered values for the pre-magmatic and hydrothermal zircons, ranging from 0.0008 to 0.0034. In addition, for the pre-magmatic and hydrothermal zircons, $^{176}$Hf/$^{177}$Hf ratios systematically increase slightly with the $^{176}$Lu/$^{177}$Hf ratio. The average value of the $^{176}$Hf/$^{177}$Hf increase is 0.0218% when compared with volcanic zircon. It suggests the same lithospheric reservoir and weak hydrothermal influence. All of the same, it is impossible to distinguish magmatic and hydrothermal zircons by Lu–Hf isotope systematics after magmatic zircon has been modified by hydrothermal fluids.

Hf model (TDM1 and TDM2) ages are also calculated, despite their possibly altered Lu–Hf isotope systematics in the pre-magmatic and hydrothermal zircons, and we find that all zircons have relatively concentrated Hf model ages. Given the 2 percent uncertainty of TDM, it is interesting to see that: (1) for the pre-magmatic zircon, the mean TDM1 and TDM2 ages are 2575±13 Ma and 2577±13 Ma (2 sigma; n=15), respectively, which are closely coincident with the mean $^{207}$Pb/$^{206}$Pb age of 2568±5 Ma; (2) unaltered volcanic zircon has ages of 2558±23 Ma and 2574±23 Ma (2 sigma; n=5), which are older than the mean $^{207}$Pb/$^{206}$Pb age of 2507±5 Ma, but similar to the TDM age of the pre-magmatic zircon within error; and (3) hydrothermal zircons have similar TDM1 and TDM2 mean ages of 2580±9 Ma and 2599±9 Ma (2 sigma; n=36), respectively, which are older than the mean $^{207}$Pb/$^{206}$Pb age of 2507±4 Ma, but also similar to the TDM age of the pre-magmatic zircon within error. These results probably indicate that (1) the pre-magmatic activity represented by the pre-magmatic zircons was ultimately sourced from synchronous depleted mantle with limited contamination from crustal materials, (2) acidic volcanics and hydrothermal fluids were extracted from that pre-magmatic event and followed by post-volcanic hydrothermal processes within ca. 100 Ma, and (3) increasing Lu–Hf isotopes commonly increase the corresponding Hf model ages, causing Hf model age to be less reliable. That constraint causes us to interpret Hf isotopes cautiously, as they may be related to either crustal contamination or variable $^{176}$Lu/$^{177}$Hf ratios, especially in hydrothermal and metamorphic zircons.

In situ O-isotope analyses were conducted on the same zircon zones used for U-Pb analysis (Fig. 1). The δ18O values of magmatic zircons from the biotite plagioclase gneiss range from 5.3 to 5.8 ‰ (averaging 5.5 ‰), similar to modern mantle δ18O value (δ18O =5.3 ± 0.6 ‰; Valley et al. 1998). The zircons from disseminated ore have a homogenous O isotopic composition, with δ18O ranging from 7.0 ‰ to 7.7 ‰ (averaging 7.4 ‰) except one anomalous value of 6.7 ‰ (not shown). The δ18O values of zircons from the massive sulfide ore and the banded ore occur as two groups according to their core-rim structure. The values of cores have a typical characteristic of modern mantle ranging from 5.3 ‰ to 5.8 ‰ (averaging 5.5 ‰), whereas the values of rims range from 5.6 ‰ to 7.0 ‰ (averaging 6.2 ‰), indicating a metamorphic or hydrothermal origin. A higher δ18O in the rim than its core demonstrates input of O-enriched materials during overgrowth. The successive elevation of δ18O indicates...
increasing input of high-$\delta^{18}$O materials under high-temperature during evolution of the magmatic hydrothermal convective system.

4 Conclusion

On the basis of the zircon geochronology and in situ oxygen isotopic analyses, we can conclude the following.

(1) The Hongtoushan Cu-Zn mineralization occurred at ~2570 Ma and was further Cu–Zn enriched by later hydrothermal processes at 2507 Ma.

(3) The hydrothermal fluid of Cu-Zn enriched mineralization is sourced from $^{18}$O-enriched post-magmatic hydrothermal solution.

(4) The Lu/Hf ratio has an obvious elevation, resulting in the increase of the $^{176}$Lu/$^{177}$Hf ratio due to Lu substitution, but an impervious modification on $^{176}$Hf/$^{177}$Hf.

(5) The protoliths of the gneisses have mantle-like source, likely indicating an intensively extensional setting related to the rift or mantle plume.

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References


S08 – From fertility to footprints: New vectoring tools for mineral exploration

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Advances in integrated exploration targeting

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Abstract. Over the last 15 years or so, there has been significant innovation in integrated exploration targeting to support how and where mining companies are to search for new deposits. Exploration is increasingly focused on targets at depth or under cover where the remote sensing role of geophysics takes on a new role in the exploration process. Strategies relying on the identification of geophysical anomalies are giving way to the integrated characterization and identification of mineralized systems footprint(s), helping vector towards ore. Integrated exploration targeting is the process by which exploration geoscientists merge, quantify and weigh the contribution of geology, geophysics, and geochemistry to produce a coherent 3D earth model to support mineral exploration decisions, from survey planning to drillhole targeting. This approach relies on, but also forces key technological innovations in data management, quantitatively-integrated geological and geophysical modelling, and pattern recognition through machine learning. We describe four instrumental advances in integrated exploration targeting: 1) the ore system footprint versus anomaly paradigm; 2) the use of geophysical data in the interpretation of alteration; 3) machine learning to reveal subtle relationships amongst data that are diagnostic of ore forming processes and their footprint; and 4) data acquisition simulations to optimize exploration strategy and plan data acquisition.

1 Introduction

As in other domains, the “big data” revolution applies to mineral exploration. We are collecting increasing amounts of digital geochemical, geophysical, and remote sensing data as measurement technology continues to advance and exploration becomes more challenging as we explore at depth or under cover. These new challenges are forcing us to better understand our data streams as well as the relationships among them. Innovative data analysis tools and workflows have become a requirement for ore system recognition and targeting. At the centre of these innovations is the Common Earth Model (CEM), a 3D spatial model of the earth (Fig. 1) that contains, and is consistent with, all current geological, geochemical, and geophysical data, as well being consistent with conceptual geological thinking (McGaughey 2006, 2007). It is a working hypothesis subject to change as interpretational thinking evolves or new data are acquired. It is the 3D container in which all spatial data reside within a coherent structural, formational, and facies context. As such, it provides the necessary basis for understanding ore systems footprint(s) and deposit targeting, for interpreting geophysical data in terms of alteration, for structuring data for machine learning algorithms to gain interpretational insight, and to simulate data acquisition for the optimization of strategy and the planning of cost-effective field data acquisition.

Figure 1. The Flin Flon volcanogenic massive sulfide (Cu-Zn-Au-Ag) camp Common Earth Model (CEM). In addition to the visible structures and formational contacts, the 3D model is fully attributed with physical properties that correspond to the modelled geology and all geophysical data.

2 Mineralization footprints and the CEM

Exploring deep or under cover means that there is no expectation of a direct signature of an ore deposit within exploration data sets. The ore deposit, however, is part of a mineralized system with alteration assemblages that may extend many kilometres. Where the architecture of such systems is known in terms of a reasonably consistent pattern of alteration domains (the “footprint”), exploration strategy can focus on the identification of such domains and vectoring to the ore deposit. The current NSERC-CMIC Industrial Research Network project, “Integrated Multi-Parameter Footprints of Ore Systems: The Next Generation of Ore Deposit Models,” is focused on characterizing the multi-disciplinary, multi-variate, and multi-scale characteristics of alteration domains and their spatial relationships to ore deposits (http://cmic-footprints.ca). From a data integration perspective, there are three major challenges: 1) recognizing the different alteration domains within the footprint; 2) characterizing the multi-variate signature of those domains; and 3)
vectoring from distal to proximal alteration domains identified in field data towards ore.

Research in the multi-disciplinary characterization of footprint alteration domains, and its use to recognize the footprint in field data, require the development of Common Earth Models from whatever data sets are available. The reasons for this are two-fold. First, many of the important variables are either topological (within, under, over) or geometric, such as proximity measures to 3D geometrical structures such as faults or intrusive contacts. Away from drilling, the only way to construct a 3D earth model, consistent with field data, in which topological or geometric variables can be developed, is to integrate geological and geophysical interpretation through the CEM. A necessary CEM validation test is that the 3D geological model is attributed with physical properties that are consistent with the modelled rock types and consistent with the geophysical data. Consistency with geophysical data must be demonstrated by forward modelling. Second, physical properties are critically important to the footprint characterization because they are typically the only rock properties that are interpretable over the entire exploration volume. Volumetric physical property interpretation is accomplished through inversion of geophysical data using the integrated interpretation workflow described in the next section.

3 Geophysical signatures of geochemical alteration

Recognition of footprint-scale geochemical alteration from the interpretation of geophysical data is important not only from the perspective of footprint-domain recognition, but more generally from the perspective of maximizing the exploration value of the data sets with the greatest and most uniform areal coverage. Potential fields data are common, with high-quality airborne magnetic data nearly ubiquitous in modern mineral exploration. Geophysical data are only sensitive to variations in physical rock property in the earth’s subsurface (e.g. gravity data respond only to variations in rock densities). On the other hand, the sources of those physical property variations are generally associated with geological features and processes. Those include rock forming, tectonic, structural, geochemical, and mineralization processes. Away from ore and its immediate alteration halo, alteration usually has a limited effect on physical rock properties that are then controlled by the primary nature of the rocks.

The integrated interpretation workflow we use to create Common Earth Models can often reveal the geophysical signature of geochemical alteration by, in effect, removing the primary control on geophysical data—the changes in physical properties across structural and formational contacts. A geophysical modelling framework that can act on a 3D geological model, directly modifying structural and formational contact geometry, is required for this purpose. The workflow (for the case in which both gravity and magnetic data are available) can be summarized as:

1. Construct an initial 3D geological model.
2. Attribute the model with homogeneous densities and magnetic susceptibilities per geological formation.
3. Forward model to estimate the gravity and magnetic data that would be theoretically generated from the model, and compare to the gravity and magnetic field data;
4. Adjust the geological model in any way suggested by the difference between the forward modelled and field data, with the restriction that geological units remain homogenous in density and magnetic susceptibility, and that the physical property values used are consistent with the interpreted rock types;
5. Repeat steps 3 and 4 until no further improvement in fit between forward modelled and field data is possible.
6. In a final step, alter the model to allow the physical property heterogeneity within formations required to achieve a match between forward modelled and field data.

The heterogeneity permitted in step 6 may be considered, with proper interpretational caution, as variation in physical properties within geological formations due to alteration. The key assumption of this workflow is that variation in physical properties in the earth is primarily controlled by structure, contact geometry, and rock type, with alteration having a secondary effect.

In practice, the most technically complex step in the above workflow is step 4, adjusting the model composed of homogeneous units so that it better fits the data. For this step, we use “VPmg,” a magnetics and gravity modelling and inversion program that directly inverts for the shape of contact geometries (Fullagar and Pears 2007) and both homogeneous or heterogeneous formation densities. We operate VPmg from the GOCAD® earth modelling platform, directly integrating geological and geophysical modelling in the same workflow (The notion of the Common Earth Model was originally developed in oil industry application of GOCAD, integrating geological modelling with seismic interpretation.) The geophysical inversion philosophy of VPmg is based on two fundamental concepts: 1) a global inversion result is built as a sequence of individual, user-defined inversions; 2) each inversion addresses a possible source of change in physical rock properties. This is made possible by the different inversion types offered. Geometrical inversions (perturbation of selected lithological contacts constrained by drillhole pierce points) are used to model the contacts between homogeneous domains and the fault blocks that delimit them (step 4), while changes due to heterogeneous physical rock properties within a single rock type or a group of rock types can be associated with an alteration process (step 6). The capability of this integrated geology and geophysics workflow to model geochemical alteration effects through physical properties ultimately provides insights into vectoring in 3D, whether interpreted through the footprint-recognition paradigm or not.
4 Machine learning for multivariate analysis of mineralization footprints

The multivariate nature of ore system footprints presents a further important interpretational challenge. Recognizing the complex and often subtle associations of variables that define footprint alteration domains and their relationship to geophysical proxies is beyond the capability of conventional statistical techniques when there are many variables in play. Recent advances in machine learning technologies in other fields have presented an opportunity to investigate the multivariate associations that define footprint domains in a new and powerful way.

There are two main approaches to machine learning, unsupervised and supervised. Unsupervised machine learning finds natural groups or “clusters” in a set of data, to which an interpreter must give meaning. Supervised machine learning is used to train an algorithm to identify a class or target variable (such as “mineralization is present”), based on a group of known examples.

There has recently been a surge of interest and research into the application of machine learning methods to better understand the complex, multi-disciplinary data we must deal with in mineral exploration. We have experimented with machine learning in conventional prospectivity analysis, replacing standard weights-of-evidence with a machine learning algorithm called HyperCube® (http://hypercube.bearingpoint.com), that searches for rules of association between input variables and the target variable or class. Our finding is that machine learning significantly outperforms standard non-machine learning prospectivity algorithms such as weights-of-evidence. HyperCube, along with several unsupervised machine learning tools such as k-means clustering and self-organizing maps, has also been used successfully within the NSERC-CMIC Footprints project for interpretation (Feltrin et al. 2016). There are numerous other recent examples of the successful application of machine learning to mineral exploration appearing in the literature (e.g., Caté et al. 2017).

5 Exploration data simulation

The development of the CEM has permitted the simulation of realistic exploration data sets. Simulations can be used for several applications: 1) for the formulation of targeting strategy by exploration teams based on realistic simulation of field data; 2) for detectability studies of a specified footprint or for direct detection of mineralization using geological, geochemical or geophysical data; 3) to identify the best sampling parameters (survey design) to capture the desired exploration criteria; and 4) to train students by providing a realistic, simulated data-acquisition platform.

Realistic simulations at a given scale require a fully attributed CEM. We have developed an application called MinSim (Mineral Exploration Simulator) for CEM-based data simulations. MinSim allows users to design, simulate, and visualize results from drilling and geophysical surveys. An initial MinSim package for volcanogenic massive sulfide exploration, based on the Flin Flon CEM (Fig. 1), has been developed. An example of an interface panel for airborne gravity surveys is shown in figure 2, with results of the survey shown in figure 3.

Figure 2. MinSim interface panel for design of a simulated airborne gravity survey.

6 Conclusions

Significant advances in integrated exploration targeting have occurred over the last 15 years or so. A recurring element is the development of the Common Earth Model paradigm, in which a self-consistent 3D earth model is created through workflows that provide a quantitative, integrated interpretation of geological, geochemical, and geophysical data. The CEM provides a sound basis for research into the alteration footprint(s) of mineral systems. Its construction through an integrated interpretation workflow provides a means of interpreting alteration using geophysical data and physical-property proxies to alteration. It provides key input variables for the application of machine learning to an understanding of the associations of input variables and target conditions that we need to recognize for exploration success. Finally, it is the basis of realistic mineral exploration data simulations that can be used to develop strategy and to train the next generation of explorationists.
Figure 3. Simulation result, showing a realistic gravity response (Gzz) along the specified survey flight lines.

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References


Distinguishing between barren and fertile batholiths in the same porphyry-Cu district using zircon trace element geochemistry

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Abstract. Zircon trace element chemistry, particularly when combined with U–Pb dating of zircon, can provide crucial information on the temporal, and chemical evolution of magmatic-hydrothermal systems. Sixteen samples representing six different igneous units were analysed for 33 elements using LA-ICPMS. Zircons from the mineralised Luhr Hill intrusion have smaller negative Eu/Eu* anomalies than zircons from the post-mineralisation Shamrock intrusion. Zircons from the Shamrock intrusion show a different trace element chemistry to zircons from either pre- or syn-mineralisation intrusions. Zircons from the Shamrock batholith contain elevated Ho, P, U, Yb and Er. Zircons from the Yerington batholith contain elevated Dy, Tb, Y, Lu, and Yb.

1 Introduction

The Eu anomaly (Eu/Eu*) and trace element patterns in zircon can be used to distinguish barren batholiths from fertile batholiths that generate porphyry-copper deposits (PCDs) (Dilles et al. 2015; Lu et al. 2016). PCDs are typically associated with hydrous, oxidised magmas (Richards 2009; Dilles et al. 2015). Low Eu anomalies (Eu/Eu* ≥ 0.4) are characteristic of fertile, oxidised magmas (Dilles et al. 2015). A large negative Eu anomaly is typically attributed to the presence of Eu³⁺ in the melt, or reducing conditions since Eu²⁺ partitions less readily into zircon than Eu³⁺.

2 Yerington porphyry-Cu – Mo – Au district

The Yerington mining district (Yerington) occurs in west-central Nevada, United States, approximately 80 km southeast of Reno (Fig. 1). Yerington has long been a site of intensive porphyry deposit research due to excellent outcrop and numerous Cu ± Mo ± Au porphyry deposits, with a total endowment of over six Mt Cu in sulfide ores and > 100 Mt of Fe in oxide ores (Dilles et al. 2000).

The oldest rocks recorded in the district are middle Triassic volcanic rocks that have been intruded by middle to late Triassic plutons (Fig. 1; Dilles and Wright 1988). The Mid – Late Triassic McConnell Canyon volcanics comprise a thick package of marine sedimentary and volcanic rocks. A quartz porphyry dike that has intruded the volcanic sequence has been U–Pb dated at 232.2 ± 2.3 Ma (Dilles and Wright 1988). This porphyry does not appear to have intruded the overlying sedimentary sequences, and therefore this age is interpreted as a minimum age constraint for the formation of the McConnell Canyon volcanics. The McConnell Canyon package includes: basal aeolian sandstone, evaporate gypsum, marble, tuffaceous siltstone, a thick upper Triassic limestone, tuffaceous limy beds and black argillite (Dilles et al. 2000). Basement rocks were regionally metamorphosed to biotite-bearing schistose texture sometime between emplacement (232.7 ± 2.9 Ma) and the emplacement of unmetamorphosed, crosscutting early quartz monzodiorite of the Yerington batholith (169.4 ± 0.4 Ma; Dilles and Wright 1988).

The Jurassic-aged Yerington batholith is a polyphase intrusion comprising the McLeod Hill (169.4 ± 0.4 Ma), Bear, and Luhr Hill (168.5 ± 0.4 Ma) intrusions (Dilles 1987; Dilles and Wright 1988). The Luhr Hill granite is the causative intrusion associated with multiple Cuporphry and Cu-skarn deposits in the Yerington district.
Figure 1. Geology map of the Yerington district, Nevada. Modified from Dilles and Proffett (1984). U–Pb in zircon ages from Dilles and Wright (1988). The Shamrock batholith (165.8 ± 0.4 Ma) is a post-mineralisation Jurassic-aged intrusion located immediately south of the Yerington batholith (Fig. 1; Knopf 1918; Harris and Einaudi 1982; Dilles 1987; Dilles and Wright 1988). The Shamrock batholith is not associated with any known Cu-porphyry or Cu-skarn mineralisation in the district (Harris and Einaudi 1982).

3 Methods

Zircons from 16 samples collected across the Yerington district were separated using heavy liquids. All samples yielded > 100 zircons. Zircons were analysed by LA-ICPMS at the Rio Tinto Laboratory, Melbourne, Australia. Zircon cores were preferentially targeted for analysis. Eu/Eu* values were calculated as $\frac{[Eu_{ppm}/0.0563]}{\sqrt{[Sm/0.148]([Gd*0.199])}}$.

4 Zircon trace element geochemistry

The average Eu anomaly in zircons from the mineralised Luhr Hill granite is smaller than the average Eu anomaly of zircons in either the pre-mineralisation intrusion or the post-mineralisation Shamrock intrusion (Fig. 2a). Zircons from the Shamrock batholith returned Eu/Eu* values ≤ 0.4, with half the analyses ≤ 0.25, whereas samples from the Yerington batholith returned values between 0.25 – 1.05. A small number of analyses from zircons in the McLeod Hill and Luhr Hill samples returned values > 0.40. No zircons from the pre-mineralisation Bear intrusion returned values > 0.40.

Zircons from pre- and syn-mineralisation intrusions have higher (Eu/Eu*)/Y values, and higher (Ce/Nd)/Y values than zircons from the Shamrock intrusion (Fig. 2b). Greater than 95% of zircons from the post-mineralisation Shamrock intrusion have a 10000*(Eu/Eu*)/Y value < 3, and a (Ce/Nd)/Y value < 0.02. Greater than 95% of zircons from the syn-mineralisation Luhr Hill intrusion have 10000*(Eu/Eu*)/Y values of > 3 and (Ce/Nd)/Y values > 0.05. Zircons from pre-mineralisation intrusions have 10000*(Eu/Eu*)/Y and (Ce/Nd)/Y values that overlap with zircons from both syn- and post-mineralisation intrusions.

Discriminant projection analysis using 26 variables (trace elements) was used to analyse the trace element chemistry of zircons in pre-, syn-, and post-mineralisation intrusions (Fig. 2c). Discriminant projection 1 (DP1) discriminates between zircon populations of the Yerington and Shamrock batholiths. Zircons from the Shamrock batholith contain elevated Ho, P, U, Yb and Er. Zircons from the Yerington batholith contain elevated Dy, Tb, Y, Lu, and Yb. There is significant overlap between zircons from pre- and syn-mineralisation intrusions. However, a population of zircons from pre-mineralisation intrusions contained higher Y, Lu, Eu, Ti, and Sm than zircons from syn-mineralisation intrusions.

5 Summary and implications

Previous studies from multiple porphyry-Cu districts (e.g., Chuquicamata-El Abra; Ballard et al. 2002; Yerington, Yanacocha; Dilles et al. 2015) have shown that zircons with small negative Eu/Eu* values are associated with ore-forming magmas (Lu et al. 2016). Large Ce³⁺/Ce⁴⁺ ratios (> 300) can also be characteristic of ore-forming magmas however the calculation of Ce⁴⁺/Ce³⁺ ratio is controversial (Dilles et al. 2015; Lu et al. 2016). Lu et al. (2016) proposed the use of Ce/Nd as a proxy for the Ce anomaly due to its power law relationship with Ce/Ce* and the typically elevated concentrations of Ce and Nd in zircons.

Results from this study show that zircons from pre- and syn-mineralisation intrusions have higher Ce/Nd values than zircons from the post-mineralisation Shamrock.
batholith. This suggests that pre- and syn-mineralisation intrusions were more oxidised than the post-mineralisation intrusion. High Eu/Eu* values in zircons from pre- and syn-mineralisation intrusions support the conclusion that ore-forming magmas in the Yerington district were either very hydrous, very oxidised, or both (Dilles et al. 2015; Lu et al. 2016). Conversely, the Shamrock batholith was more reduced and less hydrous as compared to pre- and syn-mineralisation intrusions.

The entire Yerington batholith was emplaced within one million years (Dilles and Wright 1988). The results from this study indicate that the McLeod Hill intrusion (pre-mineralisation) was more reduced than the Luhr Hill intrusion (syn-mineralisation). Progressive oxidation over time of intrusions sourced from the same magma chamber has also been observed at the Los Picos-Fortuna/Pajonal-El Abra igneous complex (Ballard et al. 2002). Ballard et al. (2002) suggested a number of reasons why this might occur including: (1) metasomatism of a mantle source region before or during the partial melting process; (2) fractional crystallisation of Fe2+-bearing silicate, oxide, or sulphide phases; (3) addition of SO2 into a mature magma chamber from a degassing mafic magma ponded below; and (4) degassing of magma at low pressure with preferential removal of reduced species. The last explanation is unlikely for the Luhr Hill intrusion as it was emplaced deepest in the crust as compared to the McLeod Hill and Bear intrusions.

The Shamrock batholith was intruded approximately three million years after the Luhr Hill intrusion. This timing relationship indicates that in a span of three million years, magma composition changed from relatively oxidised to more reduced. The mechanisms attributed to this change in redox conditions is not well understood; however, a number of factors may have affected redox processes including: (1) changes in the degree of magma mixing between felsic and mafic magmas at the base of the crust; and/or (2) assimilation of more reduced crustal material during magma ascent. Further work is necessary to fully understand the significance of changing redox conditions in an arc environment.

### 6 Conclusions

Zircons from the post-mineralisation Shamrock intrusion exhibit very different trace element chemistry as compared to ore-forming intrusions in the Yerington district, Nevada. Zircons from fertile intrusions have small negative Eu/Eu* anomalies, and higher Ce/Nd values indicative of a hydrous, oxidised melt. Zircon trace element geochemistry is a valuable, relatively inexpensive tool for early-stage district-scale exploration that can help the explorer to focus efforts on fertile search spaces.
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Geochemical characteristics of magmatic mica as a monitor of metal fertility in Devonian intrusions of the New Brunswick Appalachians

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Abstract. The Canadian-Appalachian and specifically Acadian-related felsic intrusions host many different types of granophyric element mineralization. Geochemical characteristics of biotite from thirty of these intrusions were used to develop fertility indices for potential use as an exploration tool to distinguish barren and mineralized granitic intrusions. Results clearly showed distinctive geochemical characteristics for biotite from barren, Cu-Mo mineralized, and Sn-W-Mo mineralized intrusions. Biotite from barren intrusions classify as magnesian-siderophyllite, containing more Ti, Mg, V, and Cr with lower Mn and halogen content. On the other hand, biotite from Cu-Mo systems classifies as ferroan-phlogopite, whereas biotite from Sn-W systems classifies as lithian-siderophyllite. Grains from Sn-W-Mo systems shows the highest Fe, Li, Mn, W, Rb, and halogen contents. In general, Sn, Mo, Sb, Co, Ni, Sr, Cs, and Br are slightly higher in biotite from mineralized intrusions. Biotite from Cu-Mo systems contains slightly higher values of almost all the analysed elements compared with the barren intrusions. A new classification diagram was introduced using Li, V, and Na content of biotite as a discriminant between barren and mineralized felsic intrusions.

1 Introduction

Biotite is a significant ferromagnesian mineral in most intermediate and felsic igneous rocks. Biotite crystallizes under a wide range of physiochemical conditions and typically equilibrates with the latest volatile phase; therefore, its chemical composition has long been used to study different geochemical characteristics of the parent magma. For instance, they have been used to examine the genesis of mineralization in many porphyry deposits (Monteiro et al. 2008; Boomeri et al. 2009, 2010; Siahcheshm et al. 2012; Afshooni et al. 2013), rare-element pegmatites (Lentz 1992), and Sn-bearing granites (Wang et al. 2013; Akoh et al. 2015). The halogen contents of biotite predict the fluoride and chloride activity of the aqueous volatile phase (Munoz 1984; Coulson et al. 2001; Zhang et al. 2016) and can be used as a thermometer to test equilibrium by assessing the extent of subsolidus recrystallization and (or) exchange processes between biotite-apatite pairs (Sallet 2000). Furthermore, the Mg/Fe versus F/ OH in biotite can be used to study crustal contamination in I-type granites (Ague and Brimhall 1988). Interestingly, some studies have tried to use biotite chemical characteristics to differentiate barren and mineralized systems (Zhang et al. 2001; Rasmussen and Mortensen 2013; Maydagán et al. 2016); however, this goal has not been fully achieved yet.

Two sets of felsic intrusions were emplaced during the later parts of the Appalachian orogenic cycle in New Brunswick (van Staal et al. 2009). However, just those associated with crustal thickening processes of Acadian orogeny and post Acadian uplift are mineralized with different concentrations of granophile elements. These intrusions geochemically defined affinities ranging from primitive to highly evolved A-, S-, and I-types granitoids.

Thirty of these Devonian intrusions were studied to examine the use of detailed biotite compositions as a proxy to differentiate between barren and mineralized granitoid intrusions. Empirical and experimental research has shown that biotite continuously equilibrates with their host melts. Therefore, core-to-rim compositional zoning of biotite and hornblende can provide a record of magma evolution so that the origin and evolution of granitoids can be discerned.

In this paper, we present comprehensive in situ analyses of biotite from seven of the studied intrusions (Lost Lake and Juniper Barren granodiorites represent barren intrusions, Nicolas Deny, Blue Mountain, and McKenzie Gulch represent Cu-Mo systems, and Mount Douglas and Mount Pleasant represent Sn-W-Mo mineralized intrusions) to clearly show the geochemical contrast between the two end members. The new data helps us to investigate the genetic relationship between Sn-W-Mo and rare Sb mineralization and magmatic-hydrothermal evolution of the Acadian-related granitoids of New Brunswick.

2 Tectonic setting

Studies have shown that biotite colour and major element content can be used as a tool to identify the tectonic setting of its host magma (Lalonde and Bernard 1993; Abdel-Rahman, 1994; Shabani et al., 2003). Biotite from the Lost Lake and Juniper Barren granodiorites are greenish-brown in colour indicating an oxidized I-type magma, whereas biotite grains from the mineralized intrusions (both Cu-Mo and Sn-W-Mo systems) are brownish-red indicative of a more reduced environment. Oxidation state of the granitic magma has a direct relationship with the associated ore mineralization (i.e. Sn vs. Cu-Mo) and partially dictate the compatible/incompatible behaviour of elements toward mica (Blevin and Chappell 1992, 1995). However, mica crystallization in leucogranites does not seem to be dependent on oxygen fugacity (Pichavant et al. 2016). The examined biotite grains are mostly located in
calc-alkaline and alkaline fields of the biotite discrimination diagram of Abdel-Rahman (1994). This in terms means subduction-related orogenic suites that are enriched in Mg. However, data from the Mount Pleasant granite plot within the P domain of the classification indicating the peraluminous nature of its parent magma (Fig. 1a).

3 Analytical procedure

We collected polished thin sections of thirty granitoid samples from previous studies (McLeod 1990; Whalen 1993; Yang 2005; Beal et al. 2010; Shinkle 2011; White 2013) and used transmitted light microscopy to choose the freshest and largest biotite crystals for our study. These grains were analysed with both electron microprobe and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) at the University of New Brunswick.

Major elements and halogen analyses were obtained on carbon coated polished thin sections using JXA-JEOL-733 Superprobe, equipped with dQant32 and dSpec automation from Geller Microanalytical Laboratories. The microanalysis was conducted with 15 kV accelerating voltage, 30 nA beam current, the maximum counting interval of 120s and the beam size of 2 µm.

The biotite grains were then analysed at the same spots by LA-ICP-MS using the Resonetics M-50-LR 193 nm Excimer laser ablation system coupled to an Agilent 7700× quadrupole ICP-MS. A different beam size of 17, 24, and 33 µm (based on the grain size), 4 Hz pulse rate, 10 J/cm² energy was used. The K content of each spot measured by EPMA was used with an internally-standardized data reduction scheme to obtain the most accurate trace element data. The NIST 610 and NIST 612 were used for external calibration, whereas the BC2RG glass was analysed as a secondary standard. The relative deviations for trace element data are generally within 10%. Biotite formula calculation is based on 22 atoms of oxygen. Water contents were calculated by stoichiometry (Yang and Lentz 2005).

4 Biotite mineral chemistry

4.1 Biotite classification

Biotite from barren and mineralized intrusion show contrasting major element geochemistry. Analysed grains from the barren intrusions classify as magnesian-siderophyllite, whereas the ones from the Cu-Mo systems classify as ferroan-phlogopite and those from Sn-W-Mo systems classify as lithian-siderophyllite according to the classification scheme of the International Mineralogical Association (IMA) (Rieder et al. 1998). The classification of Nachit et al. (2005) was used to identify the source of the analysed grains and the data indicated a magmatic origin for most of the spots with TiO₂ ranging from 2.69 to 4.97 wt.%. However, data from the magmatic biotite of the Mount Pleasant granite plot in the secondary biotite domain due to its more evolved geochemical characteristics (i.e., the lower TiO₂ content of about 0.1 wt.%) (Fig. 1b).

4.2 Halogen chemistry of biotite

Biotite from barren intrusion contains much lower halogen elements. For instance, Lost Lake and Juniper Barren granodiorites contain less than 1.5 wt.% F, whereas mineralized intrusions have up to 5 wt.% F. In contrast, Cl content shows no systematic changes between biotites of barren and mineralized intrusions. In general, Cl values are much lower than F and vary from 0.001 to 0.4 wt.%. This is mainly due to the Mg–Cl avoidance introduced by Munoz (1984). The biotite from Sn-W systems is distinct from the other groups by its low IV(F) (0 to 0.3) and consequently low IV(F/Cl) (2.78 to 3.2). Biotite from Cu-Mo systems and barren intrusions have a higher IV(F) value of 1.79 to 2.23 and IV(F/Cl) of 3.50 to 6.59 due to their lower F content.

On the IV(F/Cl) versus IV(F) diagram, biotite from Mount Pleasant, one of the most mineralized intrusion in New Brunswick, shows the highest F enrichment (almost zero IV(F)). Biotite from the North Pole and Mount Douglas plot within the Sn-W-Be deposits, while McKenzie Gulch, Blue Mountain, and Nicolas Deny plot within porphyry copper field. On the other hand, biotite from barren intrusions displays a wide range of IV(F/Cl) varying from 3 to 5.5 and plot outside of all the mineralization types outlined in the diagram (Fig. 1c).

4.3 Halogen fugacity of associated fluids

The halogen fugacity of the associated magma or fluids can be calculated using the halogen content of biotite (Munoz 1984, 1992; van Middelaar and Keith 1990; Yang and Lentz 2005; Ayati et al. 2008; Boomeri et al. 2009, 2010). The log(HF/HCl) ratio increase gradually from barren to Cu-Mo and reaches to its highest value of 0.95-1.46 and consequently lower log(H₂O/HF) (2.58-3.92) in Sn-W-Mo systems. Moreover, the analysed biotites do not form a linear trend on both logs (XCl/XOH) vs. XMg and log (XF/XOH) vs. XFe plots, which may indicate possible continuous equilibration of these grains with fluids over a range of fluid composition and/or temperatures. This is typical for magmatic fluids during cooling of granitic plutons, displayed by an increase in /HF/HCl ratios of magmatic fluids with differentiation (Yang and Lentz 2005; Zhang et al. 2016).

4.4 Trace element composition

Biotites from mineralized and barren intrusions show distinctive trace element characteristics. K/Rb ratio decreases gradually from core to rim in almost all the analysed samples (i.e., Rb increase from core to the rim) indicating fractional mineralization in their parent magma. Furthermore, biotite from the Sn-W-Mo systems has the highest values of Li (0.1 to 1.1 wt.%), Mn (5100 ppm), W (1 to 60 ppm), and Rb (800-9000 ppm). Biotite from Cu-Mo
systems shows the highest Cu value of 50 to 100 ppm among the studied grains with all the other analysed elements having the value in between barren and Sn-W systems. Lastly, biotite from the barren intrusions have much higher V (300-400 ppm) and Cr (50-100 ppm) values. All the other analysed trace elements, including Sn, Mo, Sb, Co, Ni, Sr, Cs, and Br are slightly higher in biotite from mineralized intrusions. Based on these result, a new classification diagram was introduced using Li, V, and Na content of biotite as a discriminant between barren, Cu-Mo, and Sn-W-Mo systems (Fig. 1d).

![Figure 1](image.png)

**Figure 1.** Chemical compositional diagrams of biotite from the Acadian-related granites of New Brunswick. a TiO₂*10-Fe+MnO-Mgo classification of Nachit et al. (2005). b MgO-FeO-Al₂O₃ classification of Abdel-Rahman (1994). c Intercept value IV(F/Cl) plots against IV(F). d proposed ternary diagram of Na-Li-V.

## 5 Conclusions

Results of this study clearly show differences in geochemical characteristics of biotites from barren and mineralized felsic intrusions in Acadian-related felsic intrusions of New Brunswick. Biotites from barren intrusions classify as magnesian-siderophyllite and have higher Mn, Ti, and lower halogen content. These biotites also have much higher V and Cr values, whereas biotites from Cu-Mo and Sn-W-Mo systems classify as ferroan-phlogopite and lithian-siderophyllite, respectively. Biotite from the Sn-W systems contains lower Ti and much higher halogen content. These grains show highest values for Li, Mn, and Rb. Biotite from Cu-Mo systems has trace element values between barren and Sn-W-Mo mineralized intrusions.

Results of this study clearly show that biotite geochemical characteristics reflect its parent magma and can be used as a reliable method to distinguish barren and mineralized granitic intrusions. We introduce new ternary diagrams using Li-V-Na to differentiate barren, Cu-Mo mineralized, and Sn-W-Mo mineralized felsic intrusions.

## Acknowledgements

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Identification of hydrothermal alteration related to mineralisation using epidote mineral chemistry

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Abstract. The sorosilicate mineral epidote is a commonly occurring and easily recognisable mineral found within the alteration halo surrounding mineralised hydrothermal deposits that are hosted in volcano-sedimentary and igneous terranes. Epidote is also a product of greenschist and amphibolite facies regional metamorphism. As a result, in ancient arc-volcanic terranes it can be unclear whether epidote encountered during regional exploration has formed via metamorphic or magmatic-hydrothermal processes. In this study, we compare mineral chemical analyses of epidote from regional metamorphic terranes with epidote sampled from the hydrothermal alteration halos surrounding porphyry and skarn mineralisation in the Baguio district, Philippines. The results are subsequently used to test the ‘fertility’ of epidote-bearing samples collected from the Aconcagua river valley of central Chile. It was determined that there are measurable differences in trace and rare earth element chemistry that can be used to effectively discriminate between epidote formed from regional metamorphism and hydrothermal alteration related to mineralisation. The ability to geochemically distinguish between these two styles of epidote has substantial implications for mineral exploration in regionally metamorphosed terranes, as well as for situations where porphyry-style mineralisation is not exposed at surface.

1 Introduction

The detection of hypogene geochemical dispersion halos surrounding mineralisation in volcanic belts has previously relied on whole rock geochemical or assay sampling, and geophysical techniques. Recent advances in laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) have led to the recognition that these geochemical dispersion halos can be detected up to several kilometres beyond the limits of conventional rock-chip sampling techniques (Cooke et al. 2014; Wilkinson et al. 2015).

In this paper, we present mineral chemistry results from epidote sampled from greenschist to amphibolite facies metamorphic terranes in northern Australia. These results are compared with epidote sampled from the hypogene geochemical dispersion halos surrounding porphyry Cu-Au deposits and skarn prospects in the Baguio district, Philippines (Cooke et al. 2014). We then use a suite of altered samples from central Chile (Fig. 1) to show that subtle geochemical variations of trace and rare earth elements in epidote can be used to discriminate between epidote formed from metamorphic and magmatic-hydrothermal processes. In addition, epidote trace element chemistry may provide information on the fertility of mineralised systems, helping explorers to focus on prospective areas for exploration within mineralised districts.

2 Results

Analysis of epidote grains was completed on samples collected from two Paleoproterozoic regional metamorphic terranes (Harts Range and Georgetown Inlier, Australia) and outcrops of Miocene volcanic and intrusive rocks from the Rio Aconcagua valley, central Chile (Fig. 1). The methodology used for the LA-ICP-MS
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microanalysis of epidote follows the process outlined in Cooke et al. (2014). A summary of the results obtained from this study are provided in Table 1.

2.1 Epidote chemistry – metamorphic terranes

A total of 75 valid epidote analyses from samples from regional metamorphic terranes were used for this study, including 46 analyses from eight samples from amphibolite facies-altered rocks of the Harts Range, Northern Territory, Australia, and 29 analyses from seven samples from greenschist facies-altered rocks of the Georgetown Inlier, Queensland, Australia (Wade et al. 2008; Baker et al. 2010).

Major element concentrations in metamorphic epidote are within typical ranges, including for Ca (15.8 – 16.8 wt %; avg. 16.6 wt %), Al (11.9 – 14.9 wt %; avg. 13.1 wt %) and Fe (5.2 – 12.0 wt %; avg. 9.3 wt %). Concentrations of typical pathfinder and ore elements such as As, Sb and Cu are very low (<10 ppm) compared to epidote formed proximal to porphyry-style mineralisation (Fig. 2; cf. Cooke et al., 2014). In many analyses the concentrations of these trace elements fall below detection limits. Concentrations of Sn (>10 ppm), Yb (>75 ppm) and Y (>250 ppm) were found to be higher on average than for propylitic epidote (Table 1).

Table 1. Summary of epidote mineral chemistry data.

<table>
<thead>
<tr>
<th>Regional metamorphic terranes</th>
<th>Rio Aconcagua valley</th>
<th>Baguio district*</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of analyses</td>
<td>75</td>
<td>99</td>
</tr>
<tr>
<td>Ca (wt %)</td>
<td>15.8-16.8</td>
<td>15.5-17.0</td>
</tr>
<tr>
<td>Al (wt %)</td>
<td>11.9-14.9</td>
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</tr>
<tr>
<td>Fe (wt %)</td>
<td>5.18-12.0</td>
<td>6.83-13.7</td>
</tr>
<tr>
<td>As (ppm)</td>
<td>BDL-13.8</td>
<td>3.33-230.4</td>
</tr>
<tr>
<td>Au (ppm)</td>
<td>BDL-0.020</td>
<td>BDL-0.077</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>BDL-56.4</td>
<td>BDL-71.9</td>
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<tr>
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<td>Mn (ppm)</td>
<td>521-4,253</td>
<td>642-11,494</td>
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<td>Mo (ppm)</td>
<td>BDL-0.394</td>
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<td>Pb (ppm)</td>
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</tr>
<tr>
<td>Sb (ppm)</td>
<td>BDL-8.92</td>
<td>0.349-36.2</td>
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<tr>
<td>Sn (ppm)</td>
<td>0.270-161.8</td>
<td>0.122-50.4</td>
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<td>Y (ppm)</td>
<td>0.050-2,096.7</td>
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<tr>
<td>Zn (ppm)</td>
<td>1.37-15.2</td>
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<tr>
<td>Zr (ppm)</td>
<td>1.72-732.8</td>
<td>0.275-358.9</td>
</tr>
</tbody>
</table>

* Data from Cooke et al. (2014)

2.2 Epidote chemistry – central Chile

A total of 99 valid epidote analyses were collected from nine samples from the Rio Aconcagua valley of central Chile (Fig. 1; Piquer et al. 2017). As with epidote analyses from the metamorphic terranes, the epidote analyses from the Rio Aconcagua valley have major element concentrations that are within typical ranges for epidote (Table 1). Collectively, the average trace and rare earth element concentrations in epidote for the central Chile samples are higher than in metamorphic epidote (Table 1). In particular, central Chile epidote is high in Cu, Zn, Pb, As, La and Ce relative to metamorphic epidote. Pb concentrations are particularly anomalous, and may be a regional feature.

Figure 2. Plot of As versus Sb concentrations in epidote. Red symbols: Baguio district data (Cooke et al. 2014); blue symbols: Harts Range and Georgetown Inlier (metamorphic epidote); black symbols: Rio Aconcagua valley epidote, central Chile. Rio Aconcagua valley symbols denote respective locations shown in Figure 1.

3 Discussion

Epidote analyses from both the metamorphic terranes of central Australia and volcanic rocks of central Chile are compared to epidote analyses from the Baguio district, Philippines, collected by Cooke et al. (2014). The Baguio district contains several porphyry, epithermal and skarn deposits that have formed in the last 3 million years. For the study of Cooke et al. (2014), epidote from the hydrothermal alteration halos surrounding the Black Mountain and Nugget Hill porphyry Cu-Au deposits, the Thanksgiving skarn, and the Mexico porphyry-skarn prospect was analysed.

A graphical comparison of epidote analyses from each district is shown in figures 2 and 3. In these diagrams, there is a clear separation in trace element concentrations between epidote formed in regional metamorphic environments (blue symbols) relative to epidote formed in the alteration halos surrounding the Philippine porphyry Cu-Au and skarn deposits (red symbols). Regional metamorphic epidote generally contains low concentrations of the key pathfinder metals (Cooke et al. 2014), and this is illustrated in the diagrams by the trend towards low As-Sb concentrations, and high Sr/As (Fig. 2 and 3).
The central Chile epidote analyses are sub-divided based on their location in figure 1. Analyses of epidote from samples of Abanico Formation volcanic rocks adjacent to the late Miocene-aged Rio Colorado granodiorite (9.71 ± 0.23 Ma; Piquer et al. 2017) have trace element concentrations most similar to metamorphic epidote (Fig. 2), suggesting that they may have formed as a contact aureole around the intrusion. Conversely, samples from the central part of the Rio Aconcagua valley, shown as square symbols in figures 1, 2 and 3, have higher trace element concentrations that are analogous to porphyry-related epidote. These samples are proximal to small, structurally-controlled NE-trending Cu-veins, collectively known as the Mina Julia vein system. The third group of samples, from the NE corner of the district (Fig. 1), consist of strongly epidote-altered rocks of the Abanico Formation near Portillo. There is no known mineralisation associated with these samples, and based on their epidote trace element concentrations (Fig. 2 and 3), they are most likely related to contact aureole metamorphism surrounding an intrusion not exposed at surface.

4 Conclusions

Our results show that regional metamorphic epidote has pathfinder element concentrations that are chemically distinct from epidote associated with magmatic-hydrothermal alteration. Specifically, concentrations of pathfinder and ore elements such as As, Sb and Cu are very low (<10 ppm) compared to epidote formed proximal to porphyry-style mineralisation. In some cases the concentrations of these trace elements in regional metamorphic epidote fall below current microanalytical detection limits. Concentrations of Sn (>10 ppm), Yb (>75 ppm) and Y (>250 ppm) were also found to be much higher on average in metamorphic epidote than for propylitic epidote. The ability to geochemically distinguish between these two styles of epidote formation has substantial implications for porphyry-style and related magmatic-hydrothermal mineral exploration in regionally metamorphosed terranes. This may be especially useful where porphyry and epithermal mineralisation is not exposed at surface, but their associated hydrothermal geochemical dispersion halos can be sampled.

Acknowledgements

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Paleodepth indicators for targeting and vectoring of epithermal Au-Ag deposits: examples from the Hauraki Goldfield, New Zealand

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Abstract. Paleodepths of epithermal Au-Ag mineralisation have been estimated for Miocene-Pliocene, low sulphidation Au-Ag deposits in the Hauraki Goldfield, New Zealand. The estimates were made using various features including: paleosurface indicators (e.g. sinters), depth estimates from fluid inclusion homogenisation temperature measurements, hydrothermal alteration mineralogy, ore mineralogy, and vein textures. Paleodepth estimates to the base of the ore zone range from 200 m to 950 m. Fluid inclusion studies suggest that electrum in economic concentrations are in a temperature window of 260 to 180°C. This means that for dilute, gas-poor fluids that follow the boiling point for depth curve, Au deposition is limited to a vertical extent of about 400 m, with its upper boundary at about 100 m below the paleo-water table. We have catalogued, and mapped various paleosurface and paleodepth indicators, in order to define regional variations in erosion levels, and predict areas most likely to preserve the optimum depth window for Au. Regional stream sediment geochemical data have been used to broadly define erosion levels in terms of anomalous Zn, Pb and Cu representing a deep base metal sulphide zone.

1 Introduction

The Hauraki Goldfield in the Coromandel Volcanic Zone covers an area about 120 km long by 40 km wide (Fig. 1). The goldfield contains about 50 known low sulphidation epithermal Au-Ag deposits with a recorded production of more than 11 Moz of Au and 50 Moz of Ag from 1862 to the present (Christie et al. 2007). Following cessation of the early period of mining in 1952, the Martha underground mine at Waihi reopened in 1988 as an open pit mine. Golden Cross, adjacent to the historic underground mine of the same name, was mined by open pit and underground methods from 1991 until closure in 1997. New discoveries of the Moonlight (1997), Favona (2000) and Trio (2003) veins in Waihi were mined by underground methods, and mining in Waihi is currently focussed on the Correnso (discovered in 2009), Daybreak and Empire veins. Exploration is continuing on several other deposits in Waihi and elsewhere in the goldfield.

The Au-Ag mineralisation was deposited in hydrothermal systems associated with volcanism during the Miocene and Pliocene (Brathwaite et al. 1989; Mauk et al. 2011). Mineralised quartz veins are hosted in andesitic, dacitic, rhyolitic and Jurassic greywacke basement rocks, but most Au-Ag has been produced from quartz veins in andesite and dacite.

This paper describes estimation of paleodepths of some of the deposits from various paleosurface (e.g. sinters, hydrothermal breccias, silica blankets) and paleodepth (e.g. fluid inclusions, hydrothermal alteration and vein minerals) indicators in order to assist exploration vectoring and targeting in the goldfield.

2 Paleosurface and paleodepth indicators

2.1 Sinters and hydrothermal eruption breccias

Sinters and hydrothermal eruption breccias are the main indicators of paleosurface (Brathwaite and Christie 2000; Sillitoe 2015). Sinters occur at Black Jack (Kuaotunu), Kohuamuri, Broken Hills, Ohui, Onemana, Ascot (Mackaytown near Karangahake) and Favona (Fig. 1; Hamilton et al. 2017). Several occurrences of silicified volcanoclastic sediments at Cooks Beach, Tairua, Kauaeranga valley, Neavesville (Pakirarahi), St Hippo (Golden Cross), Waiharekeke, Te Ramarama, and Gladstone Hill, Winner Hill and Monument in Waihi have been suggested as sinters (Schofield 1967; Skinner 1975; Williams 1974). These silicified zones resemble the “silica blankets” that occur above the water table level in active geothermal systems, and whilst not sinters, they are indicators of proximity to the paleosurface.

Silicified hydrothermal breccias have been identified at Onemana (Robson and Stevens 1991) and in the Waihi area at Monument (Skinner 1975), Favona and Gladstone Hill (Torckler et al. 2006), and appear to be backfilling hydrothermal eruption vents rather than being surface deposits.

Silicified hydrothermal breccias at Kapowai (Williams 1974), Broken Hills (Moore 1979) and Neavesville (Barker et al. 2006) occur in pipe structures, but are of uncertain depth, although they probably formed in the near surface environment. The association of the Neavesville breccias...
with tuffs and lacustrine sediments indicates that they were diatreme breccias (Torckler 1997; Barker et al. 2006).

2.2 Fluid inclusions

Brathwaite and Christie (2000) and Christie et al. (2007) listed estimates of the depth of formation below the water table of many of the Au-Ag deposits based on fluid inclusion evidence. Under hydrostatic conditions that prevail in fracture systems open to the ground surface, as in epithermal/geothermal systems, boiling in an up-flowing hydrothermal fluid is controlled by the boiling point for depth (BPD) curve. Using the BDP curve, fluid inclusion homogenisation temperatures ($T_h$), particularly where there is evidence of boiling conditions from co-existing vapour-and liquid-rich inclusions, are used to determine the hydrostatic pressure and hence the depth below the surface. Brathwaite and Christie (2000) and Christie et al. (2007) used these data, along with information on the depths of former mining, to estimate the vertical extents of Au ore deposition for the deposits, e.g. Kapanga 140 m, Tokatea 330 m, Success 80 m, Hauraki 120 m, Kuautunu 155 m, Monowai 300 m, Sylvia 135 m, Thames 150 m, Broken Hills 170 m, Ohui <50 m, Onemana >150 m, Neavesville 150 m, Mararoto 100 m, Golden Cross 190 m, Komata 200 m, Jubilee 185 m, Owharoa 100 m, Karangahake 700 m, Waihi 575 m, Tui 260 m, and Waiorongomai 80 m.

2.3 Hydrothermal alteration

Some hydrothermal minerals are indicators of the temperature range and fluid conditions in geothermal systems. Specific mineral assemblages are diagnostic of distinct fluid types that, when integrated with other data, provide broad indicators of depth levels, boiling and mixing zones. For example, at shallow depths and on the margins of geothermal systems, alteration by steam-heated waters produces an argillic interlayered illite-smectite-calcite-kalinite assemblage (e.g. Simmons and Browne 2000). Smectite typically dominates at <150°C and illite dominates at >220°C, with interlayered illite-smectite occurring between 150°C and 220°C, although Tillick et al. (2001) noted that permeability, rock type and water/rock ratios may also influence the distribution of these clay minerals. Adularia (c. 180-320°C), epidote (c. 240-300°C) and the zeolites such as laumontite (c. 120-220°C) and wairakite (c. 220-310°C) also give an indication of temperatures (Browne 1978; Reyes 1990).

2.4 Mineralisation type and textures

Ore minerals and associated geochemistry may be indicative of specific paleodepth. For example, mineralisation rich in chalcopyrite, sphalerite, and galena is indicative of a relatively deep level in epithermal systems (Christie 1982). These base metal sulphides occur in deposits of the Thames-Waiomu area, the deep levels of the Karangahake and Waihi deposits, and the deposits of Tui and Waiorongomai. Also, porphyry style mineralisation at Miners Head, Pariitou, Waiomu and Ohio Creek is indicative of formation at deep levels (c. 1 km at Ohio Creek, Brathwaite et al. 2001). Uplift coupled with erosion was required to expose this style of mineralisation at the current surface.

At the other end of the spectrum, deposits with cinnabar and, to a lesser extent stibnite, are indicative of formation in a shallow environment. Cinnabar deposits occur in the Kaeuranga valley and Mackaytown (Ascot). However, cinnabar is found at depth in the late stages of vein formation in some deposits at Thames and at Tui and likewise stibnite at depth at Te Ahumata and some Thames deposits (Christie 1982). Thus, use of cinnabar and stibnite as a depth indicator needs to be evaluated in conjunction with other geological depth indicators.

Vein and mineral textures may also broadly provide information on paleodepth. Although usually equivocal, to the experienced eye, textures such as the type of banding in quartz veins (e.g. colloform/crustiform at intermediate levels and coarse comb quartz at deeper levels), and the crystalline form of vein minerals (e.g. chalcedonic, finely crystalline and coarsely crystalline quartz representing increasing depth) may provide information on the depth of mineral deposition (cf. Dong et al. 1995).
2.5 Regional stream sediment geochemistry

The differences in vein mineral abundances described above are reflected in the regional exploration stream sediment geochemistry data. Regional patterns in the concentrations of Zn, Pb and Cu in stream sediment geochemical surveys broadly distinguish areas with deeper levels of erosion exposing the chalcopyrite-sphalerite-galena style of mineralisation.

3 Gold deposition window

An assessment of the fluid inclusion $T_h$ data for the Hauraki Goldfield deposits suggests that deposition of electrum in economic concentrations appears to be confined to a temperature window of 260° to 180°C, similar to that determined for some other epithermal Au-Ag deposits (e.g. Hishikari - Izawa et al. 1990; Osilo - Simeone and Simmons 1999) and active geothermal fields (e.g. Rotokawa - Seward 1991; Ohaaki - Simmons and Browne 2000). On a BPD curve for hydrostatic pressures in low-salinity, low-gas systems, Au deposition is therefore generally limited to a vertical depth zone of about 400 m, with its upper boundary at about 100 m below the ground surface. The lower limit may be extended deeper (c. 300 m at Karangahake and c. 200 m at Waihi) by sector collapse, uplift, erosion or fluid mixing (Brathwaite and Faure 2002; Simmons 2002), causing telescoping of the mineralisation.

4 Prospectivity

Individual paleodepth features for the Au-Ag deposits, regional patterns of stream sediment Zn, Pb and Cu geochemical anomalies, and stratigraphic relationships enable delineation of areas of the Hauraki Goldfield where the optimum window for Au deposition has been substantially eroded or deeply buried (Fig. 2). In general, the western deposits have much deeper depths of erosion than the eastern deposits. Six areas of deep erosion are identified and characterised by one or more of: 1) porphyry copper deposits, 2) base metal sulphide bearing veins, and 3) anomalous Cu, Pb and Zn values in stream sediments. These are northern Great Barrier Island, Paritu, Tokatea-Tararu, Maratoto, Waitekauri, and Tui-Waiorongomai (Figs 1 and 2). We consider that these areas have poor potential for an epithermal Au-Ag deposit of large vertical extent, although this does not totally preclude them from being economically significant, since large amounts of bonanza grade Au were extracted at both Thames and Coromandel over narrow vertical intervals.

In contrast, areas with sinters and shallow sinter-like features provide potential for hosting deposits with a large depth extent. These include: Ohui, Onemana, Broken Hills, Neavesville, Waiharakeke, Waihi, Monument, and Karangahake.

Areas with substantial caldera fill (Fig. 1; Skinner 1993, 1995; Malengre et al. 2000; Smith et al. 2006) imply that any potential deposits hosted in the underlying andesite will be buried very deeply (c. 1-2 km) beneath rhyolitic cover rocks, and are therefore less prospective. The calderas do however offer potential on their margins, in terms of providing a potential deposit-hosting structural environment buried at shallower levels.

5 Conclusions

The majority of Au-Ag deposits in the Hauraki Goldfield have limited depth extents (<200 m) of economic grade...
mineralisation, although Martha and Karangahake are notable exceptions with depth extents of 575 m and 700 m respectively. The limited depth extents of economic ore, fluid inclusion data, and modelling of Au deposition in geothermal systems suggest that deposition of electrum in economic concentrations is confined to a vertical depth zone of about 400 m, with its upper boundary at about 100 m below the paleo-water table. However, the lower limit can extend up to 300 m deeper by sector collapse, uplift, erosion or fluid mixing.

The paleosurface and paleodepth indicators enable reconstruction of the geographic distribution of the optimum depth window for Au deposition for some areas. This enables definition of several areas where the Au window has largely been eroded, and other areas where the Au window for andesite-hosted veins is deeply buried (Figs 1 and 2). This significantly reduces the prospective area for this target type, helping to focus the exploration effort.

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Airborne hyperspectral surveying as a tool for mineral exploration at high latitudes: a pilot study over porphyry Cu deposits, eastern Alaska Range, Alaska

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Abstract. The U.S. Geological Survey collected airborne imaging spectrometer data over unmined porphyry Cu deposits in the eastern Alaska Range using the HyMap²™ sensor in 2014. The objective was to test whether this technology could aid regional mineral exploration efforts in rugged remote parts of the State. Maps of the distributions of predominant minerals, made by matching reflectance signatures in HyMap²™ data to reference spectra in the shortwave infrared region, do not uniquely discriminate individual rock units but do identify hydrothermal alteration associated with porphyry deposits and prospects hosted mostly within the Nabesna pluton. In the footprints of porphyry Cu deposits at Orange Hill and Bond Creek, unique spectral signatures are related to variations in chlorite and muscovite abundance and their chemical composition. This is best revealed by variations in 2.2 µm Al-OH absorption feature positions in pixels spectrally dominated by muscovite. Electron microprobe analyses confirm that these longer wavelength 2.2 µm absorption features are the result of chemical differences in micas spatially associated with the porphyry deposits. The same chlorite classifications and absorption feature positions also delineate new mineral occurrences. Our study suggests that airborne imaging spectroscopy has application for regional mineral exploration in mountainous terrain in Alaska.

1 Introduction

Alaska is a region with high potential for world-class mineral resources, but geologic mapping and exploration are hampered by Alaska’s immense size, remoteness, and rugged terrain. Airborne imaging spectroscopy (often referred to as hyperspectral remote sensing) can rapidly provide information on rock and alteration mineral compositions over broad areas that can help guide mineral exploration. However, the technology has historically not been used in Alaska because of low sun angle, unpredictable weather, and abundant vegetation. The U.S. Geological Survey (USGS) completed an airborne survey using the HyMap²™ sensor (Cocks et al. 1998) flown over a portion of the eastern Alaska Range (Fig. 1) to test whether, despite these factors, shortwave infrared spectroscopy would identify unmined porphyry Cu deposits and occurrences (including Orange Hill and Bond Creek). The airborne data were calibrated using targeted ground-based field spectra and combined with historic and new geochemical and mineralogical data to improve and validate results.

2 Geologic background

The study area lies near the leading edge of the Wrangellia terrane, which was accreted to the North American margin in the Jurassic to Cretaceous (Plafker and Berg 1994). Mid-Cretaceous plutons, including the Nabesna pluton intruded the Wrangellia terrane volcanic rocks and landward flysch basins (Richter 1973). A number of porphyry Cu deposits formed during this magmatic event; the largest of these in the current study area are Orange Hill and Bond Creek (Fig. 1). The Orange Hill deposit is partially exposed on the eastern edge of the Nabesna Glacier valley in intermediate igneous rocks of the Nabesna pluton. The Bond Creek deposit is well exposed between the west and middle forks of Bond Creek.

Figure 1. Location map (inset) and geologic map showing the distribution of porphyry prospects. Modified from Richter (1973). Grey zone is highly altered rock at Bond Creek.
prospects, including the Copper King skarn are localized in the southwestern portion of the pluton margin. Widely distributed small Cu and Au occurrences are reported in the Wrangellia terrane rocks (not shown).

3 Methods

3.1 Spectral analyses

In July 2014, approximately 2,000 line kilometers were collected using the HyMap2™ sensor over several areas including the focus area of this paper. The imaging spectrometer measured reflected sunlight in 126 narrow channels spanning the 0.4 to 2.5 micron (µm) wavelength region of the electromagnetic spectrum. The nominal pixel size was ~6 meters. Additional ground calibration and field spectral measurements were taken using an Analytical Spectral Devices (ASD) FieldSpec4™ spectrometer.

The HyMap2™ data were converted from radiance to reflectance using a multi-step calibration process (Kokaly et al. 2013). Reflectance images were processed using the Material Identification and Characterization Algorithm (MICA), a module of the USGS PRISM (Processing Routines in IDL for Spectroscopic Measurements) software (Kokaly 2011). The MICA analysis identifies the spectrally dominant mineral(s) in each pixel of imaging spectrometer data by comparing its reflectance spectrum to a reference spectral library of minerals, vegetation, water, and other materials. Since the spectral library contains multiple chlorite samples of different compositions, we were able to map qualitative differences in chlorite-dominated pixels across the study area. Shifts in the 2.2 µm Al-OH absorption feature (due to vibrational effects of the aluminium-oxygen-hydrogen bond) in pixels containing dominant muscovite signatures, related to chemical differences in micas (e.g., Duke 1994), were also mapped across the area.

Spectral analysis of hand specimens was completed using the Corescan Hyperspectral Core Imager Mark III™. These analyses identified spectral shifts in muscovite across specimens for follow-up microprobe analyses to confirm a relationship between spectral shifts and mineral chemistry. Corescan reflectance data were processed with MICA as above.

3.2 Geologic/geochemical investigations

Stream sediment, soil, and rock sampling was conducted to characterize the deposit geochemical signatures. Targeted sampling was also completed in areas away from known deposits in order to 1) establish background concentrations, and 2) test whether spectral anomalies similar to those in the known deposit areas reflect previously unrecognized porphyry Cu occurrences.

Electron microprobe analyses of muscovite/illite with different 2.2 µm absorption feature positions were completed on four thin sections to establish if there is a correlation between observed spectral shift and chemical signature.

4 Results

4.1 Spectral results

The spectrally predominant mineral(s) mapping at the regional scale indicates that the Nabesna pluton away from porphyry deposits is dominated by muscovite signatures, but that near the porphyry deposits shows much more complex mineralogy, with lesser muscovite and more chlorite, epidote, clay, and sulphate pixel classifications. Similar complexity (excluding sulphates) is observed in the Wrangellia terrane rocks, which display a patchwork of different predominant minerals. Comparison with regional mapping by Richter (1973) indicates that mineral predominance mapping alone does not distinguish specific geologic units.

Spectra from chlorite-dominated pixels demonstrated best spectral matches (based on the R² value from the linear regression of the spectral feature of the reference spectrum and the same wavelength region of the pixel spectrum) to one of three chloride-bearing reference standards. Two of these classifications are nearly ubiquitously mapped within the volcanic arc rocks of the Wrangellia terrane. The third is mapped almost exclusively in and around the porphyry cluster defined in figure 1. Notably, this class extends into the volcanic arc rocks where altered by the Bond Creek porphyry system and into two additional zones on the north side of the east fork of Bond Creek, just outside of the defined porphyry deposit/prospect cluster.

The 2.2 µm absorption feature position in muscovite/illite-bearing pixels ranges mostly from ~2.196 to ~2.209 µm (Fig. 2). The majority of the muscovite pixels in the region have relatively short (<2.203 µm) absorption positions. However, the rock exposures in and around the porphyry deposits (Orange Hill and Bond Creek) display mostly >2.204 µm wavelength absorption feature positions. Pixels displaying these longer absorption feature positions are spatially coincident with but more aerially extensive than the chlorite classifications.

Similar to that shown by the chloride mapping, additional areas north of the east fork of Bond Creek also contain pixels with long wavelength absorption features (areas 7 and 8; Fig 2). Only small scattered areas with abundant long wavelength signatures are observed in Wrangellia terrane rocks, with the most extensive located along the southern edge of the survey (loc. 11, Fig. 2). Similar ranges of absorption feature positions are observed in Corescan data of individual hand specimens.

4.2 Geochemical results

In the study area, sediments and soils with anomalous concentrations of Cu + Au and (or) Mo are mostly centered about the known porphyry deposits (Fig. 2). Samples in
the Wrangellia terrane typically contain only anomalous Cu and lack Mo and Au. Two areas identified by the chlorite and long 2.2 \( \mu \text{m} \) absorption feature positions that are outside of the known porphyry deposits are located along and at the headwaters of the east fork of Bond Creek (locs. 7 and 8; Fig. 2). Targeted sampling around the hyperspectral anomalies confirms that these rocks are also mineralized because rock, soil, and sediment samples in these areas contain anomalous Cu-Au and (or) Mo concentrations.

Electron microprobe analyses of micas characterized by shortward and longward wavelengths shift of the 2.2 \( \mu \text{m} \) absorption features based on Corescan data of hand specimens indicate that the absorption feature positions are a consequence of mineral chemistry (Fig. 3). Micas with longest wavelength position have higher Si and Mg, and lower Al (±Na) than shorter wavelength micas.

5 Discussion

The spectral mineral predominance mapping as a proxy for geology is only interpretable to the level of detail of the existing reconnaissance geologic mapping (Richter 1973). Complexity in the distributions of mineral classifications in the predominance mapping arises from several factors, such as lithologic variations (and structural complexity?) which are most prominent in the volcanic arc rocks of the Wrangellia terrane, unit mixing from mass wasting, and weathering and hydrothermal overprinting. The evidence for hydrothermal overprint, most strongly suggested by the abundance of chlorite, epidote, sulphates and clays in the Nabesna pluton porphyry cluster area is of particular interest to mineral explorationists.

Empirically, the distinct chlorite classification and observed longward 2.2 \( \mu \text{m} \) absorption feature position for muscovite-dominated pixels further record the hydrothermal activity. Associated fluids primarily altered parts of the Nabesna pluton but also adjacent Wrangellia terrane rocks at the Bond Creek deposit (Figs. 1, 2) and produced a chemically and spectrally distinct suite of minerals. The similar spectral signatures and follow-up geochemical sampling at locations 7 and 8 (Fig. 2) indicate that this hydrothermal activity and mineralization extended beyond the previously recognized porphyry cluster footprint.

Spectral feature wavelength shifts related to changes in mineral chemistry in hydrothermal mineral deposits have been recognized in a number of deposit types, including other porphyry Cu deposits (e.g., Halley et al. 2015; Harraden et al. 2013). The porphyry studies typically suggest that shorter wavelength positions associated with the mica chemistry are produced during main stage mineralization. However, porphyry systems are complex, and our longer wavelength signatures may result from mica formation during the waning stages of deposit formation. Regardless of the causes, the key observation is spectral contrast with surrounding rocks, particularly of supposed similar primary composition.

Although there have been spectral investigations of VMS systems in Canada (e.g., Laakso et al. 2014), to our knowledge there has been no concerted effort to apply
Airborne hyperspectral surveying as a tool in regional mineral exploration in Alaska, likely due in part to the assumed significant limitations of its application (requires clear weather, collection within short data acquisition window near solar noon, exposed bedrock with limited lichen cover). However, our study demonstrates that rapid acquisition and subsequent processing of data can be successful in distinguishing alteration mineralogy of both known and new mineral occurrences in a remote rugged area. Therefore, extensive underexplored mountainous regions remaining in Alaska are prime targets for this technology. With additional research efforts, it is plausible to further expand the applications of airborne imaging spectrometry in mineral exploration to even more challenging vegetated areas at northern latitudes.

6 Conclusions

Imaging spectroscopy provided important geologic information even though data were collected at high latitudes in rugged terrain.

1) Although not uniformly effective for mapping different geologic units, spectrally predominant mineral mapping identified areas of complex alteration mineralogy related to hydrothermal activity in the porphyry Cu deposit cluster area.

2) Chlorite-dominant pixels within the porphyry Cu deposit cluster are spectrally distinct and interpreted to reflect the porphyry alteration/mineralization processes.

3) Muscovite-dominated pixels in the porphyry Cu cluster are generally characterized by longward 2.2 µm wavelength positions because of different chemical compositions and genetic origins (i.e., formed during magmatic hydrothermal activity.)

4) Follow-up sampling around areas with chlorite and muscovite wavelength signatures similar to those displayed in regions with known deposits demonstrated additional previously unrecognized Cu-Au-Mo occurrences.

5) Airborne imaging spectrometry can be a useful guide in reconnaissance regional exploration in exposed mountainous regions of Alaska.

Acknowledgements

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Classifying propylitic alteration in complex porphyry systems; a case study of the Oyu Tolgoi Cu-Au porphyry deposits, Southern Mongolia

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Abstract. The trace element chemistry of epidote and chlorite in the propylitic halo of porphyry copper deposits has been shown to vary systematically with distance from the core of the system. These patterns provide a new tool in mineral exploration to help focus in on the most prospective areas within exploration licenses prior to costly drilling. However, in older, complex terranes such as the Central Asian Orogenic Belt, within which the Oyu Tolgoi porphyry deposits are situated, post-mineralisation arc accretion, magmatism and hydrothermal activity can lead to complex overprinting relationships which need to be resolved if a mineral chemistry vectoring approach is to be viable. At Oyu Tolgoi, Carboniferous plutonism has led to propylitisation of the post-mineralisation volcanic sequences and has also overprinted the Devonian porphyry-related alteration in the pre-mineralisation units. The two main generations of epidote alteration have been successfully fingerprinted by use of K-means cluster analysis using five key trace elements (U, As, Sb, Zr and La), so that the Devonian porphyry signature can be identified through the overprinting alteration. Furthermore, these two different generations have some distinct characteristics that can be observed in hand sample, which can inform sample selection for future ‘greenrock’ analysis in the region.

1 Introduction

The development of new exploration tools has been of great interest in recent years, driven by the fact that large deposits are likely to be located at greater depths and are therefore more difficult to explore for, often requiring costly, deep reconnaissance drilling. Geochemical vectoring using mineral chemistry is a method that is currently being investigated to help significantly narrow down exploration targets. Studies have shown that the propylitic alteration footprints that surround porphyry deposits can be fingerprinted by the trace element chemistry of propylitic epidote and chlorite; moreover, the concentrations of key elements vary systematically with distance from the system core (Wilkinson et al. 2015; Cooke et al. 2014). As the propylitic halo is the largest and most laterally extensive alteration zone, it is a useful guide to blind ore deposits where other evidence is lacking, so a better understanding of the propylitic zone is critical for this type of exploration. To date, little is known about how these trace element patterns are affected in situations where later metasomatic or metamorphic events have overprinted earlier propylitic assemblages. Understanding these effects is an important consideration in the application of these tools in older, geologically complex, porphyry belts, such as the Central Asian Orogenic Belt (Fig. 1). This highly prospective terrane contains several Palaeozoic porphyry deposits, including the world-class Oyu Tolgoi system of southern Mongolia.

2 Oyu Tolgoi geology

The Oyu Tolgoi porphyry district comprises eight, closely spaced deposits along 26 km of the NNE-oriented Oyu Tolgoi trend. The ore bodies are associated with Late Devonian (~372 Ma) porphyritic quartz monzodiorite (QMD) stocks and dykes, intruded into the Lower Devonian Oyu Tolgoi island-arc volcanic and volcanioclastic sequence (Fig. 2; Crane and Kavalieris 2012). Mineralisation occurs in a central stockwork of A-type quartz veins, and is predominantly hosted within the inferred causative intrusions themselves and the porphyritic augite basalt of the Oyu Tolgoi sequence into which they were emplaced (Crane and Kavalieris 2012). Hydrothermal alteration around the Oyu Tolgoi deposits is typical of porphyry systems, with early sodic-calcic and potassic alteration in the system core grading laterally outwards to propylitic alteration, which is overprinted proximally by widespread sericitic and advanced argillic alteration.
Propylitic alteration within the Oyu Tolgoi sequence is widespread, primarily within the augite basalt, and is locally very intense, characterised by the assemblage epidote-chlorite-albite-calcite-hematite-magnetite-pyrite. A proximal chlorite alteration zone is observed at Oyu Tolgoi associated with magnetite. Epidote appears beyond this zone, most commonly replacing plagioclase phenocrysts or in veins. It may also occur with chlorite replacing augite phenocrysts in the augite basalt, or in its groundmass with disseminated or clotty pyrite. There is also a fracture-controlled epidote alteration in which massive epidote floods outward from fractures into the surrounding rock. At the Hugo Dummet deposits in the north of the Oyu Tolgoi trend, the propylitic halo is truncated to the east and west by Carboniferous normal faults within the chlorite-magnetite-sericite zone, thus epidote is absent.

The post-mineralisation succession consists of the Heruga Sequence, a suite of interbedded volcanogenic and sedimentary rocks that have been thrust over the Oyu Tolgoi sequence from the east by the district scale Contact Thrust Fault (Fig. 2). Some basalt flows in the Heruga sequence are very similar to the porphyritic augite basalt of the Oyu Tolgoi sequence, suggesting that they may be locally derived. Carboniferous volcanogenic and sedimentary rocks of the Sainshandhudag Formation unconformably overlie the Devonian sequences (Fig. 2), and are separated by an erosional hiatus due to uplift in the Early Carboniferous. Mid-Carboniferous north- to northeast-trending normal faults, for example the major West Bat fault, truncate Devonian rocks to the west (Fig. 1), and are exploited by hornblende-biotite granodiorite plutons (Gd) (Crate and Kavalieris 2012). Other intrusive units include upward flaring, late- to post-mineralisation Devonian biotite granodiorite dykes, a series of Carboniferous hornblende-biotite andesite (HbBiAnd) dykes that intruded along the same axis as the Oyu Tolgoi trend, and the Permian Khanbogd granite, an alkaline, riebeckite-bearing batholith ~5 km east of the northernmost deposits with a reported 1 km-wide contact aureole. Younger epidote and chlorite alteration events are widespread in the Carboniferous and Heruga sequence rocks, as well as in the post-mineralisation intrusions.

### 3 Epidote classification

#### 3.1 Methodology

The trace element chemistry of epidote from 42 drill core and surface samples were analysed using LA-ICP-MS in the LODE Laboratory, Imaging and Analysis Centre, at the Natural History Museum, London. Textural information was collected and recorded for each sample using SEM backscattered electron imaging. The samples were selected to cover the propylitic halos of all known deposits and potential exploration targets within the district. Additionally, samples span the entire stratigraphic column including all major pre- to post-mineralisation units.

K-means cluster analysis was chosen to be the most suitable statistical method for this study because the main objective of such clustering algorithms is to statistically separate distinct natural groupings of multi-dimensional data. K-means is a suitable hard-partitioning algorithm to group the epidote data, as the number of clusters (K) is known, or decided, to be two, i.e. porphyry related and non-porphyry (post-mineralisation) epidote. Other supervised learning algorithms, such as random forest, require that the class of each data-point be pre-assigned for a training set of data, which is not possible here as the classification of epidote cannot confidently be determined prior to the statistical grouping due to the complex overprinting nature of the alteration. Two iterations of the cluster analysis were run in order to narrow down the selection of trace element inputs required to optimally separate the data. The initial trace element inputs were selected based on key magmatic-hydrothermal pathfinder elements identified in previous studies by Wilkinson et al. (2015) and Cooke et al. (2014). Once the preliminary groups were assigned by the initial iteration of the cluster analysis, discriminant projection analysis (DPA) was used to provide diagnostic output to determine which of the selected trace elements carried the most weight in discriminating between the two groups. Based on the DPA results, the final classification of porphyry versus non-
porphyry epidote required only five key trace elements (U, Sb, As, Zr and La) as the required inputs for the final cluster analysis and DPA.

3.2 Textural classification

Epidote at Oyu Tolgoi can be classified texturally into four major groups: vein epidote, vein halo epidote, epidote that has flooded the groundmass of volcanic rocks, and replacement epidote. Vein epidote is common throughout the stratigraphic sequence and can occur with pyrite in proximal mineralised samples, but more commonly occurs with quartz and calcite in all units. Titanite and andradite have also been observed to occur in epidote veins in the porphyritic augite basalt host rock. Epidote veins often have a reddened halo where pink albite has selectively replaced plagioclase. Epidote in halos around epidote-quartz veins has pervasively replaced the ground mass of the rock on a centimetre scale (Fig. 3a) and appears to have overprinted existing alteration. This flooding is fracture controlled and generally occurs on decimetre scales through the drill core. The intensity of the epidote overprint decreases away from the central fracture or vein.

Within the augite basalt, the phenocrysts of augite have often been replaced by chlorite-quartz-titanite so that they conspicuously stand out within the epidote-flooded groundmass (Fig. 3b). The vein halo epidote and the epidote flooding have a similar massive habit which could indicate that they are related. Where epidote has replaced specific minerals, most commonly plagioclase, it can be seen to have either selectively replaced the mineral phase whilst preserving the primary crystal form (Fig. 3c), or have replaced the mineral phase and bleb out over the edge of the crystal forming clots or patches, and destroying the primary texture locally (Fig. 3d).

3.3 Geostatistical classification

All epidote data were fed into the cluster analysis and were classified as either cluster 1 or 2, and projected into a simple 2D classification diagram through DPA (Figs. 4a-d). The full dataset could be described by two polygons, cluster 1 by polygon 1 (P1) and cluster two by polygon 2 (P2). Inspection of the data based on host rock unit shows clearly that epidote from the mineralising quartz monzodiorite (QMD) falls within P1, whereas epidote from the post-mineralisation intrusive units (HbBiAnd and Gd) sits within P2 (Fig. 4b). Epidote analysed from samples of the porphyritic augite basalt of the mineralised Oyu Tolgoi volcanic sequence that is intruded by both pre- and post-mineralisation units, is relatively evenly spread across both polygons (Fig. 4c). Conversely, epidote data from volcanic units that were either structurally emplaced (Da4a) or unconformably deposited post-mineralisation (CS3) fall predominantly within P2 (Fig. 4d).

When the epidote data are plotted in their assigned
textural groups on the epidote classification discriminant projection plot, there are some interesting results. Vein and replacement epidote are broadly spread across both polygons, though vein epidote tends to fall more within polygon 1. However, both vein halo epidote and epidote that has flooded the matrix have more of a tendency to fall within polygon 2.

![Figure 5. Textural groups of epidote data projected onto the epidote classification discriminant projection plot (as in Fig. 3), a with vein epidote, b epidote from vein halos, c epidote that has flooded the matrix, and d replacement epidote.](image)

4 Discussion

The chemical discrimination of the epidote data by cluster analysis has found two groups that appear to have some real differences when the samples are considered based on their host unit and by textural type. In the discriminant projection plot, the epidote from the mineralising intrusions and the post-mineralisation intrusions are clearly separated into the two polygons described by the two clusters, indicating that these could represent porphyry-related and non-porphyry epidote. This idea is further supported by the epidote data from the volcanic suites. The pre-mineralisation porphyritic augite basalt host rock contains epidote that fall evenly across both polygons. This would be expected as this unit has been intruded by the QMD, and by the Gd and HbBiAnd, so would likely contain epidote formed by both the pre- and post-mineralisation events. However, the volcanic units emplaced after the mineralising event contain only epidote that falls within polygon 2, the same polygon that hosts the post-mineralisation intrusive units. Thus, data that fall within polygon 2 should therefore be disregarded for use in geochemical vectoring and fertility studies of the Devonian ore system.

The epidote textural data indicate that the fracture-controlled alteration that has led to epidote vein halos and massive epidote flooding falls predominantly within polygon 2 and thus characterises the post-mineralisation epidote. By feeding this information back to the geologists in the field, rocks with this type of epidote alteration can be avoided when selecting samples for future geochemical vectoring exploration programmes in the region.

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References

Element migration processes in the near-surface environment and their consequences for exploration

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Abstract. Exploration for new ore deposits will require being able to see through overburden both physically and chemically. Surface media will be the vehicle for imaging these deposits geochemically, but the processes by which elements move in the near-surface environment are complex and poorly understood. Exactly what is required for effective exploration geochemical tools and what are the caveats are examined.

1 Introduction

A basic tenant in both environmental science and exploration geochemistry is that elevated concentrations of metals and compounds from ore deposits will disperse with time and be recorded as aberrations in normal background levels. Environmental and exploration geochemistry prove that this concept is valid because there are numerous cases where “leakage” of elements is evident (e.g. Cameron et al. 2005). The new challenges are understanding the rate by which concentrations in the environment change, what processes are involved, and identifying those particular elements or compounds that truly reflect dispersion from ore deposits several hundreds of meters below the surface. Given the paucity of recent discoveries of ore deposits at the surface, most new discoveries will be made at depth, and thus we must be able to “see” them from the surface with geochemistry (Cohen et al. 2010), and distinguish elements migrating from the deposits from those resulting from other sources.

Although elemental concentrations have been used in previous studies of element migration in the near-surface environment, only rarely have they been integrated with isotopic information to fingerprint specific sources of the elements. Isotopic compositions can be used to fingerprint an element or compound because most reservoirs in natural systems are isotopically distinct (Hoefs 1999). Elements that are known to have variations in their isotopic compositions because of separation of their isotopes due to mass differences include H, Li, B, C, N, O, Mg, S, Ca, Fe, Cu, Zn, Mo, Se, Nd, Ti and U (Johnson 2004) Isotopes produced by radioactive decay, thereby changing abundance with time, include Sr, Nd and Pb. These two factors make isotopes unrivalled indicators of a variety of processes, particularly those that involve material fluxes among the hydrosphere-geosphere-biosphere.

Because most ore deposits are reduced and therefore represent areas of high electron density, they are potential havens for microbial consortia. These microbes can mobilize elements from the deposits as aqueous or gaseous complexes in waste products or from the decay products of the microbes (Dittrich and Luttge 2008; Fredrickson and Balkwill 2006). Such complexes migrate to the surface, particularly along fractures and faults and become fixed on clay and Fe-Mn oxide surfaces, and make their way into the biosphere. These complexes will have specific element and isotopic signatures (Wasylenki et al. 2007) that reflect the deposit at depth. If these signatures are not altered during ascent or diluted with components at the surface, such as from anthropogenic activity, they should be recorded in media at the surface (Cameron et al. 2005).

The two main processes by which elements are dispersed in the near-surface environment include mechanical dispersion and chemical dispersion. The mechanisms involved in mechanical dispersion processes such as erosion or glacial effects are reasonably well understood, but those involving chemical dispersion processes are predominantly theoretical and based largely on interpretations of field data. In reality, the reasons for chemical dispersion anomalies are poorly understood. Furthermore, the influences of transported materials such as till or groundwaters on chemical dispersion of elements at the surface are unknown.

Figure 1. Processes involved in element dispersion as a result of primary (syn-mineralization) and secondary (post-mineralization) processes. After Cameron et al. (2004).
Understanding element mobility in the near-surface environment (Fig 1) requires determining (a) what elements and isotopes are most likely mobilized from natural ores, (b) what specific sites in the overburden and soils trap them (c) do microbes play a role in mobilizing elements from the deposits and in fixing them at the surface, and (d) under what circumstances do these mobile elements make their way through the geosphere and into the biosphere where we can use them to our advantage. Element concentrations at the surface are affected by migration from below through the overburden primarily along fractures, but also from above through deposition of elements from anthropogenic activities. Thus, exploration geochemistry must integrate environmental geochemistry processes, and visa versa.

2 Element migration processes and the possible complications

There have been several examples of anomalous element concentrations at the surface resulting from possible element migration from ore deposits at depth, although the exact processes involved in producing these anomalies in surface media remain contentious. Recent results initiated by Uravan Minerals over the Cigar Lake (Fig 2) and Centennial uranium deposits in the Athabasca Basin, Canada have identified specific element associations and isotopic compositions in a variety of medium that appear to originate from unconformity-related uranium deposits at depths of up to 900 m.

Figure 2. Spatial relationship of $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in clay minerals separated from the A2, B1 and C horizon soils from near the Cigar Lake uranium deposit in the Athabasca Basin, Canada. Pb from the deposit has ratios near 01 whereas background Pb has ratios near 08 Red hatched area near the center of each panel is the projection of the deposit to the surface (the deposit sits at a depth of 450 m) and the dashed lines are geophysical anomalies interpreted as faults (Kyser et al. 2016).

Among the most significant results from the research involving the Cigar Lake and Centennial deposits is the definition of specific uncertainties that must be addressed before new techniques and protocols can be applied to exploration with much greater certainty. The critical issues illustrated by these results, and many others in the literature, include: (1) what are the processes by which elements migrate to the surface and in what form do they migrate, (2) what is the best media for exploration of deep deposits and specifically for each deposit type, (3) where in various media do the mobile elements from a deposit reside so they can be identified with certainty, (4) what role do microbes play in mobilizing and fixing the elements at the surface and how do we identify their effects, (5) what role do geological structures play in producing anomalies and how can they be identified in the subsurface, and (6) whether coincident anomalies in various media such as soils, clays and vegetation are common. The studies initiated by Uravan Minerals illustrate that indeed there are geochemical anomalies in many media coincident over deep ore deposits, particularly along structures that transect the deposits at depth, but also that these anomalies are affected by components being deposited from above. Furthermore, these anomalies may originate from the till, thereby being false positive anomalies, but still have important implications for exploration.

References

Assessing the zircon compositional evolution from the Guichon Creek Batholith and Highland Valley Copper deposit, south-central B.C.

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Abstract. The Late Triassic Guichon Creek batholith formed over a period of four million years and hosts the deposits of the Highland Valley Copper porphyry Cu ± (Mo) district. The batholith consists of multiple granodiorite to quartz monzonite intrusions that have zircon as an accessory phase. Zircon compositions were investigated from fifteen samples from the edge to the centre of the batholith to evaluate their potential as an indicator of mineralizing processes. Europium and titanium concentrations were used to determine Eu/Eu* values and calculate temperatures of formation. Zircon from the early phases have Eu/Eu* values of 0.20-0.55 and calculated temperatures of 850°-750°C. Later phases that host mineralization generally have zircons with higher Eu/Eu* up to 0.75 and calculated temperatures down to 600°C. The increase in Eu/Eu* suggests increasing oxidation state in the magma towards conditions favourable for mineralization. Dikes from the porphyry copper deposits that are syn- to post-mineral have higher trace element content and trend from high Eu/Eu* values to lower, thus reflecting exsolution of fluids from the melt and subsequent ore deposition. Evaluating zircon compositions from evolving batholiths emphasizes a broad scale potential for exploration of porphyry deposits.

1 Introduction

The Guichon Creek Batholith (GCB) located in south-central British Columbia, is an elongate, concentrically zoned body that intrudes the sub-marine volcanic and sedimentary units of the Late Triassic Nicola Group. Several moderate to large tonnage porphyry copper deposits are hosted within the centre of the GCB and make up the Highland Valley Copper district (HVC) which is fully-owned and operated by Teck Resources Limited and makes up one of the largest copper resource in Canada (Byrne et al. 2013; Teck 2016). New U-Pb TIMS and Re-Os ages indicate that the GCB formed from up to three magmatic pulses that culminated in the formation of the economic ore deposits at HVC circa ~208.4 Ma (D’Angelo et al. 2017). Trace element composition of zircon from samples dated by D’Angelo et al. (2017) were analysed to characterize evolutionary changes in zircon chemistry from the early edge of the batholith to the syn- to post-mineral dikes at the HVC deposits. Zircon (Zr[Hf]SiO₄) incorporates multiple minor and trace elements into its structure, the concentrations of which can be used to determine the temperature and oxidation state of the parental melt. Recent studies in zircon compositions from intrusive rocks associated with economic porphyry copper deposits are characterized by decrease in SO₂, increased oxidation state and water-rich composition of these granites (Ballard et al. 2002; Dilles et al. 2015; Shen et al. 2015; Lee et al. 2017). Evaluating the zircon compositions from the GCB phases and dikes with precise age dates provides a means by which the usefulness of this method as an exploration and evaluation tool can be determined.

2 Geology of GCB and HVC deposits

The Late Triassic GCB is a compositionally zoned calc-alkaline body that hosts multiple porphyry Cu ± (Mo) deposits including the past producing Bethlehem and the currently mined Valley, Lornex, and Highmont deposits (Figure 1; McMillan 1985; Byrne et al. 2013). Fifteen samples of fresh to altered rocks from the various batholith phases were collected from the margin of the batholith to the core, including late dikes from within the Bethlehem, Valley and Highmont pits (Fig.1). All ages referenced are from D’Angelo et al. (2017) except the Gump Lake phase.

2.1 Pre-GCB Gump Lake phase

The Gump Lake phase is an elongate 3x10 km granodiorite to quartz monzonite located along the eastern edge of the GCB. Sampled for this study (KB132), the intrusive phase has previously been mapped as syn- to post-GCB (McMillan et al., 2009), however, new U-Pb TIMS dating puts the age of formation at 218.01 ± 0.18 Ma. The phase is geochemically different from the early marginal phases of the GCB and this, with the new age data, suggests that magmatic activity and batholith formation is older than had been previously recognised in the region.
Figure 1. Geologic map of the Guichon Creek batholith modified after ongoing CMIC-Footprint contributions and referenced within Byrne et al. (2017). Samples referenced in D’Angelo et al. (2017) except KB132 (Gump Lake phase) from this study. Main economic deposits include Valley, Lornex, Highmont, and Bethlehem (inset).

2.2 Early GCB phases

The margin of the GCB comprises an equigranular and mafic Border phase and a Highland Valley facies, which consists of the Guichon and Chataway sub-facies. Contacts between the Guichon and Chataway sub-facies are generally gradational from granodiorite to quartz monzodiorite; however, local sharp boundaries can occur (Byrne et al. 2013; D’Angelo et al. 2017). Samples of all three phases and the transitional zone of the Highland Valley phase were collected. U-Pb ages for these phases range from 211.0 to 210.4 Ma and are generally within error of each other (Fig. 1).

2.3 Middle GCB phases

The Bethlehem facies and associated porphyry dikes, stocks, and brecciated phases from the HVC Bethlehem pit are here defined as part of the middle GCB units. The Bethlehem facies is a weakly porphyritic granodiorite that occurs between the Highland Valley phase and later Skeena facies but is in contact with the Guichon phase in the Bethlehem deposit. Dikes sampled for this study from the Bethlehem deposit include the early feldspar and quartz porphyry Bethlehem porphyry, the equigranular to porphyritic Jersey stock, and the late-mineral feldspar and quartz-phryic porphyry dike (FQPC). The age of these units ranges from 208.5 to 209.8 Ma and they are associated with an earlier mineralization event at the Bethlehem deposit relative to the main mineralization at the Valley and Lornex deposits (Byrne et al. 2013).

2.4 Late GCB phases

The youngest phases (206.9 to 208.5 Ma) of the GCB are in the centre of the batholith and consist of felsic granodiorite to monzogranite (Skeena facies) and the weakly porphyritic granodiorite and monzogranite of the Bethsaida facies. These units host the main copper mineralization at the Valley, Lornex, and Highmont deposits. Two samples of Bethsaida facies were collected from outside of the main deposits and one of Skeena facies is from the Lornex pit. Two syn- to post-mineral dikes are from Valley drill core and the Highmont pit. The biotite-phryic porphyry ‘salt and pepper’ (S&P) Bethsaida dike from Valley was dated at 208.2 Ma and the quartz and feldspar phryic, quartz-rich porphyry dike (QFPQ) from Highmont was dated at 206.9 Ma bounding the minimum age of the GCB (D’Angelo et al. 2017).

3 Methods

Twenty to twenty-four zircon grains from each sample were analysed for trace element composition using laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) technique. Approximately twenty-five, 47 μm core to rim spots (Fig. 2) were conducted on each sample over a fifteen hour session yielding >375 analyses, not including standards. Isotopes measured include Ca\(^{48}\) to monitor for apatite inclusions and Ti\(^{49}\) to calculate temperatures after Watson et al. (2006). Additional elements measured included Y, Nb, Ta, REE, Hf, U, Th, and Pb.

Figure 2. Reflected light and cathodoluminescent images of zircon with spot locations for a Gump Lake phase, and b Bethsaida phase. Hafnium concentration, Eu/Eu* (Eu*) value, and calculated temperature given for each spot location. Grains from all samples varied in zoning characteristics but where able a core and rim spot analysis was taken for each zircon grain.
4 Discussion

Hafnium content in zircon can generally be used as a proxy for crystallization percent as concentration increases due to Hf incompatibility in the parent melt (Hanchar and Watson 2003; Dilles et al. 2015). In the GCB phases Hf concentration generally varies from less than 7000 to 14000 ppm, whereas the Gump Lake phase clusters around 9000 ppm (Fig. 2). Using Hf as a proxy for crystallization and comparing with Eu/Eu* values \( \frac{[Eu]_N}{([Sm]_N\times[Gd]_N)^{0.5}} \) where \([Eu]_N\), \([Sm]_N\), \([Gd]_N\) are chondrite-normalized, the general oxidation state can be determined as increased water content decreases plagioclase crystallization resulting in a lower europium anomaly in zircon (Dilles et al. 2015). The Gump Lake, Guichon, and Guichon-Chataway (Highland Valley transitional unit) phases have Eu/Eu* values ranging from 0.20 to 0.40, whereas the Border phase varies from 0.30 to 0.55 (Fig. 3A). The Chataway phase shows a distinct trend relative to the other early phases in that the Eu/Eu* values increase from 0.30 to 0.70 with increasing Hf concentration. The middle GCB Bethlehem phases and late GCB Skeena and Bethsaida phases have Eu/Eu* values ranging from 0.30 to 0.70, suggesting an increase in aqueous fluids in the melt and higher oxidizing conditions through time (Figs. 3B, 3C). The dikes associated with or post-mineralization from the Valley and Highmont pits (‘S&P’ Bethsaida; QFPQ) trend from higher Eu/Eu* values 0.70 to lower 0.20 with increasing Hf content (Fig. 3D). Although variation within individual samples is high the overall trend shows increasing Eu/Eu* values from the early phases to the Bethsaida facies followed by a sharp decrease with the ‘salt and pepper’ Bethsaida and QFPQ dikes (Fig. 4). There is a slight difference between the two Bethsaida samples with sample SB217 located southwest of the Valley pit (Fig. 1) having a lower variation than sample SB218 located to the east. This could be the result of heterogeneity in the Bethsaida facies but the overall Eu/Eu* values in the Bethsaida facies fall above 0.40. Decreasing Eu/Eu* values with increasing Hf content within individual samples have been observed in other porphyry copper deposits (Lee et al. 2017) and indicates either early fluid saturation and release in the parental melt or alternatively mixing between an upper oxidized melt with a reduced melt. The younger ‘salt and pepper’ Bethsaida and QFPQ dikes have higher concentrations of Y, Ta, Nb, and REE relative to the other samples suggesting they crystallized from a more enriched source. Calculated Ti4+ temperatures (calculation referenced in Watson et al. 2006) for the samples show a higher temperature range for the early GCB phases relative to the later phases (Fig. 5). Additionally the temperature range for the ‘salt and pepper’ Bethsaida dike shows a subtle increase with increasing Hf content suggesting probable mixing with a late higher temperature melt (Fig. 5D). Zircon composition from these dikes reflect the melt composition during the main mineralization event at HVC suggesting that the possible mixing event released the buildup of aqueous fluids in the GCB allowing for the extraction and deposition of the main ore deposits at HVC.
Figure 5. Calculated Ti\textsuperscript{4+} temperatures after Watson et al. (2006) corrected for TiO\textsubscript{2} activity of ≈ 0.7 after Ferry and Watson (2007) vs. Hf concentration in zircon samples from: a) early GCB phases; b) middle GCB Bethlehem phases and dikes; c) late GCB phases; and d) synto-post-mineral dikes from Valley and Highmont deposits. Early phases have higher calculated temperatures except for Gump Lake phase relative to the middle and late GCB phases which are at or near solidus temperatures. The late ‘salt and pepper’Bethsaida dike has a subtle increase in temperature with increasing Hf content suggesting possible mixing with a higher temperature melt. ppy = porphyry, S&P = salt and pepper.

4 Summary

Acquisition of zircon trace element concentration via LA ICP-MS allows for lower cost, rapid analysis of multiple data points that is still viable relative to other more precise techniques such as sensitive high resolution ion microprobe - reverse geometry (SHRIMP-RG). Data acquired from the GCB and associated HVC porphyry deposits indicate an increase in Eu/Eu* values with time to conditions where fluid content is high and potential for metal extraction from the melt is greater. The youngest sampled dikes have a trend of decreasing Eu/Eu* values with crystallization, suggesting potential mixing with an oxidized upper chamber and an enriched higher temperature melt. This is interpreted to have contributed to the formation of the large tonnage ore deposit at HVC due to fluid release and metal extraction from the lower source magma. Zircon composition when analysed over a large district has potential to determine ore fertility of large regional granite systems.

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The effect of titanite crystallisation on Eu and Ce anomalies in zircon and its implications for the assessment of porphyry Cu deposit fertility

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Abstract. The redox sensitivity of Ce and Eu anomalies in zircon has been well demonstrated by experimental studies and these parameters may represent important tools in the exploration of porphyry Cu systems which are thought to be derived from oxidised magmas. However, Ce and Eu anomalies in zircon are also affected by the co-crystallisation of REE-bearing phases such as titanite. Here, we report the trace element chemistry of zircons from titanite-bearing intrusions associated with mineralisation at the world class Oyu Tolgoi porphyry Cu-Au deposit (Mongolia). Based on these data, we suggest that neither Eu/Eu*, nor Ce4+/Ce3+ are robust proxies for melt redox conditions, because they are both too strongly dependent on melt REE concentrations, which are usually poorly constrained and controlled by the crystallisation of titanite and other REE-bearing phases. In spite of this, Eu/Eu* can broadly distinguish between fertile and barren systems, so may still be a useful indicator of porphyry magma fertility.

1 Introduction

Zircon (ZrSiO4) has proved to be one of the most useful minerals in the study of igneous and metamorphic petrogenesis because of its robustness as a geochronometer, the sensitivity of certain trace element substitutions to intensive parameters (e.g. temperature; Ferry and Watson 2007), and its resistance to high-temperature diffusive re-equilibration. One aspect of zircon chemistry which has received significant recent interest is the effect of magmatic redox conditions on the partitioning of the rare earth elements (REE) Ce and Eu. Uniquely among the REE, which are usually trivalent, Ce and Eu may also exist as Ce4+ and Eu2+. Ce4+ is more compatible in zircon than other REE3+ cations (including Ce3+) as it substitutes directly for Zr4+. For the same reasons, Eu3+ is more compatible in zircon than Eu2+. Because of this, and because typical arc melts contain Eu and Ce in both oxidation states, zircons commonly have positive Ce (Ce/Ce*>1) and negative Eu anomalies (Eu/Eu*<1). The Ce4+/Ce3+ ratio of zircon may be estimated using the method of Ballard et al. (2002).

Experimental studies have shown that the magnitude of Ce and Eu anomalies varies as a function of melt fO2 (Burnham and Berry 2012). This redox sensitivity is of particular relevance in the exploration for porphyry-type copper ore deposits, which are thought to be derived from oxidised arc magmas. Zircons from magmatic rocks closely associated with mineralisation have been shown to have high values of Ce/Ce*, Eu/Eu* (Fig. 1) and Ce4+/Ce3+ (Ballard et al. 2002).

However, Ce and Eu anomalies in zircon may also be
controlled by the prior or concurrent crystallisation of other REE-bearing phases, which may act to enrich or deplete the melt in Eu and Ce if these elements are more or less compatible than neighbouring REE. Ce anomalies are extremely rare in magmas, so very few phases preferentially partition Ce over La or Pr. As a result, Ce anomalies in zircon may be a more robust proxy for melt redox conditions. On the other hand, negative Eu anomalies in zircon may be a more robust proxy for melt preferentially partition Ce over La or Pr. As a result, Ce extremely rare in magmas, so very few phases less compatible than neighbouring REE. Ce anomalies are deplete the melt in Eu and Ce if these elements are more or less compatible.

Thus, the crystallisation of plagioclase prior to zircon saturation would deplete the melt in Eu, generating a negative Eu anomaly which would be inherited by zircons crystallising subsequently. Although plagioclase is the most commonly cited example, many other major and accessory mineral phases also have Eu anomalies. Titanite (CaTiSiO$_5$) strongly partitions REE ($K_{Ds}$ all >1; Colombini et al. 2011) and preferentially partitions Sm and Gd over Eu. This means that the crystallisation of titanite has the potential to impart a significant positive Eu anomaly on residual melts, which may be inherited by phases which crystallise subsequently. Critical to this is the timing of titanite crystallisation. If titanite crystallises in-situ in the shallow crust (i.e. is not fractionated from the melt), then the REE concentrations and Eu anomalies in residual melts may be dramatically affected, but the composition of bulk magmas may be unaffected.

In this study, zircons from the causative quartz monzodiorite (QMD) intrusions at the Oyu Tolgoi porphyry Cu-Au deposit are analysed to constrain the effects of titanite crystallisation on Eu and Ce anomalies.

2 The geology of Oyu Tolgoi

Oyu Tolgoi is a cluster of Palaeozoic porphyry Cu deposits located in the southern Gobi Desert of Mongolia. The deposits form a discontinuous belt of mineralisation approximately 22 km in length and ~5 km wide, making the district one of the largest centres of porphyry mineralisation in the world. The highest-grade mineralisation is found at Hugo Dummett, the deepest ore body, with >2.5 wt. % Cu and 0.5 to 2 g/t Au, whereas the most southerly deposit, Heruga, has lower Cu (0.48 wt. %) and Au (0.48 g/t) grades (0.6 wt. % Cu equivalent cut-off).

Mineralisation at both Heruga and Hugo Dummett is hosted primarily in a thick sequence of tholeiitic augite basalt, related to the emplacement of large-volume quartz monzodiorite intrusions (QMD), dated to between 368 and 372 Ma (Wainwright et al. 2011). The upper portions of the system are cut by a district-scale thrust fault (the Contact Fault) which emplaces an allochthonous sequence of basaltic breccias interbedded with red and green siltstones, known as the Oyu Tolgoi Hanging Wall sequence. This is poorly constrained but likely of late Devonian age. Both the autochthonous (mineralised) and allochthonous (unmineralised) rocks, as well as the Contact Fault, are cross-cut by narrow, anastomosing biotite granodiorite dykes, which postdate mineralisation.

3 Analytical techniques

Zircons from 13 Oyu Tolgoi drill core samples were separated and mounted in polished resin blocks. All analytical work was conducted at the Imaging and Analysis Centre of the Natural History Museum. Zoning was characterised by SEM-cathodoluminescence imaging using a Zeiss EVO SEM, with a beam current of 3.0 ± 0.3 nA, and an accelerating voltage of 20 kV. Given the narrow range of Si values ($\sigma = 0.2$ wt.% Si, $n = 111$), a mean value of 15.3 wt. % Si was used to calibrate LA-ICP-MS data. LA-ICP-MS analyses were conducted using an ESI New Wave UP193FX laser ablation system coupled to an Agilent 7500cs quadrupole ICP-MS. NIST-612 and BCR were used as the primary and secondary standards respectively. A fluence of 2.5 to 3.0 J cm$^{-2}$ and a spot size of 30 µm were used.

4 Results

4.1 Petrography

Zircon grains analysed in this study ranged in size from 30-500 µm. Many show distinct cores and rims, separated by a dissolution boundary that truncates the zoning of the core (Fig. 2). Most rims have a brighter CL response than the cores. Titanite inclusions, ranging in size from <1 µm to 30 µm, are common in zircons from QMD samples, and are ubiquitously observed in the overgrowth rims. Inclusions of K-feldspar, albite, quartz, hornblende, apatite and magnetite are also present. Despite its frequent occurrence as inclusions in zircon, titanite is a rare accessory phase in the groundmass of QMD samples and is absent in strongly altered rocks.

Figure 2. An SEM-cathodoluminescence (CL) image of a representative zircon grain from the Oyu Tolgoi quartz monzodiorite, showing distinct cores and rims separated by a dissolution boundary. The rims contain inclusions of titanite, and have characteristically low Ta, and high Eu/Eu* and Yb/Gd. Ttn = titanite, hbld = hornblende. White circles are laser spots.
Titanite-bearing (min. – med. – max) | Titanite-absent (min. – med. – max)
--- | ---
Eu/Eu* | 0.46 – 0.81 – 2.6 | 0.02 – 0.42 – 0.77
Ce/Ce* | 2.1 – 215 – 8701 | 7.6 – 194 – 8325
Ce4+/Ce3+ | 62 – 1102 – 8330 | 12 – 218 – 7578
Yb/Gd | 26 – 110 – 191 | 9.5 – 38 – 135
Ta | < 0.2 ppm | > 0.2 ppm
Ta/Nb | 0.07 – 0.17 – 0.34 | 0.09 – 0.34 – 0.54

Table 1. A summary of the geochemical characteristics of the titanite-bearing rims and titanite-absent cores of zircons from Oyu Tolgoi. Green indicates the group with significantly higher median values, whereas red indicates a lower median.

These observations suggest that titanite was originally a more common accessory phase in the QMD but was frequently destroyed by alteration, leaving behind only those grains included within robust zircon crystals.

4.1 Trace element geochemistry

The chemistry of titanite-absent cores and titanite-bearing rims in Oyu Tolgoi zircons is markedly different. These contrasts are consistent between different rock samples (Table 1). Titanite-bearing zircon zones have higher median Eu/Eu*, Ce4+/Ce3+, Yb/Gd, and lower Ta/Nb ratios. There is little difference in Ce/Ce*.

Chondrite-normalised REE patterns for titanite-absent zircon zones are typical of zircons from barren arc rocks, with concave-downwards patterns and negative Eu anomalies (Fig. 3b). REE patterns for titanite-bearing zircon zones show MREE depletion, and smaller to positive Eu anomalies (Fig. 3b).

Estimates of crystallisation temperature were calculated using the Ti-in-zircon thermometer of Ferry and Watson (2007), using a TiO2 activity of 0.7 and SiO2 activity of 1. In general, the zircon rims yield lower crystallisation temperatures than the titanite-absent zircon cores.

5 Discussion

The chemistry of the titanite-bearing zircon rims is unusual for zircons from typical barren arc rocks. That these atypical chemical signatures are observed in the rims of zircons separated by a dissolution boundary from cores with typical zircon chemistry indicates that these grains record a change in magma chemistry and/or temperature. The exceptionally high Eu/Eu* and Ce4+/Ce3+ values of the rims could be interpreted in terms of unusually oxidising conditions with attendant implications for porphyry deposit genesis.

A possible explanation for the observed textural and geochemical characteristics is an influx of hot, mafic magma as this would decrease the bulk Ta and Nb and increase Eu/Eu*. The concomitant increase in temperature would cause the melt to become undersaturated in Zr, causing any pre-existing zircons to resorb. However, temperature estimates for the titanite-bearing rims are ~50°C lower than the cores. Also, the low Ta/Nb ratio of the rims cannot be easily explained by an influx of mafic melt as this would have a higher Ta/Nb ratio (Stepanov and Hermann 2013). For these reasons, this process, at least on its own, is considered unlikely to be the origin of the low Ta rims.

Alternatively, the depleted MREE, low Ta and Nb, and lower Ta/Nb of the titanite-bearing rims may be explained by the co-crystallisation of titanite. Ta and Nb are both strongly compatible in titanite and Ta is more compatible than Nb (DNb = 109, DTa = 145; Colombini et al. 2011). As a result, the crystallisation of titanite during late-stage petrogenesis would deplete the residual melt in Nb and Ta, and decrease the Ta/Nb ratio of subsequent zircons.

Eu/Eu* values in excess of 1, as observed in titanite-bearing zircon zones (Table 1), cannot be accounted for by changes in redox alone because even under very oxidised...
conditions, $D_{Eu}$ would be intermediate between $D_{Sm}$ and $D_{Gd}$ (Burnham and Berry 2012). Thus, $Eu/Eu^*$ $>1$ must be due, at least in part, to melts that are enriched in Eu with respect to Sm and Gd.

Positive whole rock Eu anomalies occur in intrusions associated with porphyry systems where they are ascribed to the suppression of plagioclase crystallisation due to high $H_2O_{melt}$, coupled with oxidised conditions. However, elevated $Eu/Eu^*$ in residual liquids may also be expected from the crystallisation of titanite, which may account for high $Eu/Eu^*$ values in zircon rims. To investigate this, we modelled the crystallisation of small volumes of titanite from melts of average QMD composition using Rayleigh fractionation. The results of this analysis show that melts which are crystallising small amounts of titanite would be in equilibrium with zircons that are progressively depleted in MREE with respect to HREE (i.e. higher Yb/Gd), and have increasing $Eu/Eu^*$ values (Fig. 3 a,b). Positive zircon Eu anomalies were generated by our model after just 0.34 % titanite crystallisation. Chondrite-normalised REE patterns produced by our models also show a striking similarity to Oyu Tolgoi zircons, reproducing the average REE patterns of titanite-bearing zircon zones after the crystallisation of ~0.2% titanite (Fig. 3). These results demonstrate that high $Eu/Eu^*$ in zircons can be generated easily by processes which are redox independent. Consequently, all attempts to use Eu in zircon to determine the redox condition of magmas at the time of zircon crystallisation must be treated with caution unless evidence for a lack of titanite co-crystallisation (e.g. high Ta, low Yb/Gd and Ta/Nb) is presented.

Titanite crystallisation also complicates the estimation of $Ce^{4+}/Ce^{3+}$ using the method of Ballard et al. (2002):

$$Ce^{4+}/Ce^{3+}{\text{zircon}} = \frac{Ce_{melt} - Ce_{zircon}}{D_{Ce^{3+}}} \cdot \frac{D_{Ce^{3+}}}{Ce_{zircon}/Ce_{melt}} = \frac{Ce_{melt} - Ce_{zircon}}{D_{Ce^{3+}}} \cdot \frac{Ce_{zircon}/Ce_{melt}}{Ce_{zircon}/Ce_{melt}}$$

Of the parameters used in its calculation, $Ce^{4+}/Ce^{3+}$ is most strongly controlled by $D_{Ce^{3+}}$ (Fig. 4). This is estimated using the lattice strain model by interpolating between the partition coefficients of other $REE^{3+}$ cations, which are calculated as $REE_{zircon}/REE_{melt}$. Because the REE content of the melt is difficult to estimate in granitic systems, whole rock REE contents are used instead, making the assumption that $REE_{whole\text{rock}} \approx REE_{melt}$. However, the crystallisation (but not fractionation) of titanite would cause REE depletion in the melt, but not change the whole rock REE concentration (i.e. $REE_{whole\text{rock}} > REE_{melt}$). This would cause underestimates in $D_{Ce^{3+}}$ which leads to an overestimate for $Ce^{4+}/Ce^{3+}$ for zircons in equilibrium with titanite (Fig. 4). Consequently, titanite crystallisation may drive changes in calculated $Ce^{4+}/Ce^{3+}$ ratios which are unrelated to changes in melt $fO_2$, thus compromising the ability of this parameter to measure redox conditions.

**Figure 4.** Calculated $Ce^{4+}/Ce^{3+}$ values are dependent upon estimated $D_{Ce^{3+}}$ values, which may be strongly underestimated in melts which have crystallised titanite.

$Ce/Ce^*$ is likely to be unaffected by titanite crystallisation because it does not preferentially partition $Ce$ over other $REE$. This makes $Ce/Ce^*$ a potentially more robust measure of redox. However, $Ce/Ce^*$ is difficult to calculate because of LREE contamination in zircon due to inclusions of apatite or monazite.

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Hyperspectral characterization of white mica and biotite mineral chemistry across the Canadian Malartic gold deposit, Québec, Canada

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Abstract. The Canadian Malartic gold deposit is located in the highly endowed Abitibi region of Québec. A large part of the mineralization is located within Archean metasediments, which are often challenging to characterize by conventional core logging. Hyperspectral imaging of 168 meta-sedimentary samples from Canadian Malartic reveals that, in addition to ubiquitous biotite, 70% of the samples contain significant amounts of white mica, which was previously not recognized. Additionally, compositional changes in white mica and biotite composition within the deposit reflect the degree of hydrothermal alteration. The presence of phengitic white mica (>2206 nm, <3.3 V_\text{Al} per 22 O) is indicative of altered and potentially mineralized samples, whereas distal samples are more muscovitic in composition (<2202 nm, >3.5 V_\text{Al}). Biotite composition, also derived from spectral data, similarly shows variability in Mg\# with respect to distance to mineralization, but to a spatially more limited extent than white mica. The most Mg-rich biotite (Mg\# > 70) occurs spatially associated with mineralized intervals, and no Mg-rich biotite occurs outside of the open pit.

1 Introduction

Canadian Malartic is a gold mine located in the Malartic area of Québec, immediately south of the NW-SE trending Cadillac-Larder Lake Tectonic Zone, which separates the Pontiac and Abitibi subprovinces of the Canadian Shield. It is a high-tonnage, low-grade open-pit mine (13.4 Moz Au in 372.9 Mt ore averaging 1.02 g/t Au: Helt et al. 2014), which sits atop and consolidates numerous historical underground workings. The distribution of the mineralization at Canadian Malartic is in part controlled by the E-W striking Sladen fault (De Souza et al. 2015), and is shown on figure 1. A large part of the mineralization occurs within Pontiac Group metasediments (greywacke to mudstone) (Perrouty et al. 2017).

Core logging of the metasediments can be a challenging task to do visually; we therefore aim to use hyperspectral imaging (or imaging spectroscopy) to characterize the mineral chemistry and alteration patterns of samples in and around the deposit.

2 Methodology

2.1 Sampling

Data were collected on 168 metasediment samples from 9 drill cores on a N-S section across the deposit and its footprint (Fig. 1b), forming a section that extends from the central portion of the mineralized zone to approximately 1.5 km south of the mine. They include a wide range of alteration types, sedimentary protoliths (greywacke, mudstone), and metamorphic grades (biotite to garnet zones). For each sample, both the core pieces and
associated thin section block were scanned with a SisuROCK hyperspectral core scanner.

2.2 Hyperspectral imaging

Imagery was acquired for all samples at a spatial resolution of 0.2-0.5mm/pixel, where every pixel contains an infrared reflectance spectrum in the range 1000-2500 nm (Short Wave Infrared - SWIR). Typical spectra for biotite and white mica are shown in figure 2. In this spectral range, most phyllosilicates show several characteristic absorption features due to the presence of specific cation-OH bonds (Hunt 1977).

The position of -OH related absorption features varies with mineral chemistry. For example, the 2200 nm Al-OH absorption feature of white mica varies from about 2192 to 2220 nm (Fig. 3), and is correlated to its $^{3+}$Al content (i.e., muscovite to phengite: Duke 1994). Similarly, the 2250 nm absorption for biotite varies with Mg#, from 2240 nm for Mg-rich biotite to 2260nm for Fe-rich biotite.

![Figure 2](image2.png)

**Figure 2.** Spectra of biotite and white mica, continuum removed and offset for clarity. The position of the 2200 nm (white mica) and 2250 nm (biotite) absorptions can be used to determine mineral chemistry.

![Figure 3](image3.png)

**Figure 3.** Correlation between $^{3+}$Al content of white mica (from EPMA data, for 22 O atoms) and position of 2200 nm absorption feature.

3 Results

3.1 Thin-section blocks

The 168 thin-section blocks are displayed in figure 4a with the same relative spatial arrangement as shown on figure 1b; each column represents samples from a single drill core. Samples are colour-coded according to the position of the white mica and biotite absorption features. Almost 70% of the samples contain significant amounts of white mica. End-member muscovite has shorter absorption wavelengths (2192 nm) and is displayed in red colours, whereas more phengitic muscovite (from Tschermak-like substitution) has longer absorption wavelengths (>2205 nm) and is displayed in blue to purple colours.

Biotite is ubiquitous, with variable amounts of retrograde chlorite. The position of its 2250 nm absorption feature varies with Mg#, and is displayed in blue-purple colours for Mg-rich compositions (2240 nm) and red colours for Fe-rich compositions (2260 nm).

![Figure 4](image4.png)

**Figure 4.** a Thin-section block hyperspectral imagery processed to display the position of the 2200 nm absorption feature of white mica. b Same data, processed to display the position of the 2250 nm absorption feature of biotite, reflecting its Mg#.

3.2 Core and field samples

Larger samples show decimetre-scale variability in both mineralogy and in mineral composition, which is not captured at the thin section scale (2-4 cm). Several hundred meters of continuous drill cores were therefore imaged using the hyperspectral system to illustrate the scale of mineralogical variability in mineralized samples. Similarly, field samples ranging from 30 cm to 1.5m in length were taken from an 8x12 km area around the mine to characterize mineralogical variability in unaltered Pontiac metasediments.

Figure 5 illustrates a meter-long core sample from the
mineralized zone (near drill hole CM07-1216, on figure 1), which presents an alternating pattern of phengitic white mica and white mica-free zones, with gradational and texturally complex transitions. Biotite is present throughout the length of the sample, but varies in composition from Mg#80 (2245 nm, purple) to Mg#60 (2252 nm, yellow) within one meter.

Figure 5. Core sample (1m long) from the mineralized zone (0.5ppm Au on 1.5m), showing dm-scale variations in mineralogy. Same colour scale as previously. a White mica hyperspectral image (2200 nm), showing alternating presence and absence of white mica. b Biotite hyperspectral image (2250 nm), showing a gradual composition change from Mg-rich (Mg#80, 2245 nm, purple) to intermediate Mg content (Mg#60, 2252 nm, yellow). c Photograph.

A typical unaltered distal metasediment sampled 3 km southwest of the deposit is shown in figure 6. Metamorphic white mica in mudstone beds is of muscovitic composition (2196 nm, >3.7 10Al), is compositionally homogeneous, and shows sharp contacts to white-mica free greywacke beds. Biotite is present throughout and is compositionally homogeneous (2252 nm, intermediate Mg#)

Figure 6. Typical unaltered Pontiac metasediment. Field sample (1m long) located 3 km southwest of the deposit. a Occurrence and composition of white mica (2196 nm, >3.7 10Al). b Occurrence and composition of biotite (2252 nm, intermediate Mg#). c Photograph.

4 Discussion and final remarks

Mg-rich biotite (Mg#>70, <2250 nm) in the deposit is associated with hydrothermally-altered and mineralized samples, and rapidly (m-scale) grades into background compositions (Mg# 50-60, >2252 nm). White mica of hydrothermal origin is phengitic in composition (>2206nm, <3.3 10Al), but is not always present. Small (dm to 10’s of m) scale, texturally complex changes in white mica abundance and composition are observed within the deposit.

Regionally, metamorphic grade affects white mica composition, producing Al-richer muscovite at higher metamorphic grades (Duke and Lewis 2010). From proximal to distal samples (at km scales), metamorphic white mica progressively varies from 2204 nm to 2196 nm, but is homogeneous within a given sample (m scale). Presence or absence of white mica is controlled by protolith composition, as can be seen from alternating layers of white mica-free beds (generally coarser grained greywackes) and white-mica rich beds (generally finer grained mudstones).

As data acquisition is rapid (1 minute per core box or 10 seconds per individual sample), spectrally detectable changes in white mica composition make hyperspectral imaging a useful tool for vectoring towards mineralization in similar geologic environments. Likewise, small-scale changes in biotite composition can be useful for rapidly and accurately delineating mineralized intervals in drill cores.

Acknowledgements

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Enhanced targeting tools for mineral exploration - Mineral Prospectivity Modeller (MPM)

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Abstract. Enhanced data-analysis methods and practices can also be considered time-saving, cost-effective and environmentally neutral in mineral exploration. Their importance constantly increases as digital data is collected in exploration. The Mineral Prospectivity Modeller (MPM) project investigates and implements new workflows and tools for mineral prospectivity modelling. A publically available Spatial Data Modeller toolbox is refactored and enhanced into ArcGIS 10 and ArcGIS Pro. The project also produces an on-line prospectivity modeller for easy selection of target areas for exploration. The use of the tools will be demonstrated in a case study with real exploration data. The results of the project will be published as a report of investigation, scientific papers and an open source software. The project is co-funded by the Finnish Funding Agency for Innovation - TEKES, together with the mining and exploration industry. The MPM project involves an international collaboration network composed of the top experts in mineral prospectivity mapping, including the U.S. Geological Survey, the Geological Survey of Canada and the University of Campinas (Brazil).

1 Mineral prospectivity mapping

Traditionally, evaluation of mineral potential, also known as mineral prospectivity mapping, is based on examination of geological outcrop and drill core data based on extensive field work, aided by visual inspection of geochemical and geophysical maps derived from field and airborne measurements. Today, digital maps allow quantitative analysis of these data-sets. GIS based data-analysis and spatial data mining techniques can be utilized to integrate information derived from rasterized and vectorized spatial data-sets into a single mineral prospectivity map defining the most favourable areas for the deposit type under examination (Fig. 1). Besides being able to exploit large amounts of information, modern methods are time-saving, cost effective and, simultaneously, environmentally neutral.

Prospectivity mapping methods can be divided into two main approaches (Bonham-Carter 1994): 1) Empirical or data-driven approach and 2) Conceptual or knowledge-driven approach.

The first category of techniques, empirical approach, uses prior knowledge on the locations of existing mineral deposits or occurrences, and optionally non-deposits, within the study area. The commonly used supervised techniques for prospectivity mapping are weights of evidence, logistic regression and neural networks. The empirical methods are suitable especially for the mature brownfields exploration with abundant training data available.

The second category, conceptual approach, is translating the expert knowledge into a mathematical model using for example fuzzy logic (Zadeh 1965). Known mineral deposit sites are not required. Instead, the input data is rescaled into a common scale from non-favourable to favourable based on assumed dependence of the data on prospectivity. The rescaled input data is then integrated using fuzzy operators into a spatial representation of prospectivity. This approach fits well within greenfields exploration where there is limited number of known mineral deposits available for training of the models.
Various data pre-processing methods are performed prior to the prospectivity modelling. In addition to the basic image filtering techniques and geophysical transformations, it is often useful to find natural clusters in the data. An unsupervised classification method called Self Organising Maps (SOM) (Kohonen 1998) is therefore implemented into ArcSDM. SOM are a powerful tool for dimension reduction, clustering and anomaly detection for multidimensional data.

A typical workflow for mineral prospectivity modelling project is shown in Figure 2 (Nykänen 2008). First an exploration model, a theoretical mineral systems model (e.g. Wyborn et al. 1994) or a practical exploration model (e.g. Nykänen et al. 2015), is formulated. The input data for the modelling is either extracted from the existing geoscience databases or acquired by making additional measurements and observations. The second step involves data pre-processing, which includes various methods in order to create meaningful map patterns from the raw data in the mineral exploration context. The third step is the actual prospectivity modelling applying the empirical or conceptual approaches on the data available. The output of the modelling is a single prospectivity map which summarises the information provided by the input maps. Finally, model validation is performed including various statistical or cross-validation techniques to assess the accuracy of the model. This workflow is dynamic such that parameters are modified and models are re-run to iterate until the validation shows acceptable performance levels. The final validation of the mineral exploration model is assessed by drilling the most prospective targets.

2 Arc SDM toolbox

2.1 Existing tools

The ArcSDM tool box for ArcGIS was originally developed and released by the U.S. Geological Survey and Geological Survey of Canada (Kemp et al. 2001). Since 2005 the code has been maintained by the University of Campinas, Brazil. Esri Inc. implemented the Fuzzy logic tools into the Spatial Analyst toolbox in ArcGIS.

The previous ArcSDM toolbox is available for download from the web site of the University of Campinas in Brazil (http://www.ige.unicamp.br/sdm/) including Weights-of-Evidence (WofE) tools, a neural network toolbox called GeoXplorer and some utilities. This toolbox runs on ArcGIS 10 and provides the essential tools for mineral prospectivity mapping.

The current ongoing MPM project has refactored the tools from the previous ArcSDM version into ArcGIS 10 (from 10.1 onwards) and ArcGIS Pro platforms. The new release is called ArcSDM 5 and it can be downloaded from the GitHub (https://github.com/gtkfi/ArcSDM).

2.2 New tools

In addition to the already existing tools in the previous versions of ArcSDM new tools are implemented. Receiver Operating Characteristics (ROC) curves are used to validate spatial models. They require two sets of validation points: 1) true positive sites, i.e. locations of the known mineral deposit type of interest that were not used for training the model; and 2) true negative sites represent locations of non-deposits. Nykänen et al. (2015) propose using random points as true negative sites if there is not an adequate data-set of non-deposits. Nykänen et al. (2015) propose using random points as true negative sites if there is not an adequate data-set of non-deposits available.

Other possible new tools that we are aiming at implementing are non-linear classification technique such as Regularized Least-Squares - RLScore (Pahikkala and Airola 2016). Furthermore, we are looking into methods such as random forests, support vector machines or possibly others to be implemented in the future releases of the toolbox.

2.3 Reference data-set

A reference (sample) data-set will be extracted from GTK’s publicly available geodatabase to enable continuous ad-hoc testing of the toolset during the development and to enable the new users to experiment with the tools. This data package includes geological, geophysical and geochemical data-sets and their derivatives. Original geological and geochemical data is given both in vector and raster format, geophysical data in raster format.

The geological data (Table 1) is extracted from GTK’s digital bedrock map of Finland (Bedrock of Finland - DigiKP) and mineral deposits data are derived from GTK’s “Mineral deposits of Finland” data base.
Table 1. Geological data layers in MPM demo data package.

<table>
<thead>
<tr>
<th>Layer Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic deposits and occurrences of the area</td>
</tr>
<tr>
<td>Lithological units as polygons</td>
</tr>
<tr>
<td>Lithological units as polylines</td>
</tr>
<tr>
<td>Black shales/schists as polylines</td>
</tr>
<tr>
<td>Shear, fault and thrust zones as polylines</td>
</tr>
<tr>
<td>Geological domain boundaries as polylines</td>
</tr>
<tr>
<td>Lithological units classified by lithology in raster format</td>
</tr>
<tr>
<td>Lithological units classified by type in raster format</td>
</tr>
<tr>
<td>Supracrustal rocks classified by lithostratigraphic groups in raster format</td>
</tr>
<tr>
<td>Lithology classified by era in raster format</td>
</tr>
</tbody>
</table>

The geochemical data consist of GTK’s regional till data-set (Salminen 1995). Regional till geochemistry includes the concentrations of 25 elements in basal till fine fraction (<0.06 mm). The sampled material was chemically unchanged C-horizon till preferably under the water table. The average sampling depth was approximately 1.5-2 m. Sampling was done in 1983-1991. The sampling density was one sample per 4 km². The samples were collected as a composite of 3-5 subsamples. The coordinates of each sample are calculated based on coordinates of these 3-5 subsamples. Some of the subsamples were originally collected in targeting till geochemical sampling campaigns. From hot aqua regia dissolutions abundances of 25 elements were determined (e.g. Salminen 1995). These assay results were interpolated into 500x500 m cell size grids using inverse distance weighting (IDW).

The geophysical data is comprised of the low-altitude aerogeophysical data collected during 1972-2007 (Airo 2005) and derivatives of ground gravity survey. The parameters of the original airborne geophysical data were: flight altitude 30-40 m, the nominal flight line spacing 200 m and sample distance along the survey line 6-50 m. The MPM reference data-set includes total magnetic field, apparent resistivity, quadrature (em-imaginary) and in-phase (em-real) components. The data-set has been interpolated to 500 m x 500 m cell size grids using minimum curvature (spline) method.

A data-set layer “gravity worms” represents maxima of spatial gravity gradients at different upward continuation levels. The processing technique, multi-scale edge detection, was first presented by Hornby et al. (1999) and later discussed by Archibald et al. (1999) and Holden et al. (2000). The regional Bouguer data (1 observation per 25 km²) used in the processing was provided by the National Land Survey of Finland (Kiviniemi 1980; Kääriäinen and Mäkinen 1997).

3 On-line mineral prospectivity modeller

In addition to the desktop GIS toolbox, the MPM project is also aiming at creating a conceptual on-line fuzzy logic prospectivity modelling tool, which processes geological, geophysical and geochemical data in a web map application. The first release will be using only the GTK demo data-sets from Finland. The users will be able to run various scenarios to delineate areas favourable for different mineral deposit types and make initial target area selections. The aim is to run an enhanced web map service which provides some spatial data analysis capabilities in addition to traditional data browsing and viewing.

4 Case study

Mineral exploration is done in several scales from regional to target scale. The MPM task will create workflows and tools to optimize the target scale modelling by adding new information into the models during an exploration project evolution. This will be demonstrated by using a historic case study. In a typical mineral exploration project the amount of data grows in the course of the project but the gained information might not increase parallel. This project aims to solve this issue by providing new tools for data exploration.

The stepwise prospectivity mapping, starting from regional scale conceptual model and ending up with a sequence of combined conceptual/empirical target scale prospectivity model, will be carried out using publicly available data from a gold deposit within Central Lapland Greenstone Belt, Northern Finland. The selection of the target area will be based on a comprehensive publicly available exploration data-set. Thus this target area can be used to demonstrate the model optimization procedure with annually increasing exploration data.

5 Summary

The MPM project will produce two main products: 1) the ArcSDM 5 tool box for ArcGIS 10 (from 10.1 onwards) and ArcGIS Pro. The mineral prospectivity mapping toolbox includes the algorithms from the previous version and additional enhanced tools. The usage of the tools will be demonstrated by applying the techniques into a gold prospectivity model using regional and target scale data from the Central Lapland Greenstone Belt, Northern Finland. 2) The on-line MPM web map service will provide simple to use decision making tools for selecting favourable mineral exploration areas in Finland. A presented case study will demonstrate the possibilities offered by this technology.

The users of the results are junior mining companies and mining companies conducting mineral exploration, and companies providing exploration services to exploration industry. In addition, the tools can be utilized by many other disciplines requiring spatial data analysis.
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References

Integrated multi-parameter footprint of the Canadian Malartic gold deposit, Québec, Canada

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Abstract. The metasomatic halo of the Canadian Malartic gold deposit has been investigated using and integrating multiple geological and geophysical methods. Over 50 structural, lithogeochemical, mineralogical, petrophysical and geophysical parameters were identified and they provide the spatial distribution of alteration zones within the deposit footprint as well as vectoring information. This communication highlights the main parameters that define the Canadian Malartic footprint and on-going progress regarding their geological, geospatial and geostatistical integration.

1 Introduction
The NSERC-CMIC Multidisciplinary Mineral Exploration Footprints project (http://cmic-footprints.ca/), aims to characterize the distal signature of major ore systems, to identify new exploration criteria, and to develop exploration methodologies by integrating geological, structural, lithogeochemical, mineralogical, petrophysical and geophysical datasets.

This communication presents a synthesis of some of the multi-parameter footprints and vectors toward the mineralization that have been identified for the world-class Canadian Malartic deposit (>18.6 Moz, Gervais et al. 2014), which is located south of the Cadillac Larder Lake Deformation Zone, Abitibi Subprovince, Canada (Fig. 1).

2 Geological setting
2.1 Host rocks and deformation

The Canadian Malartic gold deposit is hosted by Archean meta-sedimentary rocks (Pontiac Group) and quartz-monzodiorite intrusions of the Pontiac Subprovince, and by meta-volcanic rocks of the Abitibi Subprovince (Piché Group). These lithologies were intruded by basic dykes prior to the mineralization event(s). Upper greenschist metamorphism overprints all host rocks, mineralization and associated alteration.

Three major deformation events have been recognized in the area (Derry 1939; Perrouty et al. 2017) and include: 1) a pre-mineralization and pre-intrusion D1 deformation event that produced isoclinal F1 folds and a pressure-solution bedding parallel S1 cleavage, 2) a syn-mineralization D2 deformation event that produced open to tight steeply dipping F2 folds, an east-plunging L2 stretching lineation and a NW-SE-trending penetrative biotite/amphibole foliation, and 3) a post-mineralization minor D3 deformation event that produced open F3 folds, a subtle NE-SW-trending crenulation S3 cleavage and kinks.

The D3 event postdates the metamorphic peak and may correlate with late dextral transcurrent movement along the Cadillac Larder Lake Deformation Zone (Bedeaux et al. 2017).

2.2 Mineralization

Low grade, large-tonnage gold mineralization in the Canadian Malartic deposit is structurally controlled by the E-W Sladen Fault Zone (which is connected to the Cadillac Larder Lake Deformation Zone) and NW-SE high-strain bands (Derry 1939). Ore zones are spatially associated with quartz monzodiorites intrusions (Helt et al. 2014). The proximal alteration mineralogy consists of biotite, K-feldspar, albite, white mica, quartz, carbonate, pyrite, rutile, scheelite in the meta-sedimentary rocks (Helt et al. 2014, De Souza et al. 2015, 2016) and biotite, quartz, carbonate, chlorite, pyrite, rutile, epidote in the meta-basic dykes (Perrouty et al. 2015).

3 Integrated multi-parameter footprints
3.1 Structural footprint

Orogenic and intrusion-related gold systems are all structurally controlled. At Canadian Malartic, the relationship between the deformation and the mineralization was recently investigated by De Souza et al. (2015, 2016), who demonstrate a syn-D2 timing for the main gold mineralization event and estimate it to be around 2664 Ma.

Perrouty et al. (2017) showed that gold occurrences in the Canadian Malartic district are systematically associated with structurally complex zones, which are interpreted to be joined F1 and F2 fold hinges. They also highlighted spatial variations in the intensity of the S2 biotite foliation in greywacke and tentatively interpreted it as a consequence of the alteration by mineralizing fluids during the D2 deformation event.
3.2 Geochemical footprint

Lithogeochemical variations throughout the footprint of the deposit are controlled by the protolith composition and by alteration. Whole-rock geochemical analyses were conducted by ACTLABS, ALS and SGS laboratories and were supplemented by a whole-rock stable isotope study (see Raskevicius et al. 2017).

Mass changes were calculated for meta-sedimentary rocks and meta-basic dykes in order to generate a series of representative mass gain and loss maps. Gold and associated elements (Ag, Te) have the most significant mass gains proximal to the deposit in both rock types. Elements such as S and C are intimately associated with gold mineralization and are enriched in the vicinity of the deposit. Significant mass gains are also observed for large-ion lithophile elements and for light rare-earth elements, but their distributions highlight a more distal alteration signature, which is particularly well recorded in the meta-basic dykes (Fig. 2).

Differences in analytical methods (partial vs total leaches) can also be used to detect alteration.

3.3 Mineralogical footprint

Mineralogical changes within the footprint of the Canadian Malartic gold deposit are linked with lithogeochemical changes during the hydrothermal alteration process. Major mineral proportions are highly dependent on the protolith in the meta-sedimentary rocks (greywacke vs siltstone vs mudstone) and the resultant variations can therefore be difficult to interpret. However, the relative abundances of minor minerals such as carbonates, pyrite, and rutile increase in the vicinity of the mineralized zones.

The meta-basic dykes are more reactive to the hydrothermal fluids than the Pontiac meta-sedimentary rocks. Their mineralogy evolves from a distal amphibole-rich composition to a proximal biotite–carbonate–quartz–pyrite–rutile mineral association (Perrouty et al. 2015).

Mineral chemical variations were also evaluated. Biotite and white mica compositions are highly dependent on the protolith and metamorphic conditions (Gaillard et al., 2015), but a distinct “hydrothermal” signature can nevertheless be identified around the Canadian Malartic deposit. Hyperspectral (SWIR) methods have also been shown to efficiently detect and map mineral compositional changes (see Lypaczewski et al. 2017).

Glacial dispersion from the Canadian Malartic deposit in the surficial till is also being investigated (Taylor et al. 2017).
3.4 Petrophysical footprint

Rock physical properties are controlled by multiple parameters including mineralogy and structures. Measurements were acquired at the Geological Survey of Canada Paleomagnetism and Petrophysics Laboratory and at École Polytechnique de Montréal.

Density is highly dependent on the mineralogy and porosity. Major mineralogical changes during alteration result in density variations across the Canadian Malartic footprint, which are particularly strong for meta-basic dykes.

Magnetic susceptibility and remanence are mainly controlled by minerals such as magnetite and pyrrhotite. The spatial distributions of these minerals in the footprint is complex. Pyrite is the most common sulfide mineral in the deposit and is commonly associated with destruction of magnetite. It is, however, progressively replaced by pyrrhotite towards the south, which is tentatively interpreted to be a metamorphic overprint on the alteration assemblage. The anisotropy of the magnetic properties along geological structures is also being investigated and correlated with structures.

Low-frequency electrical properties were also measured and interpreted based on rock texture, sulfide mineral proportions and grain size distribution (Bérubé et al. 2017).

3.5 Geophysical footprint

The detection of orogenic intrusion-related disseminated gold deposits by geophysical methods is very challenging because the petrophysical contrasts are often not sufficient to provide a perceptible geophysical signature.

Geophysical datasets in the area consist of airborne magnetic and EM surveys provided by Canadian Malartic Corporation, and several ground IP lines that were acquired in collaboration with Abitibi Geophysics during this project. Airborne data were used mainly to delineate geological structures and units, and are not sensitive to alteration signature. High resolution (meter-scale) time-domain and spectral induced polarization ground surveys were conducted at the Bravo gold occurrence and appear to detect graphitic mudstone and mineralized greywacke layers (Bérubé et al. 2017).

3.6 Data integration

Three major data integration analyses are being conducted in this project: 1) geological “physical” integration between parameters (e.g., carbonate alteration => density

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**Figure 2.** Schematic diagram summarizing the main parameters that define the footprint of the Canadian Malartic gold deposit from the most distal (left) to the most proximal (right).
decrease), 2) geospatial integration (e.g., gold, quartz-monazodie intrusion and F1-F2 fold hinges are spatially associated), and 3) geostatistical integration (e.g., principal component analysis, K-means clustering, machine learning), which are still in progress.

Over 50 individual vector and footprint parameters can be used to characterize the proximal, medial, and distal alteration zones. Combinations of these parameters enhance their capacity to vector toward the deposit and decrease the possibility of false positive results. The identification of a minimum set of parameters that best describe the footprint and that are applicable to exploration is a critical goal of this project.

4 Summary and conclusion

Many individual mineralogical, lithogeochemical and petrophysical parameters vary across the Canadian Malartic footprint (Fig. 2), and therefore define the footprint of the deposit. However, some of these parameters are physically linked together (e.g., mass gain in potassium => biotite formation => density decrease in meta-basic dykes.). Extensive data integration will be used to identify the best combination of variable that define the Canadian Malartic footprint and permit vectoring from the periphery toward the high grade core, which can then potentially be used to target similar ore systems.

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Vectors to mineralization in the carbonate-hosted Grasberg-Ertsberg porphyry district from calcite C-O isotope and trace element geochemistry

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Abstract. Trace element analyses of calcite veins, marbles, and skarn in the Grasberg-Ertsberg district reveal distinctive characteristics in distal and proximal skarn and porphyry environments. C-O isotopic values correlate with trace element variations and both can be attributed to magmatic fluid mixing with rock-buffered meteoric waters. A negative correlation is observed between δ18O and Mn:Mg values, which change systematically towards the center of the Grasberg Intrusive Complex (GIC). Evidence for fluid migration for up to 5km away from the GIC along permeable fracture and fault networks is indicated by magmatic-hydrothermal signatures in distal calcite vein chemistry. Isotopic and trace element analyses of calcite present a new and potentially effective tool for the detection of porphyry deposits in carbonate-hosted terrains which to date have proven challenging to explore.

1 Introduction

The Grasberg-Ertsberg district is located in the Central Range of Papua, Indonesia. Cu-Au mineralisation in the district is hosted by multiple porphyry and skarn deposits with an estimated resource of 7.5 billion tonnes (grading 0.70% Cu and 0.64 ppm Au) and 3.6 billion tonnes (grading 0.60% Cu and 0.44 ppm Au) for the Grasberg and Ertsberg systems respectively (Leys et al. 2012). The Grasberg and Ertsberg igneous complexes formed ~3.5-2.5 Ma during minor left lateral movement on NW trending strike slip faults (Sapiie and Cloos 2013). This permitted magma ascent via structural corridors and focused hydrothermal fluid flow (Cloos et al. 2005; Sapiie and Cloos 2013).

Host rocks in the district are predominately limestone with minor sandstone and shale of the New Guinea Limestone Group (NGLG) deposited on the marine shelf of the Australian plate in the early Tertiary (Quarles van Ufford 1996). At ~12 Ma a north-dipping subduction zone formed off the northern coast of Australia and related compression in Papua caused uplift, reverse faulting and folding, resulting in large amounts (~80 km) of ENE-WSW shortening in the region (Quarles van Ufford 1996). Strike-slip reactivation of reverse faults with a maximum of 1 km left-lateral offset occurred prior to Grasberg-Ertsberg district magmatism which is dated at about 4-2.5 Ma (Cloos et al. 2005; Sapiie and Cloos 2013).

The Grasberg porphyry Cu-Au deposit is hosted by monzodiorite intrusions and subvolcanic breccias of the Grasberg Igneous Complex (GIC) within a diatreme that intrudes NGLG sediments. Outside the diatreme, porphyry-related alteration comprises narrow replacement sulphide and minor skarn beyond which an average 200m wide marble halo is developed. Calcite is found as pods in left lateral faults as well as veins of similar WSW-ESE orientation in NGLG carbonates within the marble halo (Sapiie and Cloos 2004). The temporal association of movement on these left-lateral faults with magma emplacement and ore formation, together with alteration calcite chemistry can be used to characterize hydrothermal fluids in carbonate hosted ore deposits (eg. Barker et al. 2013; Vaughan et al. 2016).

2 Sampling and methodology

Sampling aimed to investigate significant changes in fluid chemistry with distance from the center of the Grasberg deposit. Samples were taken of GIC intrusions, the Dalam Diorite, and Main Grasberg Intrusion as well as NGLG limestones and skarns surrounding Grasberg and the nearby weakly mineralized West Grasberg porphyry. In total 255 samples were collected on two main transects across the deposit. Transect 1 trends WNW-ESE across the GIC and extends up to 6 km away from it over NGLG carbonates lying close to the axis of a major district syncline. Transect 2 starts within the GIC and trends SSW along the main mine access road for ~2.5 km, crossing many of the strike-slip faults in the southern part of the district. Samples were preferentially taken of marble, skarn and calcite veins from outcrop, however near deposit samples were taken from drill core.

Each calcite-bearing sample was photographed using longwave and shortwave ultra-violet light (LW-UV, SW-UV). One inch epoxy rounds were made from about half of these samples, and microscope UV photography and CL-SEM was captured using a FEI MLA650 environmental scanning electron microscope.
Calcite from 81 vein, marble, and skarn samples was analysed for trace elements by laser ablation inductively coupled mass spectrometry (LA-ICP-MS) with at least 10 spots per sample for a total of 915 individual analyses. An ASI Resolution laser ablation system coupled with an Agilent 7900 ICP-MS was used for analyses. NIST 612 measured at ~80 µm was used as the primary standard, with GSD-1g measured at 32 µm and MACS-3 run at 60 µm as secondary standards. Secondary standards were used as instrument checks and as long term data reproducibility constraints. Fluence used was ~3.5 J/cm² and all spots were ablated at 5 Hz. Elements analysed were: Li⁷, C¹³, Na²³, Mg²⁴, Al³⁷, Si²⁹, K⁳⁹, Ca⁴³, Ti⁴⁷, V⁵¹, Cr⁵³, Mn⁵⁵, Fe⁵⁷, Co⁵⁹, Ni⁶⁰, Cu⁶⁳, Cu⁶⁵, Zn⁶⁶, Zn⁶⁸, Ga⁶⁹, Ga⁷¹, As⁷⁵, Se⁸⁸, Y⁹⁸, Zr⁹⁰, Ag¹⁰⁷, Ag¹⁰⁹, Cd¹¹⁰, Sn¹¹⁸, Ba¹³⁷, La¹³⁸, Ce¹⁴⁰, Pr¹⁴¹, Nd¹⁴⁰, Sm¹⁴⁷, Eu¹⁵₁, Gd¹⁵⁷, Dy¹⁶⁴, Er¹⁶⁶, Yb¹⁷², Lu¹⁷⁵, Hf¹⁷⁸, Ta¹⁸¹, Au¹⁹⁷, Pb²⁰⁸, Th²³², U²³⁸.

Stable isotope analyses of samples were analysed using a MultiFlow Isoprime 100 automatic system. Microdrilled powder sample weights of 20-100 µg were taken to end up with 20-30 µg of pure calcite. 200 mL of 100% phosphoric acid was added to evacuated sample vials and digested for 10-18 hours. Duplicate standards were run after every 6 samples and included NBS-18, NBS-19, ANU-M1, and ANU-PRM2, which include limestone, calcite, and carbonatite C-O isotope standards. Precision for this method based upon blanks, instrument drift and standard reproducibility is ±0.12 ‰ for δ¹³C and ±0.20 ‰ for δ¹⁸O measurements. An average trace element composition was calculated for the area sampled for isotope analysis, which allows for direct comparison of trace element and isotope variability in each sample.

### Figure 2. Multiple generations of calcite growth in veins within interbedded micritic limestone and carbonaceous shales of the NGLG Kais formation (GB11MB061). Sample is located ~1.5 km NW of the center of the GIC, proximal to the Grasberg West intrusion. Multiple imaging techniques used including CL-SEM (a) of the lower circle, plain light photography (b), SW-UVF (c), and LW-UVF (d). Blue, white, and pink colours in UV-photography can be correlated to different generations in CL-SEM imaging. Regions analysed for O-C isotopes are shown by red circles.

### 3 Trace element and stable isotopic composition

The results of imaging were presented by Thompson et al. (2016) and showed a correlation between calcite mineral
chemistry and UV fluorescence (UVF) colour. Calcite veins with a red UVF response occur proximal to the GIC. Grasberg district NGLG limestone stable isotope geochemistry was published for the Big Gossan skarn deposit (Meinert et al. 1997) Prendergast (2003). The blue box in figure 3b displays the range of isotopic variability in unaltered limestone reported by Prendergast (2003), but many samples from our study plot significantly outside this field. This suggests that not readily visible late stage alteration or chemical exchange such as partial dissolution has occurred. Whether such alteration is associated with Grasberg-Ertsberg district intrusions or meteoric water circulation during earlier compressional tectonism is unknown. Some chemical variability due to interaction with magmatic-hydrothermal fluids is likely, as indicated by an increase in Mn and decrease in Mg (Fig. 3a) with decreasing distance to intrusions that does not correlate with dolomite abundance. Variations in Pb, Sr, LREE, and U from proximal to distal environments are also observed.

The black ellipse on figure 3b displays calcite analyses from calcite partially replacing amphibole within GIC and nearby district skarn deposits Kucing Liar and Big Gossan. These analyses represent the assumed isotopic composition of the magmatic-hydrothermal fluids, and match the range of magmatic C-O isotopic variability in Sheppard and Harris (1985). Calculated δ18O of calcite values of 10-15‰ from the Ertsberg skarn (Meinert et al. 2003) are similar to δ18O values from skarn calcite measured in this study. The red ellipse shows results from breccias found at the contact between the GIC and surrounding limestones. The lower δ13C of these breccias and their similar δ18O compared to unaltered samples may indicate rock buffered δ18O isotopic conditions, with the lower δ13C isotope values due to CO2 rich magmatic fluids. This is supported by the work of Fu et al. (2003) who showed that fluid inclusions from the center of the GIC associated with early high temperature magmatic brines (>800°C) have higher metal contents and are CO2 rich and H2O poor.

A small number of calcite veins exhibit chemical signatures similar to NGLG limestone, however these may have formed pre-GIC emplacement during collision-related district deformation around 12 Ma.

**Figure 3.** Calcite C-O isotopic data from within and around the GIC. Values plotted are calcite isotopic concentrations, not water, as the temperature of calcite precipitation is unknown. a: average trace element concentration of the area sampled for C-O isotope analysis versus the δ18O value. The proximal (within 1 km) to distal (up to 6 km away) arrow shows the location of the samples relative to the GIC. b: δ13CVPDB ‰ versus δ18OVSMOW ‰. The black ellipse contains analyses of calcite from veins and amphibole replacements in samples from the GIC and nearby skarns. The red ellipse contains a population of limestone breccias with calcite matrix. The blue box depicts the isotopic range of unaltered NGLG limestone (Prendergast 2003).

**Figure 4.** Calcite δ18O versus distance from the center of the GIC. Filled blue squares are limestone, unfilled blue squares are veins, triangles are breccias, and green symbols are marble. Red stars show the position of West Grasberg and the center of the GIC.

The C-O isotopic and trace element compositions of calcite have been shown to be useful indicators of mineralizing processes and alteration footprints (Escalante 2008; Pass 2010; Vaughan et al. 2016). Proximal to intrusions and some distal calcite veins in the Grasberg-Ertsberg district show magmatic-hydrothermal signatures as indicated by their low δ18O. Calcite δ18O versus distance from the center of the GIC (Figure 4) shows that some calcite veins have magmatic-hydrothermal signatures up to 5 km to the east of Grasberg. These veins lie near the Meren Valley Fault, a major bounding structure on a transpressive strike-slip fault zone which was active during magma degassing and the emplacement of Grasberg (Sapiie and Cloos 2013). That calcite veins in limestone up to 5km from a major porphyry deposit are likely related to
that deposit is significant, but more importantly their systematic Mn:Mg increase with proximity to Grasberg (Fig. 3a) has great potential to be used for carbonate-hosted deposit vectoring. This parameter is thus a potentially valuable tool to identify hydrothermal deposits in carbonate terrains and other deposits hosted in similar geologic terrains need to be similarly investigated.

4 Conclusions

Veins found within the carbonate host rocks around Grasberg display systematic variations in δ18O and Mn:Mg content. These chemical variations are due to contributions from magmatic-hydrothermal fluids. Strike slip faulting during emplacement of the Grasberg porphyry deposit provided pathways for magmatic fluids to reach the distal environment (~5 km).

The presence of calcite veins in a carbonate hosted porphyry deposit cannot be immediately correlated with the emplacement of the Grasberg ore body as some veins show no textural or chemical evidence of magmatic-hydrothermal fluids. Isotopic and trace element analyses of calcite present a new and potentially effective tool for the detection of porphyry deposits in carbonate-hosted terrains which to date have proven challenging to explore, as they lack the widespread and characteristic alteration zones found around porphyry deposits hosted within volcanic or clastic sedimentary rocks.

Acknowledgements

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References


Exploration targeting in porphyry Cu systems using propylitic mineral chemistry: a case study of the El Teniente deposit, Chile

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Abstract. The mineral chemistry of epidote and chlorite from the propylitic halo at El Teniente, in samples collected at distances up to 6.6 km from the deposit centre, was determined by microprobe and LA-ICP-MS analysis. Results show that both minerals incorporate a range of trace elements in a systematic way that define a much larger footprint to the system than is easily recognised using conventional means. In chlorite, geothermometry temperatures, Ti and V are high proximal and Li, As, Co, Sr, Ca and Y are low proximal (high distal); ratios of these elements define gradients towards ore varying over 3-5 orders of magnitude. In epidote, As defines a broad proximal low and is generally elevated at distances of at least 3 km from the edge of the ore shell. Zn, La, Yb, Y and Zr amongst others appear to define a geochemical shoulder that surrounds the deposit. These patterns are broadly similar to those observed in previous work at Batu Hijau and in the Baguio District suggesting that these minerals behave consistently and can therefore provide useful exploration tools within propylitic “green rocks”.

1 Introduction

Porphyry ore deposits represent remarkable accumulations of metals, in particular Cu, Mo and Au, precipitated from hydrothermal fluids in an intrusive host and its surrounding country rocks. Deposits are typically centred within an alteration halo with characteristic mineralogical and chemical zoning patterns (Cooke et al. 2014a). This footprint is a key guide for exploration, providing a larger (up to 10 km radius) target area within which mineralization may exist. The most distal alteration facies, the propylitic zone, has been traditionally regarded as a largely isochemical alteration domain containing little information of use in exploration. Furthermore, the mineral assemblages that characterise this zone may be present within barren hydrothermal systems, or produced by processes such as regional metamorphism. The lack of research in this environment means that the controls on the formation of these huge alteration zones are incompletely understood. However, because they are so laterally extensive and frequently encountered, an enhanced capability to explore within this domain would be extremely powerful. Indeed, recent work (Cooke et al. 2014b; Wilkinson et al. 2015), part of a series of AMIRA research projects led by the University of Tasmania, has shown that valuable chemical information is locked up in epidote and chlorite that can provide useful exploration insights. Here, we present the results of a study of the propylitic halo of El Teniente, one of the largest porphyry Cu-Mo systems known, in order to assess whether previously documented patterns are reproduced. We consider the differences between the giant El Teniente system and previous results from the smaller porphyry systems studied in the Baguio District, Philippines and Batu Hijau, Indonesia.

2 El Teniente geology

El Teniente is located on the western margin of the Andean Cordillera, approximately 70 km southeast of Santiago, within the confines of the Central Chilean porphyry copper belt. It is the world’s largest underground Cu mine, hosting a pre-mining resource of approximately 95 Mt of fine Cu (Camus 2002; Stern et al. 2010) and is the world’s largest known resource of Mo (Sillitoe 2010) with current+mined resource total of approximately 2.5 Mt (Camus 2002).

The deposit is hosted by a late Miocene volcanoplutonic complex (Fig. 1), referred to as the Teniente Mafic Complex (TMC), within the mid-late Miocene Farellones Formation, a >2,500 m thick sequence of extrusive and intrusive rocks of basaltic to rhyolitic composition (Skewes et al. 2002). In the late Miocene-Pliocene (~6.5-4.5 Ma), the TMC was intruded by a series of diorite to granodiorite intrusions, with which multiple igneous and hydrothermal breccia complexes are associated. Mineralisation appears to have developed in concert with three main magmatic episodes (Spencer et al. 2015), each of which was associated with its own pulse of hydrothermal activity (Vry et al. 2010). Thus, it has been concluded that the deposit represents a nested Cu-Mo porphyry system formed by the emplacement and overprinting of a number of porphyry intrusions that evolved separately in space and over time (Vry et al. 2010; Spencer et al. 2015).

Propylitic alteration at El Teniente forms a distal halo surrounding a core of potassic alteration (intense biotite-magnetite alteration, and K-feldspar within intermediate-felsic intrusive rocks). It has not been extensively studied but is mostly characterised by replacement of hornblende and augite in the TMC by chlorite, and plagioclase phenocrysts by epidote.
3 Methods

Approximately 130 samples of the Teniente Mafic Complex (basaltic to andesitic volcanic rocks) and intrusions (dolerite, tonalite, diorite, granodiorite, monzonite) were sampled for analysis (Fig. 1). Sub-samples containing minerals of interest were prepared as polished resin mounts for SEM backscattered electron imaging of mineral relationships, electron microprobe wavelength dispersive analysis (EMP-WDS) and laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS). Major and minor elements in individual chlorite and epidote grains were determined using a Cameca SX100 electron microprobe housed in the Central Science Laboratories at the University of Tasmania. Major, minor and trace elements in the same grains were measured using a New Wave 193 nm solid-state laser coupled to an Agilent 7500cs quadrupole mass spectrometer, located in the School of Physical Sciences, Discipline of Earth Sciences, University of Tasmania. Typically, 5–10 spot analyses were acquired from each sample, from within 3–5 separate mineral grains. In total, 651 LA-ICP-MS spot analyses of chlorite (from 116 samples) and 617 of epidote (from 110 samples) meeting quality control criteria were obtained.

Aluminium and calcium concentrations determined by microprobe were used as the internal standards for chlorite and epidote respectively, and NIST612 standard reference material was used for external calibration of the LA-ICP-MS results according to standard practice.

4 Results

4.1 Chlorite geochemistry and thermometry

Major element compositions of chlorite correspond to the clinochlore-chamosite solid solution with a wide range in Fe (8-23 wt%) and Mg (16-6 wt%) content. Median Al and Si contents are 10.2 and 13.2 wt% respectively. Mn contents determined by microprobe range up to 6.1 wt% but the vast majority are <2 wt% Mn.

Chlorite crystallisation temperatures were calculated from microprobe data using the thermodynamic model of Walshe (1986). Sample average temperatures are in the range 113-356°C with an overall mean of 241°C. Gridding the data (Fig. 2) shows that the temperatures define a clear thermal anomaly associated with the ore deposit.

4.2 Chlorite trace element zonation

After the major elements, Mn, Ca, Zn, V, Co and Ni are the most common components (in decreasing order of abundance). However, As, Ba, Ce, Cu, K, La, Li, Na, Pb, Sn, Sr, Ti, Y and Zr were also detected in more than two-thirds of the analyses, with the lowest limits of detection for some elements at ~4 ppb.

Clear spatial zonation patterns are observed around El Teniente for a number of trace elements in chlorite, including proximal lows for Li, As, Co, Sr, Ca, La and Y and proximal highs for Ti and V (Figs. 3, 4).
Figure 3. Gridded chlorite compositional data (log of sample average, cell size 200 m, minimum smoothing distance 4 cells) for trace elements showing proximal lows. Outline of the 0.5 wt% Cu shell is shown for reference. Note the apparent westward offset between some of the chlorite anomalies and the location of the orebody at depth.

Figure 4. Gridded chlorite compositional data (log of sample average, cell size 200 m, minimum smoothing distance 4 cells) for trace elements showing proximal highs. The Ti anomaly coincides with the ore shell; the V anomaly forms a very proximal shoulder. Outline of the 0.5 wt% Cu shell is shown.

4.3 Epidote geochemistry

Major element compositions correspond to epidote, with a systematic inverse correlation between Fe and Al representing compositions along the epidote-clinozoisite solid solution. Fe concentrations are mostly in the range 6-13 wt% (median 10.0 wt%) and Al in the range 10-15 wt% (median 13.3 wt%). The median Ca and Si contents are 16.5 and 17.3 wt% respectively. Mn contents determined by microprobe range up to 2.4 wt% but the vast majority are <1 wt% Mn.

4.4 Epidote trace element zonation

Systematic patterns in the trace element composition of epidote are observed for several elements, including As, La, Yb, Zn, Y and Zr (Fig. 5). Arsenic shows a very broad proximal low that is roughly centred on the ore body and extends for >3 km from the edge of the ore shell. Halo-type anomalies appear to be present for the other elements shown with peak concentrations reached about 1-2 km from the edge of the orebody.

Figure 5. Gridded epidote compositional data (log of sample average, cell size 200 m, minimum smoothing distance 4 cells) for trace elements showing proximal lows. Outline of the 0.5 wt% Cu shell is shown for reference. Note the apparent westward offset between some of the epidote anomalies and the location of the orebody at depth.

5 Discussion

5.1 Chlorite vectoring

Results from chlorite geothermometry confirm that the El Teniente deposit sits within a strong thermal anomaly that extends beyond the ore zone into the propylitic halo. This is comparable to that previously observed for Batu Hijau (Wilkinson et al. 2015).

Chlorite is enriched in Ti in a bullseye-type anomaly that is coincident with the thermal anomaly, consistent with the conclusion from Batu Hijau that Ti substitution into chlorite is thermally controlled (Wilkinson et al. 2015). The Ti content of chlorite is a more sensitive vector towards the porphyry centre than temperature because it varies over two orders of magnitude (6–650 ppm). V shows a proximal anomaly, but forms more of a geochemical shoulder that sits on the fringe of the ore shell; behaviour that is also very similar to Batu Hijau.

A number of elements show proximal lows, with Li being a particularly good example. This is attributed to mobility of Li (and also Co, Sr, Ca and REE-Y) in potassic and proximal propylitic fluids as has been constrained in
the Northparkes Cu-Au porphyry cluster, New South Wales, Australia (Pacey 2017).

As vectoring tools, element ratios in chlorite are particularly effective because they can enhance significantly the signal gradient around a porphyry centre and provide a better discrimination from background. Ratios identified at Batu Hijau are shown in Figure 6 for El Teniente, with the addition of V/Li. These ratios vary over 3-5 orders of magnitude and clearly define the mineralised centre of the system. The Ti/Li anomaly is rather remarkable in that it precisely maps the ore shell, including its triangular form, and extends up to ~5 km from the system centre. The ratios involving Ni appear to define a proximal shoulder rather than the bullseye patterns of the others, and a similar effect is noted for the ratios with V as numerator. In particular, the V/Ni ratio defines a halo maximum situated at 1-2 km from the edge of the ore shell. The V/Li ratio is interesting in form, with a distinct ridge extending to the south into the area of the new resource that has been defined to the south of the main mine. The Mg-bearing ratios proposed for Batu Hijau do not clearly define the system at El Teniente, probably because of the influence of protolith composition: proximal samples are dominated by intermediate to felsic intrusive lithologies as opposed to the basaltic to basaltic andesite composition of the majority of the remainder. However, there is no indication that the trace element patterns are significantly protolith controlled, with the possible exception of Ni.

Figure 6. Gridded chlorite trace element ratios (log of sample average, cell size 200 m, minimum smoothing distance 5 cells). Outline of the 0.5 wt% Cu shell is shown for reference.

5.2 Epidote vectoring

Epidote trace element patterns generally define a broader, but less well-defined footprint than chlorite. Arsenic is the best vector element, displaying a broad low in proximity to ore, with a distal enrichment to at least 5 km from the system centre. Other elements appear to define a geochemical shoulder with maxima at varying distances from the centre, but typically at 1-2 km from the edge of the ore shell. These patterns are broadly similar to those identified in the Baguio District (Cooke et al. 2014).

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References

Chalcopyrite as an indicator mineral to fingerprint mineral deposit types: a preliminary study

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Abstract. Chalcopyrite is a reliable indicator mineral in exploration as it occurs in numerous mineralization types, is resistant to weathering, and its trace element composition varies substantially from one deposit type to another. It is possible to recognize the major types of mineral deposits using Se, Zn, Ba, Ag, Ni, and Sn concentrations of chalcopyrite analyzed by electron probe microanalysis (EPMA) as they are significantly higher than the detection limits. Ni-Cu and Opemiska Cu vein chalcopyrites are enriched in Ni, VMS in Zn-Ag, and PGE and porphyry deposits are moderately enriched in Zn. Silver, Ni, Pd, Se, In, and Zn data obtained by laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) are also commonly above the detection limits and are particularly useful to distinguish the types of mineralization. Ni-Cu and PGE chalcopyrite is richer in Pd-Ni, VMS and porphyry in Ag, and VMS, Ni-Cu, PGE deposits show high Zn contents. Chalcopyrite from VMS, skarn, and Opemiska Cu vein deposits contains high In contents. PCA analysis of the LA-ICP-MS data indicate that Ag, As, Au, Cu, Ni, Pd, Sn, Te, and Zn are discriminant elements to differentiate chalcopyrite from distinct deposit types.

1 Introduction

Chalcopyrite has the potential to be a useful indicator mineral for exploration. It is a common mineral in various types of mineralization and is resistant to mechanical and chemical weathering. Furthermore, the recent works of Plouffe et al. (2016) on the till geochemistry and mineralogy near Cu porphyry deposits in British Columbia (Canada) demonstrated that chalcopyrite represents a good indicator mineral for Cu-Au porphyry mineralization even if it is less abundant in weathered/oxidized till. However, this mineral is poorly studied compared to magnetite, garnet, and other indicator minerals, as it contains low abundance of most trace elements. Fleischer (1955) and Hawley and Nichol (1961) were the first to analyze the trace element content of chalcopyrite. Afterward, studies were mainly focussed on the chalcopyrite composition in a specific deposit or on the partitioning of trace elements between sulphides (Harris et al. 1984; Cabri et al. 1985; Steininger 1986; Huston et al. 1995; Butler and Nesbitt 1999; Titley and Ruiz 2005; Barnes et al. 2008; Masslenikov et al. 2009; Dare et al. 2010; Dare and Barnes 2011; Wang et al. 2015; George et al. 2016). Among these studies, Huston et al. (1995) interestingly noted that Ag, In, Sn, Zn, and Se substitute in the lattice of chalcopyrite, whereas Pb, Bi, and Ba occur as mineral inclusions. It is only recently that Lazich (2010) highlighted the potential of the trace element compositions of chalcopyrite to discriminate ore deposit types.

In this preliminary study, we report chalcopyrite trace element compositions analyzed by electron probe microanalysis (EPMA) and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) from 16 deposits from a range of deposit types, including Ni-Cu, PGE, VMS, porphyry, skarn, IOCG, Opemiska Cu vein, Kupferschiefer, and orogenic gold (Table 1), in order to outline the geochemical signatures characteristic of each mineral deposit type.

Table 1. Total number of grains analyzed by EPMA and LA-ICP-MS.

<table>
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<th>Deposit type</th>
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<th>Number of grains (LA-ICP-MS)</th>
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</table>

2 Methodology

2.1 EPMA

Minor and trace element contents of chalcopyrite (Ag, Ba, Cd, Co, Cr, Cu, Fe, Hg, In, Mn, Ni, Pb, S, Se, Sn, Ti, V, W, Zn) were determined with a CAMECA SX-100 five spectrometer EPMA at Université Laval (Québec, Canada). Analytical conditions included an accelerating voltage of 25 kV, a 100-nA beam current, and a counting time of 40-60 s on peak and 20 s on background. Calibration standards used were simple oxides (GEO Standard Block of P and H developments) and minerals (Mineral Standard Mount MINM 25-53 from Astimex Scientific Limited; Jarosewich et al. 1980).
2.2 LA-ICP-MS

Chalcopyrite were analyzed to obtain the average composition of a grain by abating a linear trench or a deep pit, especially for those with micro-inclusions, as described in Dare et al. (2012). Trace element contents (Ag, As, Au, Bi, Cr, Cu, In, Ir, Mn, Mo, Ni, Os, Pb, Pd, Pt, Ru, S, Sb, Se, Sn, Te, Ti, V, W, and Zn) were determined using a RESolution M-50 Excimer 193 nm laser coupled to an Agilent 7700xx ICP-MS at the Université du Québec à Chicoutimi (UQAC, Québec, Canada). Beam sizes of 55 μm and 44 μm (rarely 33 μm) were used depending on the grain size. For the trenches, a speed stage of 7.5 μm/s, a laser frequency of 15 Hz, and a power of 2.5 J/cm² were used. For the point analysis, a laser frequency of 15 Hz and a power of 13 J/cm² were used for 35 s analyses. Three certified reference materials (MASS1-C, LAFLAM_C, B_MSS5_A) were used for calibration and the quality of the data was monitored using two different reference materials (B_MSS5_A, AI3-1). Data reduction was completed with the software Iolite.

3 Statistical analysis

Chalcopyrite typically contains low abundance of most trace elements. Hence, several data measured by EPMA or LA-ICP-MS are censored because their value is below detection limits (Helsel 2005). A number of methods exist to process these censored data, such as the exclusion of data or the arbitrary substitutions. In this study, the data were imputed using the imputation of k-nearest neighbors as described in Makvandi et al. (2016). The data were also transformed to centered log-ratio to overcome the effect of closure (Makvandi et al. 2016). Centered log-ratio transformation is symmetric with an orthonormal basis and recommended for multivariate statistical techniques like principal component analysis (PCA). Our transformed results were then analyzed using PCA, following Makvandi et al. (2016), in order to investigate the complex variance in compositional data by sorting out discriminator elements which differentiate the geological samples based on their chemical composition.

4 Results

Samples from the 16 deposits include a variable proportion of chalcopyrite grains (~4-90%) in the mineral assemblage. These grains are fine- to coarse-grained, anhedral, and typically contain inclusions of oxides, sulphides, and/or silicates.

4.1 EPMA

EPMA data are mostly below or close to the detection limit. Among the 16 minor and trace elements analyzed, Se, Zn, Ba, Ag, Ni, and Sn display concentrations significantly higher than the detection limits. Chalcopyrite from Ni-Cu and Opemiska Cu vein deposits are enriched in Ni compared to the other deposit types. VMS chalcopyrite is characterized by high Zn and Ag contents (>450 ppm and >135 ppm, respectively) as well as higher values of Se, Sn, and Ag. PGE and porphyry deposits also contain chalcopyrite moderately enriched in Zn (>100 ppm).

4.2 LA-ICP-MS

The LA-ICP-MS data of 18 (Ag, As, Au, Bi, Cu, In, Mn, Ni, Pb, Pd, Ru, S, Sb, Se, Sn, Te, Ti, V, W, and Zn) out of 25 elements measured contain less than 40% censored values. Overall, chalcopyrite from VMS and porphyry deposits has high Ag concentrations (~100 ppm), whereas orogenic gold chalcopyrite is typically depleted in Ag (Fig. 1), as well as in Se. High Zn contents (~100 ppm) are measured in VMS, Ni-Cu, and PGE deposits, whereas Zn values in skarn and Kupferschiefer deposits are low (<10 ppm; Fig. 1). Palladium and Ni contents in Ni-Cu and PGE deposits are generally higher than Pd-Ni contents in the other deposit types. In particular, Pd concentrations in skarn deposits are very low. Furthermore, chalcopyrite from VMS, skarn, and Opemiska Cu vein deposits contains high In contents (>10 ppm).

![Figure 1. Zn versus Ag discriminant diagram (LA-ICP-MS data) for chalcopyrite from different type of ore deposits.](image)

4.3 PCA

Principal component analysis was carried out to classify various mineral deposit types based on trace element compositions of chalcopyrite (Fig. 2). The loadings plot illustrates positive correlations among elements plotting in the same quadrant, and negative correlations among those in opposite quadrants. The correlations among elemental variables control the samples distribution in the PCA scores scatter plot (Fig. 2b). As a result, chalcopyrite from VMS deposits forms a distinct cluster in the low t1, high t2 region indicating that these grains mainly contain higher Ag, Zn, Sn, and Sb contents relative to those from other deposit types. In contrast, chalcopyrite from orogenic gold deposits forms an overlapping cluster in the high t1, low t2 region because of enrichment in Cu, Ru, and S and depletion in Ag (Figs. 2a & b). The 2 analyses from Kupferschiefer deposit plot in the vicinity of orogenic gold chalcopyrite indicating that they share similar chemistry. Chalcopyrite from PGE deposits forms a distinct cluster and has the same signature.
as Ni-Cu deposits (low t1, low t2).

The dispersion of Ni-Cu and IOCG deposit samples in figure 2b suggests that these deposits are characterized by variable compositions of chalcopyrite. Although some chalcopyrite groups such as Opemiska Cu vein, skarn, and porphyry make overlapping fields in PCA t1-t2, their scores contribution plots (Fig. 2c) indicate that these groups are discriminated by distinct mean compositions. Positive/negative contribution of an element indicates that the average composition of that element for a group of interest is greater/lower than the average composition of the whole dataset (Makvandi et al. 2016). For instance, chalcopyrite from skarn deposits is mainly separated from the others because of positive contribution of In and negative contribution of Ni, Pd, and Zn. Figure 2c also indicates that in comparison with the other groups, chalcopyrite from Opemiska Cu vein is poor in Ag and Pd, and enriched in In and Ni.

Our preliminary results are comparable to the results obtained by Lazich (2010). In general, he observed that individual samples are chemically uniform but that there is small but distinct difference in the geochemistry of various generations of chalcopyrite from one deposit. We observed such chemical uniformity among distinct samples but have yet to test different paragenetic stages of chalcopyrite. Lazich (2010) identified high Ni-Se contents in

Figure 2. Principal component analysis results of LA-ICP-MS data for chalcopyrite from different deposit types. a PC1-PC2 (first and second loadings) shows correlations among elements in chalcopyrite. b t1-t2 (first and second scores) shows the distribution of chalcopyrite from different deposit types in the latent variable space defined by PC1-PC2. c Examples of score contributions plots for some deposit types (note change in scale of score distributions between diagrams).
chalcopyrite from magmatic deposits as well as higher Pd values in Ni-Cu deposits. We also find that Ni-Cu and PGE chalcopyrite is characterized by higher Pd-Ni contents. Our VMS and porphyry chalcopyrite samples are enriched in Ag-Zn ± Sn, as shown by Lazich (2010) in granite related deposits. Orogenic gold deposit chalcopyrite is depleted in Ag and is enriched in Au. Lazich (2010) similarly observed that orogenic gold chalcopyrite has high Au contents.

5 Conclusion

The EPMA and LA-ICP-MS data show a large range of composition for chalcopyrite from various types of deposits. PCA results indicate that it is possible to distinguish the different deposit types based on the chalcopyrite trace element compositions. VMS chalcopyrite appears to be best discriminated using Ag, Sn, Zn, and ± Se, Ni-Cu and PGE chalcopyrite using Ni, Te, and Pd, orogenic gold and Kupferschiefer chalcopyrite using Au, As, and Cu, porphyry and skarn chalcopyrite using Sb, In, and ± Se, and IOCG chalcopyrite using ± Zn and ± Ba. This preliminary study will be followed by a worldwide investigation of chalcopyrite chemistry from a larger sample database, improved LA-ICP-MS and EPMA methodologies to measure more trace elements, and a more thorough study of the mineralogy and ore-forming processes that control partitioning of trace elements in chalcopyrite. This will give the capacity to use chalcopyrite as a reliable indicator mineral in exploration.

Acknowledgements

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Quantifying and improving the quality of gold grain counts in heavy mineral concentrates

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Abstract. Mineral exploration in glaciated terrain is limited by the capacity to characterize indicator minerals (identification, abundance, size, and shape). Identification and characterization of indicator minerals is a time-consuming technique that requires a great amount of human and technical resources. There are presently no reference materials available for gold grains within heavy mineral concentrates from glacial sediments. The lack of proper reference material makes it difficult to assess the quality of gold counts and thus, gold counts remain impossible to quantify. A new reference material has been produced by mixing gold grains with sterile heavy mineral sediments, followed by homogenization (bed blending), and mass reduction. To be statistically significant and to properly simulate real life conditions, the mass test portion is approximately 1 g and contains about 80 gold grains, thus being above typical background levels for the Canadian Shield. The number of gold grains is then assessed through optical and scanning electron microscopy (SEM) counting and X-ray microtomography. The reference material is tested using an automated optical reconnaissance system developed to characterize grams of indicator minerals over the course of a few minutes. This is a first step in bringing quantitative quality assessment to gold grain counting.

1 Introduction

Gold exploration in glaciated terrains is an important economic activity. Glacial overburden covers most outcrops thereby masking bedrock. However, glacial sediments (tills) are used as a proxy in exploration geology (Averill 2001). For assessing till, the most efficient technique is the use of indicator mineral grain counting in heavy mineral concentrates. Extensive exploration programs are based this technique without any tool to address quality. For example, a large number of gold grains found in heavy mineral concentrates within a till sample suggests a proximity to a gold deposit (Genes and Nichol 1987). The shape and size of gold grains and other indicator minerals also provide important characteristics that indicate the proximity of mineral deposits (DiLabio 1982, 1985, 1991; Townley et al. 2003). Typically, thousands to millions of heavy minerals grains are extracted from a 10-kg till field sample from which a few gold grains are counted (10 to 50).

Identification and characterization of indicator minerals, which are few in a mass of gangue minerals, is a time-consuming technique that requires a significant amount of human and technical resources. Grains are either counted and picked by trained personnel under an optical microscope or counted using a SEM. To our knowledge, there are no quantitative assessments to assure the quality of counting or picking nor the quantification of the uncertainty.

The main goal of this project is to develop a technique for quantifying the quality of gold counts. We propose that a reference material having a known number of gold grains in a matrix that mimics heavy mineral separates can provide a quantified means for assessing the quality of gold counts, either for use in routine analysis or for training a mineralogist in gold grain counting. At present, counting techniques are approximately at the same stage as geochemistry prior to the advent of reference materials. At that time, different laboratories would produce strikingly different results for the same material (Abbey 1980). The advent of matrix matching reference materials permitted the production of consistent results between laboratories. We believe that this new reference material will be the first step in assuring the quality of gold counting.

2 Reference material production

We selected the number of gold grains for test mass portions to represent a reasonable number of grains to count and to represent a statistically significant number above typical background counts from heavy mineral concentrates recovered from the Canadian Shield. Typical heavy mineral concentrates (derived from a compilation of 811 Geological Survey of Canada reports) tend to vary between 1 to 15 gold grains with counts trailing rapidly off to a maximum of 50 gold grains (Fig. 1). For a skilled mineralogist, counting 100 grains is considered a significant task. As such, the number of gold grains in a test portion was to be fewer than 100 gold grains. However, counts of only 25 grains were statistically difficult to be reproducible given that a mineralogist missing a single grain would produce a 4% error. To be statistically reproducible, 70 grains per test mass portion was considered as a good goal to minimize counting uncertainties and to keep processing time reasonable.
Natural gold grains from the tailings of a formerly exploited deposit (Fig. 2; Anacon Mines, Montauban les Mines, Québec, Canada) were mixed with barren heavy minerals. Two tons of sediments collected at the tailings were initially concentrated using a shaking table (Fig. 2) and characterized using X-ray microtomography to ensure their number and shape were appropriate for test purposes. Heavy minerals from a barren till collected north of Saguenay (Québec, Canada) were concentrated on a shaking table. The heavy mineral concentrate contained minerals that could be misidentified (Fig. 3) for gold, such as sulfides (but no contamination such as brass chips) to ensure reference materials reflected conditions similar to natural samples. Gold grains and the heavy mineral concentrate were homogenized using a technique that mimics bed blending (Gy 1981); we repeatedly spread the heavy minerals in a slanted V-shaped support. Over multiple passes, we then added gold grains to the heavy mineral concentrate in a similar manner described above. Test mass portions were then extracted by multiple alternate micro-scooping of the blended bed to produce 1.5-g testing samples (Boivin et al. 2016).

X-ray microtomography was used to count the number of gold grains number in a test mass portion. An advantage of this approach is that the sample container remains closed thereby eliminating grain loss or contamination. Our initial results gave the number of gold grains per sample as being closer to 80 (Table 1). Preliminary results also showed that nearly half of the gold grains were smaller than 60 µm (Table 2), thus explaining the discrepancy between our expected and actual counts. The smaller grains were missed by the initial visual observation. Further testing of the reference material using SEM is currently underway. At the end of this testing period, our reference material will be available for distribution for assessing the quality of gold grain counting by trained personnel or automated systems.
3 Optical reconnaissance

Our gold grain reference material was used to calibrate a newly developed system that uses optical reflectance spectrum recognition to identify and determine grain size and shape to characterize heavy mineral concentrates (Néron et al. this volume). Gold has a unique optical reflectance spectrum having a steep slope between 450 and 800 nm (Clark et al. 1990; 2007). This unique reflectance spectrum makes it an ideal mineral for optical reconnaissance. Silver substitution was tested with an optical spectrometer, however gold grains with up to 20% Ag did not deviate significantly from pure gold spectrum (Simard et al. in preparation). Gold is easily identified in the developed optical reconnaissance system by subtracting the red minus blue spectral reflectance from a digital RGB (red-green-blue) image (Fig. 4).

4 Other minerals

There are several potential indicator minerals other than gold (Averill 2001; Turner et al. 2016) that warrant interest. With the acquired experience from developing our gold grain reference material, other indicator materials will be prepared, such as garnets, zinc oxides, etc.

Figure 4. Photomicrograph of heavy minerals with gold grains (red) identified by the developed optical reconnaissance system. Note that gold is effectively discriminated from sulfides.

5 Conclusion

Heavy mineral concentrates are useful for exploration geology, however their reliability is limited by the lack of a quantitative assessment of count quality. To address this issue, we produced a gold grain reference material that will permit a quantification of uncertainties related to grain counting. Given that a quantified assessment of counting is commensurate to the advancement of the field, the development of a reference material for gold grain counting is a major step toward for ensuring more robust exploration techniques. We are currently developing similar reference materials for other indicator minerals to permit quantitative assessments of grain counts.

Acknowledgements

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Primary halo zonation of the Luziyuan skarn-hydrothermal lead-zinc-iron deposit and its prospecting pattern vectoring concealed orebodies

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Abstract. Application of the variability index of indicator elements defined by Beus, A. A. and Grigorian, S. V., a detailed zonation sequence of indicator elements of the Luziyuan Pb-Zn polymetallic deposit is obtained as follows: Sb→Ni→Ag→Zn→Pb→Cu→Mo→W→Au→Co→As. According to the zonation, an index to vector orebody such as \((Sb\times Ni)/(Co\times As)\) can be constructed, which is ranged from 130 to 59 in the upper part of the deposit, 59 to 0.13 in the middle part of the deposit, and 0.13-0.09 in the lower part of the deposit. Therefore, the vectoring index can be regarded as a criterion for predicting the ore potential at a given depth.

1 Introduction

The recently discovered Luziyuan skarn-hydrothermal lead-zinc-iron deposit is located at the axis of the Luziyuan anticline, the southern segment of the Baoshan block which extends southwards to the Myanmar (Fig. 1a and b). It is the super-large Pb-Zn-Fe polymetallic deposit, which has a proven reserve of 4.5 Mt (Pb+Zn) with an average Pb grade of 2.61 wt% and average Zn grade of 3.42 wt%, 500 Mt TFe with an average grade of 33.16 wt%. In addition, it contains approximately 150 t of gold with an average grade of 0.35 g/t, and 0.35 million tons of copper with an average grade of 0.33% (Jiang et al. 2013).

In addition to the Luziyuan skarn-hydrothermal lead-zinc-iron deposit, significant skarn-hydrothermal lead-zinc polymetallic deposits have been discovered over the past 20 years in this block. These mineral deposits include the Hetaoping lead-zinc polymetallic deposit (Chen et al. 2005), the Jinla lead-zinc polymetallic deposit across China and Myanmar (Chen et al. 2009a). Most of these deposits are Himalayan in age (Chen et al. 2009b).

The Luziyuan deposit with 510m long, 200m – 500m wide, is made of three ore segment such as the Luziyuan, the Xiaohebian, and the Tianshengqiao from South to North. The orebodies are mainly hosted in the marbles and marbleized limestones, which were formed from Middle Cambrian marine carbonate rocks (Shahechang Group) metamorphosed by regional thermal dynamo metamorphism. The orebodies occur in bended and/or stratified veins which are fault-bounded by NNE-NE-trending, steeply northwest dipping thrust faults (Fig.1C). Recent drill holes with more than1000m deep illustrate that the Luziyuan ore segment is plunged to south, upper Pb-Zn orebodies (average grade Pb wt 4.6%, Zn wt 3.1%) with 61-89 m thick, lower Fe orebodies (TFe 27.65 %) with 3.06-56.81m think (Jiang et al. 2013). Metal minerals include mainly sphalerite, galena, chalcopyrite magnetite, pyrite, and arsenopyrite etc. The alteration minerals include calcite, quartz, chlorite, actinolite, rhodonite, and garnet etc.

Fluid inclusion studies indicate that the mineralization has two main stages: middle – low epithermal – mesothermal stage (homogenization temperatures varying from 160°C to 280°C) and middle – high temperature hydrothermal stage (homogenization temperatures ranging from 280°C to 420°C). The δ34S (9.23-10.17)×10^{-3} and 206 Pb/204Pb ratio (18.224-18.338), 207 Pb/204Pb ratio (15.715-15.849) and 208Pb/204Pb ratio (38.381-38.874) obtained from the galena indicate the partial role of magma hydrothermal fluid in mineralization (Xia and Chen, 2005).

Figure 1. Simplified map showing geology and mineralization of the Luziyuan mine district

There is an obvious zonation of alteration mineralization on the vertical direction as follows (from top to bottom): sphalerite – galena association with carbonation (calcite) → galena – sphalerite association with chloritization (chlorite, calcite, pyrite) → galena – sphalerite – chalcopyrite association with skarnization (chlorite, actinolite, arsenopyrite, rhodonite, ) → magnetite (gold) – sphalerite – galena – chalcopyrite association with...
skarnization (actinolite, rhodonite, garnet). It is inferred from gravity and rhodonite alteration that granites might exist in deep mine area.

2 Axial zonation of primary halos

The significance of studying the element features and zonation of primary halos is to try to establish the criteria for evaluating ore potential in depth. Eighteen elements such as Zn, Pb, Cu, Ag, V, Ba, Co, Cr, Sn, Sb, W, F, Ni, Au, Mo, As, Bi and TFeO were analyzed for fifty and four of different type of ore samples from No.71 exploratory line of the Luziyuan ore segment by the Henan Rock & Ore Analysis Center, China (Table 1).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Normalized Linear productivity (10^2 \cdot \text{m}^{-1})</th>
<th>Zonation indexes of indicator elements</th>
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<tbody>
<tr>
<td>Au</td>
<td>10^4</td>
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<tr>
<td>Ag</td>
<td>10^1</td>
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<td>Cu</td>
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<td>Pb</td>
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<td>Zn</td>
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<td>Mo</td>
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<td>As</td>
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<td>Sb</td>
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<td>Ni</td>
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<td>Co</td>
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<td>Σ</td>
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</table>

*The Au values and detection limit are expressed in ppb; the oxide values and detection limit are in wt%; other element values and detection limits are in ppm; (11) represents the sample number. X represents mean; K(concentration coefficient) = the average element concentration of ore / the corresponding element concentration of the Shahechang group

Table 2. Zonation indexes of indicator elements

<table>
<thead>
<tr>
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<td>Cu</td>
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<td>Zn</td>
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<td>Σ</td>
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It is indicated by comparison with the composition of the host rocks (the Shahechang group marble) that the different types of ores are consistently enriched in Pb, Zn, Cu, Au, Bi, Ag, Sb, W, F, Co, As, and Mo, which implies that the enriched elements with clear anomaly can be
regarded as pathfinders for prospecting the ore bodies at depth within this district.

Figure 2. Geological section and primary halos of the No. 71 exploratory line in the Luziyuan mine district

Axial zonation is expressed in the direction of movement of ore-bearing solutions (Beus and Grigorian, 1977; Chen and Zhao, 1998; Chen and Han, 2010). A total of 168 samples collected from four drill cores were used for the establishment of the axial zonation of the primary halo. Eighteen variables including Au, Ag, W, Mo, F, B, As, Sb, Cu, Pb, Zn, Cr, Ni, Co, V, SiO₂, K₂O, and Na₂O were analyzed for each sample using the same analysis techniques shown in Table 1 by the Henan Rock & Ore Analysis Centre. There is obvious a zonation of primary halos of the indicator elements. The strong anomalies in Sb, Ni, Pb and Zn coincide with the middle and upper part of the orebodies; but anomalies in As, Co, and W are stronger than the formers in middle and lower part of the orebodies; and Ag, Au, Cu and Mo developed in the whole orebody (Fig. 2). These anomalies are mainly caused by the alteration and mineralization (Fig. 3). The zonation index (D) of indicator elements is defined as the ratio of the linear productivity of the halo formed by the given element, to the sum of the linear productivities of the halos of all indicator elements in the type of mineralization being studied, which can be calculated using Grigorian’s method (Beus and Grigorian, 1977). The zonation sequence of indicator elements established according to the zonation index (see Table 2) is as follows: (Sb-Ni)→(Zn-Pb-Ag)→(Cu-Pb-Mo-W)→(Au-Co-As). Some indicator elements given above in parentheses do not have exactly expressed zoning relationships, because the maximum values of their zonation indexes were found to be in the same horizons of the primary halo. To further determine the position of these particular elements in the zonation sequence, the vertical variability index (G) can be used with the help of the following formula (Beus and Grigorian, 1977):

\[ G = \frac{D_{\text{max}}}{\sum_{i=1}^{n} D_i} \]

where G is the variability index (or variability gradient); \( D_{\text{max}} \) is the maximum value of the zonation index of a given element; \( D_i \) is the value of the zonation index in the ith horizon, and n is the number of horizons (exclusive of the horizons of maximum accumulation). If \( D_{\text{max}} \) located in the upper level of \( D_i \), G is positive value, if not G is negative value.

For antimony and nickel, their maximum accumulation occurs at the level of the most upper horizon, the calculated results are as follows:

\[ G_{\text{Sb}} = 0.2316 \left( \frac{1}{0.201} + \frac{1}{0.043} + \frac{1}{0.021} \right) = 16.23, \]

\[ G_{\text{Ni}} = 0.2312 \left( \frac{1}{0.1143} + \frac{1}{0.0618} + \frac{1}{0.039} \right) = 15.43 \]

where \( G_{\text{Sb}} > G_{\text{Ni}} \), which suggests that should nickel follow antimony in the zonation sequence.

For gold, arsenic and cobalt, their maximum accumulation occurs at the level of the lowest horizon, the calculated results are as follows:

\[ G_{\text{Au}} = -0.0531 \left( \frac{1}{0.0447} + \frac{1}{0.0295} + \frac{1}{0.0295} \right) = -4.79 \]

\[ G_{\text{As}} = -0.4258 \left( \frac{1}{0.1553} + \frac{1}{0.0338} + \frac{1}{0.0298} \right) = -29.63 \]

\[ G_{\text{Co}} = -0.1368 \left( \frac{1}{0.1281} + \frac{1}{0.0116} + \frac{1}{0.0138} \right) = -22.77 \]

where \( G_{\text{Au}} > G_{\text{As}} > G_{\text{Co}} \), which suggests that should arsenic follow gold, and cobalt do arsenic in the zonation sequence.
sequence. For copper, lead, molybdenum and tungsten, their maximum accumulation occurs at the level of the middle horizons, the calculated results are as follows:

\[
\begin{align*}
G_{\text{Cu}} &= 0.0422(1/0.0053-1/0.0107-1/0.0128)=0.76 \\
G_{\text{Pb}} &= 0.1294 (1/0.0057-1/0.1293-1/0.0794)=20.07 \\
G_{\text{Mo}} &= 0.1164(1/0.0325-1/0.0355-1/0.0238)=5.27 \\
G_{\text{W}} &= 0.222(1/0.11+1/0.0289-1/0.0134)=22.23
\end{align*}
\]

where \(G_{\text{Pb}} > G_{\text{Cu}} > G_{\text{Mo}} > G_{\text{W}}\), which suggests that should lead follow tungsten, copper follow lead and molybdenum do copper in the zonation sequence.

Thus, the following sequence of indicator elements has been obtained to characterize the zonation of the halos: 

\[\text{Sb} \rightarrow \text{Ni} \rightarrow \text{Ag} \rightarrow \text{Zn} \rightarrow \text{Pb} \rightarrow \text{Cu} \rightarrow \text{Mo} \rightarrow \text{W} \rightarrow \text{Au} \rightarrow \text{Co} \rightarrow \text{As} .\]

3 Geochemical prospecting pattern

According to the zonation, the criteria of \((\text{Sb} \times \text{Ni})/(\text{Co} \times \text{As})\) can be constructed for assessment of ore potential at depth. The ratios of indexes such as \((\text{Sb} \times \text{Ni})/(\text{Co} \times \text{As})\) decreases abruptly with depth. The values are ranged from 130 to 59 in the upper part of the orebody, 59 to 0.13 in the middle part of the orebody, and 0.13-0.09 in the lower part of the orebody (Table 3 and Fig. 3). Therefore, it can be regarded as a criterion for predicting the ore potential at a given depth.

![figure 3](image)

**Figure 3.** Geochemical prospecting pattern of the Luziyuan deposit. \((\text{Sb} \times \text{Ni})/(\text{Co} \times \text{As})\) is the ratio of the multiplicative zonation index of the front indicator elements and end ones in the zonation sequence.

4 Conclusion

A detailed zonation sequence of indicator elements can be obtained using the variability index of indicator elements. According to the zonation, an index can be constructed and regarded as a significant criterion for predicting the ore potential at a given depth.

Acknowledgements

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Hyperspectral reflectance in mineral exploration: example from the Northwest Zone of the Lemarchant VMS deposit, Newfoundland, Canada

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Abstract. Hyperspectral reflectance spectroscopy has been widely available for more than 25 years and is now undertaken as a standard procedure by many exploration and mining companies. The data collected is used to characterize the mineralogy of alteration zones but is rarely used in conjunction with geochemical datasets. In this study, we integrate hyperspectral and whole rock geochemical datasets acquired at the Northwest Zone of the Lemarchant volcanogenic massive sulfide (VMS) deposit in order to determine the dominant formation processes and to establish new exploration parameters. The mineralization at the Northwest Zone is hosted in andesitic and dacitic rocks and exhibits intense hydrothermal alteration (e.g., high CCPI, AI and Ba/Sr lithogeochemical signatures) extending at least 300 m along strike of the andesitic and dacitic units. The alteration corridor has hyperspectral signatures that correlate with phengitic white micas with 2200W longer than 2215nm, and Mg-rich chlorites with 2250W shorter than 2252nm. The integration of hyperspectral reflectance, geochemical alteration proxies (i.e., AI, CCPI, Ba/Sr, Na₂O) and mass volume changes has documented specific alteration processes responsible for the alteration (i.e., seawater alteration versus silicification), which is not possible using hyperspectral reflectance or geochemistry alone.

1 Introduction

The Lemarchant deposit is a type example of an Appalachian precious metal-bearing bimodal-felsic volcanogenic massive sulfide (VMS) deposit (Gill et al.; in press; Cloutier et al. 2017). Globally, bimodal-felsic (i.e., Kuroko-type) VMS deposits are Zn-Pb-Cu-rich, stratabound to stratiform, syngenetic deposits that form on or near the seafloor by precipitation from hydrothermal fluids (e.g., Franklin et al. 2005; Hannington 2014). They are often capped by massive barite and hydrothermal exhalative mudstone. The current VMS genetic model involves hydrothermal convection of cold seawater driven by heat transfer from either oceanic crustal heat flow and/or deep subvolcanic magma chambers (Franklin et al. 2005; Galley et al. 2007; Hannington 2014). Distal alteration associated with Mg-Na-Ca-Fe ± (Si, CO₂) enrichments develops as cold seawater infiltrates the basement (i.e., kms to 10s of kms). Proximal to upflow or discharge zones (i.e., m to 100s of ms), a zoned pipe-like alteration develops. This alteration is associated with strong and pervasive Na-Ca-depletions and variable enrichments in Fe, Mg, Si, K, base metals ± CO₂.

Mineralogically, chlorite occupies the central zone whereas white mica occupies the outer zone (Franklin et al. 2005; Galley et al. 2007; Hannington 2014).

![Figure 1. Geological map of the Lemarchant deposit (modified from the resource map of Canadian Zinc Corporation)](image-url)

Traditionally, lithogeochemistry has been the dominant exploration tool for VMS deposits with most published studies focusing on establishing alteration parameters to delineate alteration zones associated with the mineralized area (e.g., Ishikawa et al. 1976; Spitz and Darling 1978; Large et al. 2001) and on determining the prospectivity of VMS belts (e.g., Lesher et al. 1986; Swinden et al. 1989; Hart et al. 2004). Hyperspectral reflectance has gained in popularity over the last 25 years in the exploration and mining sector and is now collected as standard analysis. The data obtain is used to characterize the mineralogy of alteration zones but is rarely used in conjunction with geochemical datasets. In this study, we integrate hyperspectral and whole rock geochemical datasets acquired at the Northwest Zone of the Lemarchant VMS deposit in order to determine the dominant formation processes and to establish new exploration parameters.

2 Geology of the Lemarchant deposit

The Lemarchant VMS deposit (1.24 Mt at 0.58% Cu, 5.38% Zn, 1.19% Pb, 1.01 g/t Au, and 59.17 g/t Ag; CIM-
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NI43-101; Fraser et al. 2012) is located within the Tally Pond group of the Exploits Subzone of the Appalachian orogeny of central Newfoundland, Canada (Fig.1; Copeland 2008; Fraser et al. 2012). The lithostratigraphic units present at Lemarchant comprise four volcanic packages that have been offset by faulting (Fig 2a; Cloutier et al. 2017). The lithostratigraphic units consist of two distal andesitic volcaniclastic packages (packages 1 and 2), a proximal package (package 3) consisting of andesitic to dacitic massive flows and associated autoclastic volcaniclastic, and a mafic volcanic package (package 4).

The Northwest Zone ranges in thickness from 1.8 to 29.8 m, strikes northwest, dips steeply (~60°) towards the northeast and is found in the immediate footwall of the folded LJ shear zone (Cloutier et al. 2017). It is hosted within the massive dacitic flows of package 3. The mineralization is associated sphalerite, chalcopyrite, galena, pyrite and pyrrhotite with minor sulfosalts (i.e., tetrahedrite-tennantite), bornite, stromeyerite, electrum, bladed barite, Ca-Fe-Mg-Mn-carbonate, and enrichments in epithermal suite elements (i.e., Au, As, Bi, Co, Cr, In, Mo, Ni, Sb, Se, Te; Gill et al. in press), which are atypical of VMS. Alteration associated with the mineralized zone is characterized by intense and localized Ba-enrichment, quartz, sericite and chlorite hydrothermal alteration (Fraser et al. 2012; Cloutier et al. 2017). Late mafic and felsic dikes intrude the felsic and mafic volcanic rocks of the Tally Pond group.

3 Alteration footprint – section 106+00N

3.1 Geochemistry

The rocks at the Northwest Zone have experienced variable alteration, and elevated Zn values (>1,000 ppm) correlate with high CCPI and Al values, Ba/Sr ratios and low Na2O values within the immediate footwall of the LJ shear zone and above the Lemarchant shear zone (Fig 2a-c). Low Al values and Ba/Sr ratios, and high Na2O values are found in the intermediate volcaniclastic rocks of packages 1 and 2 in the hanging wall of the Lemarchant shear zone in the western portion of section 106+00N, and in the mafic volcanic rocks of package 4, the Pacman mafic intrusion, and the various felsic intrusions in the footwall of the Lemarchant shear zone (Fig. 2a-c).

3.2 Mass balance

To quantify mass losses and gains during alteration, the multiple precursor method of MacLean (1990) was used. A subset of 4 samples from packages 1, 2 and 3 was selected based on low loss on ignition (LOI), low base metal values, minimal Na2O depletions, and trace element geochemistry following the expected fractionation on a TiO2 vs Al2O3 plot (i.e., no obvious mass gain or loss). Mineralized areas show a strong positive correlation with gain in SiO2, K2O, Fe2O3, Na2O, Zn, and BaO (Fig. 2d). Above the Lemarchant shear, an area of mass gain is observed in drill core LM08-27 and LM08-28 and may indicate a pathway used by hydrothermal fluids (Fig. 2d). This mass gain area is surrounded by a zone of overall mass loss extending outside the study area in both east and west directions (Fig. 2d).

3.3 Hyperspectral reflectance

Diagnostic shortwave infrared (SWIR) minerals present are white mica and chlorite. Long 2200 nm absorption features (2200W) towards phengitic composition (2200W > 2215 nm) are observed surrounding the VMS package, the Pacman intrusion and within felsic intrusions whereas white mica short 2200W towards paragonitic composition (2200W > 2205 nm) is observed at a 45-degree angle crosscutting rocks of packages 2, 3 and 4, and is not associated with any visual changes in the rocks (Fig. 3a). Chlorites from the dacitic rocks have distinctive short 2250 nm absorption features (2250W) between 2248 and 2254 nm corresponding to Mg and Fe-Mg chlorite (Fig. 3b). Chlorites from the other lithostratigraphic packages tend to have longer 2250W values greater than 2254 nm, closer to the Fe-Mg and Fe chlorites.

The relative abundance of white mica and chlorite can be quantified hyperspectrally by investigating the relative depth (D) of their absorption features (2200 nm and 2320 nm for white micas, 2250 nm and 2320 nm for chlorite, and 2320 nm for carbonates). Areas proximal to mineralization correlate with an increase in phengitic white mica, Mg chlorite, and carbonates (Copeland 2008; Fraser 2012; Gill et al in press; Cloutier et al 2017; this study). Areas enriched in white micas are highlighted by areas with 2200D/2320D > 1.5 (Fig. 3c), whereas areas with 2250D/2320D > 0.75 have chlorite as the dominant infrared responsive mineral (Fig. 3d).

4 Hydrothermal processes associated with the Northwest Zone

At Lemarchant, the position of the 2200 and 2250 nm absorption features in andesitic and dacitic rocks does not correlate with Al2O3/TiO2 and suggests that they are at least partly controlled by secondary alteration processes.

In VMS systems, secondary white mica generally forms by gradual hydrolysis of feldspar (e.g., Ohmoto 1996; Franklin et al. 2005; Galley et al. 2007; Hannington 2014) and produces excess Na, Ca and Si. Near the end of the convection cycle, the modified seawater fluid cools rapidly and produces zones of silicification near the surface in the stockwork and massive sulfide zones (e.g., Franklin et al. 2005; Hannington 2014). In limited Al availability areas, Si4+ substitutes for Al3+ in the tetrahedral site of the muscovite structure to produce phengite with an Si:Al ratio greater than 3. This substitution is associated with Mg2+ and Fe3+ substitution for Al3+ in the octahedral site to balance the charge (Deer et al.1992). Hyperspectrally, this substitution translates into white micas with longer 2200W absorption features. Phengitic white mica with long 2200W absorption features (2200W
Figure 2. Alteration footprint at the Northwest Zone of the Lemarchant deposit. a Geology; b Chlorite-Carbonate-Pyrite Index (CCPI) of Large et al. (2001); c Ishikawa Index (AI) of Ishikawa et al. (1976); d Silica gain (ΔSiO2)

Figure 3. Hyperspectral reflectance. a 2200W; b 2250W; c 2200D/2320D; and d 2250D/2320D
> 2215 nm) are observed at up to ~200 m below the mineralization (Fig. 2a). These zones correlate with zones of silica gain greater than 10% and suggests that addition of silica was the main factor controlling the position of the white micas absorption features (Fig. 2d).

This Mg-rich modified seawater fluid also influenced the chemistry of secondary chlorite as samples with short 2250W correlates with high Al index and low Na2O, suggesting hydrolysis of feldspars by seawater (Fig. 3b). Zones of Mg chlorite are found in the direct footwall of the mineralization and they extend up to ~300 m away along strike, suggesting intense seawater alteration (Fig. 3b).

From these parameters and the position of the absorption features, it is possible to quantify the relative proportion and intensity of the different alteration minerals. Samples with short 2250W (<2252 nm), deep 2250D and low combined ratios of 2200D/2320D and 2250D/2320D are a characteristic of Mg chlorite alteration zones and infiltration of seawater whereas samples with long 2200W (>2215 nm), deep 2200D and 2200D/2320D ratios near 2.6 are a characteristic of phengitic white mica zones and silica gain.

5 Conclusions

The mineralization at the Northwest Zone is associated with intense seawater and hydrothermal alteration (i.e., high CCPI, Al, Ba/Sr), phengitic white micas and Mg-rich chlorites. The alteration extends to at least 300 m away from the mineralization along the andesitic and dacitic units. This study demonstrates that the use of hyperspectral reflectance coupled with geochemical alteration proxies (i.e., Al, CCPI, Ba/Sr, Na2O) and mass volume changes can identify and characterize alteration haloes and fluid pathways. More specifically, hyperspectral reflectance is able to identify, quantify, and chemically characterize specific mineral phases, and relate them to specific alteration processes responsible for the alteration (i.e., seawater alteration versus silicification), which is not possible using geochemistry alone. One of the main advantages of this method is that hyperspectral reflectance can be achieved on drill core at a high resolution for a relatively low cost, and results are available instantly compared to long wait times for geochemical results, greatly enhancing decision making during exploration programs.

Acknowledgements

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The hydrothermal footprint around the Reefton orogenic gold deposit, New Zealand

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Abstract. Defining the hydrothermal footprint surrounding an ore deposit provides geochemical and mineralogical vectors to ore that can be used during exploration. We evaluate different geochemical and mineralogical characteristics surrounding the Blackwater Au deposit, Reefton, and evaluate the value of using ultra-low detection limit analytical methods. By varying the detection limit for Au between 0.5 ppb and 10 ppb, the footprint size increases by one order of magnitude. In addition, background concentrations for ore forming elements are determined with greater precision. However, the mineralogical footprint as defined by carbonate composition or sericite alteration is considerably larger than any elemental concentrations.

1 Introduction

Defining the geochemical and mineralogical footprint surrounding the ore body, and constraining criteria for vectoring to mineralization are critical aspects of exploration for orogenic gold (OG) deposits (Eilu and Mikucki 1998; Large et al. 2000). The hydrothermal footprint of an ore body is commonly significantly larger than the body itself and essentially defines a set of vectors towards the ore. In OG deposits accurate mapping of the footprint is challenging as host rocks are commonly in thermal equilibrium with Au-bearing fluids resulting in a very restricted visible alteration halo. Analytical methods used in exploration commonly have detection limits that are too high to define the concentrations of ore forming elements in the altered rock distal from the ore.

In this paper we define the geochemical and mineralogical footprint surrounding the Birthday Reef in the Reefton OG deposit, New Zealand. We use low detection limit methods to investigate their effect on the size of ore footprint at Reefton, which is a classic OG deposit. Our approach includes: (1) defining the mineralogical footprint and linking the mineralogy to the whole rock chemistry as well as (2) using ultralow detection techniques for gold and pathfinder elements to define the geochemical footprint of the deposit. We evaluate whether the detection limit for whole rock analyses of Au, As and Sb significantly increase the size of hydrothermal footprint and we compare this data to mineralogical footprints for the deposit.

2 Geological setting

The Reefton goldfield is situated west of the Alpine Fault in the South Island of New Zealand (Fig. 1). The deposits are hosted in late Cambrian-Ordovician Greenland Group metagreywacke and argillites that belong to the Buller terrane, which is considered to be an extension of the eastern Lachlan fold belt (Christie and Brathwaite 2003). The deposits show many of the classic characteristics of OG deposits (e.g Goldfarb et al. 2001). Gold-bearing lodes consist of lensoids quartz shoot, also called “reef, lode or vein”, developed along shear zones that dip steeply and usually strike parallel to fold axial surfaces in the host rocks, even though some lodes may be discordant to the bedding. The deposits are also strongly enriched in As and Sb, but some deposits are enriched in As only.

Figure 1. Reefton location (inset) and Birthday Reef veins system schematic

3 Sampling and methods

A representative set of samples from proximal ore to most distal background was collected from a >1 km long drill core at Waiuta (W22 and W22c) that intersects the Birthday Reef at the Blackwater deposit. The mineralogy was studied by optical microscopy and scanning electron
microscope (SEM) at Stockholm University. Ultralow detection limit analyses were performed for Au via inductively coupled plasma mass spectrometry (ICP MS) using a Thermo X series II mass spectrometer and for As & Sb via Analytical Millenium Excalibur hydride generation atomic fluorescence spectrometer (HG-AFS) at Stockholm University, following the method described in Pitcairn et al. (2006). Whole rock analysis was carried out at Stockholm University by X-Ray fluorescence spectrometry (XRF) and laser ablation ICP MS (LA-ICP MS). XRF analyses were produced via a ZSX Rigaku Primus II XRF spectrometer and LA-ICP MS analyses via a 193 nm Ar excimer laser coupled to a quadruple Thermo X-Series II mass spectrometer.

Figure 2. Microscope images in transmitted light: alteration minerals in some of the Blackwater samples. a Alteration commonly observed in the proximal and ore zone of Plagioclase (Albite) being replaced by Sericite. b Quartz filling pressure shadow around pyrite porphyroblasts. c Siderite alteration

Figure 3. SEM backscatter images of sulfides minerals at Blackwater. a Gersdorffite intergrowth in Pyrite associated with ullmannite replacing pentlandite. b Chalcopyrite associated with euhedral cobaltite grains, and a single grain of Bi–Te mineral. c Electrum (Au-Ag alloy) sitting next to arsenopyrite in the main Au quartz vein. d Rimmed pyrite with galena inclusions and as fracture infill.

4 Mineralogy

The alteration mineralogy comprises veins of quartz, quartz-carbonate and carbonate. Chlorite, muscovite, sericite, albite and recrystalised quartz are abundant in the altered host rock. Carbonate minerals consist of calcite, and rare dolomite, ankerite and Mg-siderite. Minor amount of epidote, tremolite, actinolite and biotite occur. Mineral replacement textures are common (Fig. 2a&c). Typical reactions are the replacement of calcite-ankerite by Mg-rich siderite and chlorite, and the substitution of albite by K-mica i.e. muscovite and sericite (Fig. 2c). The matrix is generally made of quartz or recrystalised quartz with altered wall rock clasts composed of chlorite, muscovite, sericite, albite, carbonates.

The most common sulphide mineral is pyrite, with lesser amounts of cobaltite, arsenopyrite, gersdorffite, ullmanite, chalcopyrite, galena, sphalerite, millerite and pentlandite (Fig. 3a). Pyrite occurs as euhedral or anhedral porphyroblastic patches or as euhedral and subhedral aggregates with metamorphic rims (Fig. 3d). Rimmed pyrite has commonly a solid core with alternating porous and solid rims. Some of the pyrite porphyroblasts appears to have been deformed and rotated and are fringed by pressure shadow filled with fibrous quartz (Fig.2b). Arsenopyrite occurs as replacement of pyrite and cobaltite. It commonly occurs as porphyroblasts with cobaltite, chalcopyrite, galena, gersdorffite, millerite and pentlandite. Electrum occurs either as “free” grains adjacent to arsenopyrite or as inclusions in arsenopyrite (Fig. 3c). Euheiral cobaltite grains are commonly associated with subhedral to anhedral gersdorffite, ullaminate, pyrite and chalcopyrite (Fig. 3b).

5 The geochemical and mineralogical footprint

We evaluated the footprint size of the various ore forming elements and mineralogical features. Mineral abundance and, major & trace element concentrations are plotted against perpendicular distance to ore. The footprint may extend further into the footwall but due to the limited length of drilling in the footwall, the extent of the footwall alteration can not be constrained at this time.
5.1 Carbonate footprint

The extent of the carbonate halo (carbonate spots and quartz-carbonate veins) was estimated using petrographic study (MacKenzie et al. 2016; Hamisi et al. 2017) and examination of major oxides concentrations. A scale ranging from 0 to 2 was selected to establish the relative mineral abundance (0: rare or not present, 0.25: minor, 0.5: minor but localised patches, 1: uncommon, 1.5: common, 2: ubiquitous). The carbonate spots are made of crystalline calcite and fine grains of ankerite, which are increasingly replaced toward the reef by Mg-siderite, chlorite, and quartz. Quartz-carbonate veins are common throughout the entire drill core, however they develop a brown-red coloration toward the reef typical of Mg-rich siderite alteration. Although it may be difficult to identify its exact boundary, the sideritic halo extends at least 80 m into the hanging wall and may well penetrate deeper in the footwall below the reef (Fig. 4d).

![Figure 4](image)

**Figure 4.** Minerals abundance and, major and trace elements footprint.

5.2 Silicate footprint (albite and K-mica)

The abundance of albite decreases significantly toward the reef and albite is increasingly replaced by fine-grained sericite. The sericitic halo extends for over 90 m (Fig. 4e) and is one of the most distinctive mineralogical features at Blackwater. Even though concentrations of Na$_2$O and K$_2$O are commonly low, there is a strong relationship between these concentrations and the substitution of albite by K-mica. Mass variation in Na$_2$O and K$_2$O show a clear negative correlation reflecting the sericitic footprint (Hamisi 2016 unpublished MSc thesis).
5.3 Sulphide footprint

Pyrite occurs throughout the entire drill core however near the reef pyrite is recrystallised and has developed metamorphic rims suggesting metamorphic overgrowth during a multiple stage mineralisation process. The pyrite halo based on these textural features extend up to ~35 m around the Birthday Reef (Fig. 4f). Metamorphic arsenopyrite is coeval to metamorphic pyrite. In addition arsenopyrite occurs in mineralised quartz veins. Arsenopyrite occurs in ore samples as replacement of pyrite and coberlite. Electrum also occurs only in ore samples as free grains or inclusions associated with pyrite and arsenopyrite. Other disseminated sulphides minerals including gersdorffite, ullmanite, sphalerite, chalcopyrite, galena, pentlandite, and millerite occur together with pyrite and arsenopyrite yet no distinctive halo for these could be defined.

5.4 Ore forming elements footprint

Au – Protolith and proximal samples have average concentrations of 2.9 ± 1.2 ppb and 3.5 ± 0.7 ppb respectively. The highest Au concentration in ore samples is 67 ppb and the average concentration is 34.2 ± 11.2 ppb. The Au footprint at a detection limit (DL) of 10 ppb (a common DL in the exploration industry) is <1 m from the reef intersect while the Au footprint at with a DL of 0.5 ppb is ~10m from the reef intersect (Fig. 4a).

As and Sb – Protolith, proximal and ore samples have average As concentrations of 14.2 ± 1.5 ppm, 32 ± 4 ppm and 41.3 ± 12.4 ppm respectively. The size of the As halo is ~20 m around the Birthday Reef and is not affected by a change from a DL of 10 to 0.5 ppm (Fig. 4b). Sb concentrations are low compared to other deposits in Reefton (Milham and Craw 2009). Average concentrations of protolith and proximal samples are 2.1 ± 0.2 ppm and 7.6 ± 0.75 ppm respectively. Ore samples contain average Sb concentrations of 6.2 ± 1.2 ppm. The Sb protolith signature is easily distinguishable from enriched proximal and ore samples in the Sb halo. The Sb halo at 0.5 ppm DL is approximately 20 m whereas the Sb halo at 10 ppm is just about 13 m (Fig. 4c).

6 Discussion

Sericitic alteration provides the widest footprint of the mineralisation at Birthday Reef, extending 90 m from the ore (Fig. 4e). This is slightly larger than the sericitic alteration halo (80m from ore, Fig. 4d) although in the, more distal parts of the halo sericite is difficult to observe, occurring as rare spots of partially replaced ankerite. Siderite is more clearly visible within 35 m of the ore as sideritic veins and spots that have a distinct brown-red colour. Sulphide haloes are difficult to define and Au-bearing pyrite, arsenopyrite, and electrum are restricted to within a few metres of the ore.

The background concentrations of Au vary between 0.1 and 3 ppb. The full size of the Au footprint at Birthday Reef is impossible to observe without low DL analytical methods; analysis at 0.5 ppb shows a ~20m footprint which is an order of magnitude greater than the 10 ppb halos. Background concentrations of As are relatively elevated, varying between 4 ppm and 30 ppm. The As halo is fairly well resolved with DL at 10 ppm and lower DL does not affect its size. Sb has low background concentrations varying from 0.2 ppm to 4.5 ppm, and shows a steady enrichment toward the deposit. The Sb halo at DL 0.5 ppm is 20 m compared to 13 m at DL 10 ppm.

Ultra-low detection limit analysis allows more accurate constraint of the size of the Au footprint at Blackwater but ultimately the mineral alteration halo shown by sericite and siderite are both much larger and also much more easily observable. However many orogenic gold terranes host areas of veining, sericite and siderite alteration that are not mineralised with Au, and therefore a combination of the mineralogical and low DL geochemical footprints may provide a more robust vectoring package for future exploration.

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Distinguishing adularia haloes around low-sulfidation epithermal veins using portable X-ray fluorescence

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Abstract. This study combines pXRF and XRD for the detection of adularia within the low sulfidation Waihi Au-Ag deposit, New Zealand. The pXRF was used to analyse 300 samples from the Favona vein system, we use K/Al ratios as an indicator for adularia. The presence of adularia is known to indicate system permeability and occurs associated with mineralisation. Consequently, it is used as a vectoring tool, and understanding its association to vein systems is important. We compared the ratios of 60/300 samples to XRD analysed samples. We found that adularia was almost always present in a sample with a K/Al ratio of >0.4. This “magic ratio” was used to infer the presence of adularia in the samples unanalysed by XRD. Using this technique, the adularia halo was found to be much smaller than those presented in previous studies. There are clear adularia zones before and after vein intersections and a strong anomaly at ~100m drill-hole depth in all 3 holes. Possibly marking the extent of fluid flow which leads to cooling. However, comparison of samples with known adularia concentrations to the XRD analyses shows that the XRD rarely picks up adularia in samples with <10%. Therefore, likely missing low adularia samples.

1 Introduction and geological setting

Epithermal deposits are a major source of Au and Ag within New Zealand. The Waihi deposit produces around 100,000 ounces of gold and 700,000 ounces of silver a year (OceanaGold Corporation 2017).

Low-sulfidation epithermal deposits form in shallow levels (<2km) of hydrothermal systems (Hayashi et al. 2001). The majority of gold is associated with boiling processes (Hollinger and Mauk 2002). Deposits form from neutral pH, reduced, low salinity but gas rich hydrothermal solutions (Hayashi et al. 2001).

In the Hauraki Goldfield (Fig. 1), epithermal Au-Ag mineralisation is associated with steeply dipping quartz veins (Booden et al. 2008, 2009). The Waihi deposit occurs within adularia-sericite hydrothermally altered andesite of the Waipupu Formation (c. 7.4-6.8 Ma) (Simmons et al. 2000a, 2005, Simpson and Mauk 2001, 2002; Hollinger and Mauk 2002; Simpson et al. 2003; Warren et al. 2007; Mauk 2011).

Adularia (KAlSi$_3$O$_8$) is a common alteration mineral found in low-sulfidation epithermal systems. It forms as a replacement of plagioclase phenocrysts from the primary igneous phase (Cerny and Chapman 1986). It is common and widespread both in the precious metal veins themselves and as tiny veinlets or microscopic crystals in the surrounding wall-rock (Simpson et al. 1995). It is found over a large vertical range, although is most commonly found near boiling zones (Simmons et al. 2000b). Adularia primarily deposits due to gas loss, pH increase and cooling of the system (Browne 1970). Browne & Ellis (1970) recognised that the presence of adularia was strong evidence of boiling and indicated good permeability within a system. Therefore, adularia is commonly used as a vectoring tool to highlight boiling zones and areas where large volumes of fluids have passed through; the same processes that lead to gold deposition.

This paper will build on previous studies by Simpson & Mauk, (2002) on alteration zoning within the Favona vein system, Waihi. Portable x-ray fluorescence (pXRF) is used to map K/Al ratios (as a proxy for adularia) and x-ray diffraction (XRD) analysis is used to validate the pXRF results. Therefore, assessing the ability of the pXRF to map adularia.
2 Methods

2.1 Portable x-ray fluorescence (pXRF)

Pulverised samples from three Favona drill holes were obtained from OceanaGold, Waihi. 330 samples were analysed on the 40kV pXRF on “GeoChem” mode (analysing both major and trace elements). Samples were analysed every 2m (up to 300m of core depth). The pulverised samples were placed inside a plastic ring directly on polypropylene low-sulphur pre-cut thin x-ray films (4 μm) inside the benchtop stand (Fig. 2).

Figure 2. Sample analysis method. Each sample was placed inside a PVC ring on an x-ray film inside the benchtop stand (left photo). This is at least 50% faster than the previous method of placing it in XRF pots (right photo).

2.2 X-ray diffraction (XRD)

Sixty samples were sub-sampled and analysed using XRD. Criteria for selection were ranging K/Al ratios and a wide spatial coverage. These were analysed following University of Waikato standard operating procedure on the Pananalytical Empyrean XRD. The bulk samples were already in powder form and run for 2-80 °2θ, at 50 seconds per step.

2.3 Detecting adularia

To access if adularia is present in a sample K/Al ratios from the pXRF data were used. The higher the ratio the greater the chance of adularia being present. However it can be hard to distinguish between adularia (KAlSi₃O₈) and illite (K₃(Al,Mg,Fe)₄(Si,Al)₄O₁₀(OH)₂·(H₂O)), from just elemental data. XRD analysis is used to validate which K/Al ratios contain adularia.

3 Results

3.1 XRD analysis in comparison to K/Al ratios

The 60 samples analysed using the XRD were run through the HighScore Plus software using the PDF-4 Minerals 2016 Database to detect the presence of adularia (± illite). The software picked up adularia (as various K-feldspars), it was also visually picked out using the 3.78 Å peak.

The values of K/Al were compared to adularia presence or absence. Comparing all the XRD results to the pXRF ratios it was possible to observe a “magic ratio” where by if the K/Al value was greater than this it was almost certain adularia (± illite) would be present.

This is observable in figure 3 which plots the K/Al ratios against the presence of adularia. When you reach a 0.4 K/Al ratio it is likely that adularia will be present. There are two samples above this which do not have adularia these are explained by the very low K%. Generally, the K percentage should be greater than 3%, however, this is dependent on other factors (e.g. vein material incorporation, adularia veining in unaltered rock, illite presence) which is why K is ratioed against Al. Al is immobile and has relatively consistent concentrations in the Waihi rocks. We can use this “magic” ratio of 0.4 to apply to the samples which were not analysed with XRD.

Figure 3. Graph showing K/Al plotted against whether the sample contained adularia or not. The points are coloured by their K%, ordered by 5 equal ranges. The green line marks the calculated “magic ratio” of 0.4 K/Al. Above which adularia is likely to be in a sample and below samples are unlikely to have adularia. (Y- XRD identified adularia, N- XRD did not identify adularia, U- sample not analysed on the XRD).

3.2 Adularia halos around the Favona veins

Figure 4 using the “magic ratio” of 0.4 highlights areas with high K/Al and therefore likely adularia bearing. However the halo is not as widespread as previous studies, such as Simpson & Mauk, (2002).

Hole UW67 (centre hole) shows a clear adularia halo before and after the vein intersection. UW84 also appears to show a halo before the lithological change to vein quartz.

At c.100m drill-hole depth in all 3 holes (especially
Comparing these ratios to XRD analysis without XRD or TIMA analysis (or HF staining) it is possible to distinguish between just illite, adularia & illite and just adularia from pXRF data.

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Abstract. Barren and mineralized pegmatites occur as intrusive bodies within the basement rocks of southwestern Nigeria. These have been variably mantled by deep residual profiles that pose great challenges to discovering new rare-element pegmatites. Therefore, trace element abundances in barren and mineralized pegmatites and their residual profiles were explored as diagnostic tools for discriminating between barren and rare-element pegmatites underneath lateritic covers. Abundances and geochemical interrelationships amongst relatively immobile elements in the residual profiles reveal that the rare-element pegmatite profiles are marked by enrichments in Nb, Ta, Sn, Y, and Th, relative to the barren pegmatite profiles. Similarly, rare-element pegmatite profiles indicate low Nb/Ta (0.9-3.9) and high Th/U (0.5-3.6) ratios, as compared to the high Nb/Ta (>6.0) and low Th/U (0.3-0.7) ratios obtained from the barren pegmatite profile. Zr-Th, Y-Nb, Nb-Ta-Sn and Hf-Th-Ta discrimination diagrams of the residual profiles have also proven to be potent geochemical tools for distinguishing between rare-element and barren pegmatites under lateritic covers. These geochemical patterns can be correlated with the relative abundances of accessory mineral phases that host these immobile elements in the respective pegmatite protoliths and the susceptibility of these accessory phases to intensive weathering conditions of the tropical environments.

1 Introduction

Rare-element pegmatites are the major primary host of Li, Rb, Cs, Be, Ga, Sn, Ta, Nb and rare-earth elements (REEs), while other related sources include rare-element-enriched granites, carbonatite and peralkaline complexes and their associated placers and partially altered derivatives. These essential metals are of profound interest and applications in modern day electronic, aerospace, oil and green energy industries.

Depending on magmatic sources, extent of geochemical enrichments and the degree of chemical fractionations, residual pegmatite melts can crystallize to form either barren or rare-element pegmatites. Rare-element pegmatites are formed from fluxed-enriched (Li, F, P, B) and fluid-dominated residual melts at relatively low temperature, during which high field strength elements (HFSSE; Ti, Zr, Hf, Nb, Ta and Th) and some large ion lithophile elements (LILE; Rb, Sr, Cs and Ba) are preferentially concentrated in trace amounts in the residual melts towards the late phase of pegmatite crystallization. This process results in economic concentration of these rare metals into the late accessory mineral phases, such as tantalite, columbite, cassiterite, apatite, zircon, spodumene, pollucite and amblygonite (Linnen et al. 2012). Pegmatites are generally of restricted extents, and are emplaced as dykes and sheet-like tabular bodies into pre-existing rocks. Mineralogical studies and geochemical characterization of pegmatites in different pegmatite districts around the world have indicated the occurrences of both barren and rare-element pegmatites, with the latter mostly representing less than 1.0 % of the pegmatite population (London and Morgan G VI 2012).

The Precambrian basement terrain of Nigeria falls within the humid tropical region, where rocks have been subjected to intensive weathering, resulting in the formation of deep residual profiles that hinder access to fresh outcrops. Therefore, in exploring for rare-element pegmatites in this terrain, there are challenges of extensive lateritic covers over pegmatites, the occurrences of both barren and mineralized pegmatites within the basement rocks, the poor outcrop condition and the restricted extents of pegmatite bodies, as well as the limited alteration haloes and geochemical signatures of pegmatites. The above have presented profound impediments to identifying and characterizing geochemical specialization of pegmatites underneath lateritic covers. As a result of the foregoing, prospecting and exploration for rare-element pegmatites in the study areas have largely been unguided, and more or less based on trials and error, using invasive traditional excavation methods, which have significant environmental and health implications. Therefore, it is expedient to establish systematic tools, through isolating viable geochemical signatures in pegmatite-derived residual profiles, particularly in the tropical terrains with characteristics intensive weathering and considerable deep profiles inhibiting access to fresh bedrocks. In this paper,
the abundances and geochemical interrelationships of relatively immobile elements in some selected residual pegmatite profiles from SW Nigeria have been explored. The effectiveness of these elements in discriminating between barren and rare-element pegmatites is further amplified with the use of relevant discrimination diagrams.

2 Geological setting

The Precambrian of SW Nigeria (Fig. 1) is a part of the Nigerian basement complex, which has been loosely categorized into three main subdivisions. These are the ancient migmatite-gneiss complex (ca. 2.0-3.0 Ga), the schist belts and the Pan-African (ca. 0.6 Ga) plutonic series plus affiliated minor rocks (Rahaman 1988). Among the latter, are various pegmatite bodies which are emplaced into the pre-existing basement rocks. These pegmatites and their host lithologies are generally deeply weathered due to hydrolytic processes emanating from prolonged precipitation (with pluviometric values ranging between 1900 and 2100 mm), alternate wet and dry seasons with average daytime temperature exceeding 28 ºC, as well as the acidic and oxidizing nature of the humid tropical environment.

3 Sampling and analytical methods

Six sampling locations within the Precambrian basement complex of SW Nigeria were selected; four from pegmatite mining districts at Ijero, Komu, Ofiki and Iwere areas, while Osu and Eleyele areas were respectively considered for non-mineralized pegmatite and control gneissic profile. Fresh representative lateritic samples were collected from horizons of the selected vertical profiles over the mineralized and non-mineralized pegmatites and non-pegmatite (gneissic) bedrocks. The gneissic profile serves as the control, due very low contents of pegmatophile elements in gneissic rocks. The samples were collected at regular intervals of 20.0 cm in freshly opened mine workings and hand dug pits. The bedrock pegmatite (>5.0 kg) and gneissic samples were collected from exposed outcrops directly underlying the profiles.

Representative whole-rock and lateritic profile samples were pulverized and analyzed, using X-ray fluorescence spectrometry (PaNalytical AXIOS WDXRF, 3kW, Rh-anode X-ray source) at the Steinmann Institute, University of Bonn, Germany; while selected trace elements were analyzed by inductively coupled plasma–mass spectrometry (MA250 analytical package) at ACME Labs, Vancouver, Canada. Correlation coefficients were calculated for relevant pegmatite petrogenetic elements to isolate element pairs with useful geochemical patterns in the residual profiles. Discrimination plots and relevant element ratios from the correlated elements were utilized to discriminate the pegmatite types.

4 Results and discussion

The pegmatites of the study areas have been investigated, particularly with respect to their mineralogical and geochemical characteristics and economic potentials. The pegmatites at Ijero (Okunlola and Jimba 2006), Komu (Adetunji and Ocan 2010), Ofiki (Elueze and Aromolaran 2014) have been assigned to the beryl subtype of the lithium-cesium-tantalum (LCT) petrogenetic family of Cerny and Ercit (2005), while Iwere pegmatites (Aromolaran 2007) have been identified as lepidolite subtype of the LCT clan. The Osu pegmatite is a barren type, as it lacks rare-metal and gem mineralization. The
whole-rock chemical data (Table 1) indicate elevated levels for Li, Rb and Cs in the mineralized pegmatites of the study areas, whereas these rare alkalis are conspicuously of low concentrations in the non-mineralized Osu pegmatites and expectedly much more lower in the control gneissic rock. In all the horizons of the studied profiles, these rare alkalis are generally observed to be intensely leached.

The mean concentrations of Nb, Ta and Sn are 21, 4 and 6 ppm, respectively in the Osu barren pegmatite samples, while Nb contents in the residual profile range from 6 to 11 and 15 ppm in the A, B and C-horizon, respectively (Table 1). Ta levels in the barren Osu pegmatite profile range from 1 to 2 ppm, while the Sn contents in the same profile range from 4 to 8 ppm. The mineralized pegmatites display higher contents of Nb, Ta and Sn in both fresh rock samples and their respective weathering profiles. The mean Sn contents in the mineralized pegmatites are respectively 5, 18, 17 and 8 ppm for the Ijero, Komu, Ofiki and Iwere pegmatites. The residual profiles of the mineralized pegmatites indicate Sn contents ranging from 33 to 38 ppm for the Ijero pegmatites, 3 to 27 ppm for the Komu pegmatites, 7 to 31 ppm for the Ofiki pegmatites and 1 to 2 ppm for the Iwere pegmatites, respectively. The mineralized pegmatites, therefore, show enrichment by a factor of 3-4, relative to the barren pegmatite profile (Table 1). Nb in the mineralized weathering profile of Ijero displays enhancements down the profile with values ranging from 46 to 80 and 191 ppm for the A, B and C-horizon, respectively; while Nb contents in the Komu profile ranges from 151 to 124 and 87 ppm for A, B and C-horizon, respectively. The mineralized pegmatite profile shows similar trends, as it correspondingly show enhancement of 29, 68 and 125 ppm for the A, B and C-horizon. Ta levels in the mineralized Ijero pegmatite residual profile range from 39 to 42 and 53 ppm for the A, B and C-horizon, respectively; while Komu and Ofiki weathering profiles indicate Ta contents as high as 39 and 90 ppm, respectively. Sn\(^{4+}\) (0.69 Å), Nb\(^{5+}\) (0.64 Å) and Ta\(^{5+}\) (0.64 Å) show similar ionic radii and high cation charges, and are commonly associated in pegmatite systems. The same geochemical attributes could also be replicated in the pegmatite residual profiles, as they are known to be relatively immobile. Other elements that show high contents in whole-rocks and residual profiles of the mineralized pegmatites include Y and Th (Table 1). The relatively immobile HFSE elements, such as Ti, Zr, Y, Nb, Ta, Sn, Th and Hf are utilized for bivariate and ternary plots to discriminate between rare-element and barren pegmatites. The residual profiles of the control gneissic, rare-element and barren pegmatite profiles are variedly differentiated in the Y vs. Nb (Fig. 2) and Zr vs. Th (Fig. 3) discrimination diagrams and positive correlation among these element pairs are quite apparent. The studied profiles are also sufficiently discriminated into their respective separate clusters in the Nb-Ta-Sn (Fig. 4) and Hf-Th-Ta (Fig. 5) ternary discrimination plots. The Hf-Th-Ta discrimination plot proved to be more potent as diagnostic tool for identifying rare-element pegmatites underneath thick lateritic covers. The geochemical interrelationships amongst the strongly correlated element pairs, such as Nb/Ta and Th/U ratios were also applied as geochemical guides to discriminating between rare-element and barren pegmatites. The high Nb/Ta (>6.0) and low Th/U (0.3-0.7) in the barren pegmatite profile, compared to low Nb/Ta (0.9-3.9) and high Th/U (0.5-3.6) contents in the mineralized pegmatites are characteristic of the mineralized pegmatites.
recorded in the mineralized weathering profiles are good geochemical criteria to distinguish between the mineralized and non-mineralized pegmatites hidden under lateritic mantles. The above specified distinctions are possibly a reflection of the chemistry of the pegmatite crystallizing melts, the relative abundances of the essential rock forming minerals to the exotic accessory phases and the differential dissolution of the various trace element host mineral phases in the respective pegmatites.

5 Conclusions

Faced with the exploration realities of the thick lateritic covers and the occurrences of the rare-element and barren pegmatites within basement rocks in the humid tropical regions, the use of geochemical abundances and interrelationships amongst relatively immobile trace elements in the residual lateritic profiles of pegmatites, becomes highly imperative. Enrichments in Ta, Nb, Sn, Y and Th in the residual profiles of the mineralized pegmatites, compared to the barren pegmatite profile, have been investigated to be viable diagnostic criteria for discriminating between rare metal-rich and barren pegmatites. These pegmatites can also be distinguished in their respective residual profiles using Nb/Ta and Th/U ratios plus other relevant discrimination diagrams.

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Quantifying hydrothermal alteration in exploration contexts

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Abstract. The identification and quantification of hydrothermal alteration is essential to our comprehension of mineralising processes and to the prospection of gold and base metal deposits. Numerous chemical methods enable this documentation, and each has specific advantages, limitations, and fields of application. Methods such as alteration indices, the immobile-immobile diagram, and the isocon diagram, have been extensively used since the 80s. Recently, additional normative and mass-balance methods have been proposed by the Consorem group, which work in close collaboration with the mining industry. Applying complementary methods to the Beattie Syenite enable a precise documentation of alteration in a complex setting (i.e. alkaline precursor). Alteration is also successfully quantified at Coulon, a VMS system that was metamorphosed to amphibolite-facies conditions, and enables the formulation of recommendations to estimate the intensity of alteration in the core shack using the proportions of observed minerals.

1 Introduction

Hydrothermal alteration is a key factor both for the understanding of the condition of ore deposits genesis and for mineral exploration. Several methods have been proposed in order to quantify this process. We hereafter present the results from study of alteration on two deposits in the Superior Craton and discuss the potential and limitations of the chemical methods. Through examples recently published by the Consorem group, various methods dedicated to the quantification of alteration, and their advantages and limits in an exploration context, will be discussed.

2 Beattie Syenite, Abitibi greenstone belt, Canada

The Beattie Syenite, which hosts a Neoarchean gold deposit, is located in southern Abitibi immediately north of the Porcupine-Destor fault zone that borders the northern part of the Archean composite volcano represented by the Blake River Group (Jébrak and Bigot 2015).

The quantification of alteration in this area is complicated by two factors: 1) the precursor is an alkaline, generally porphyritic, intrusion; and 2) the 185 analyses used, compiled by Bourdeau (2013), are incomplete due to their historical nature. The first factor complicates the identification of a representative precursor. The second factor is common in several exploration databases, in which many immobile trace elements necessary to some mass-balance methods have not been analysed.

In this context, the following methods have been applied (Mathieu 2016): 1) mass-balance calculation using the immobile-immobile diagram (Barrett and MacLean 1994); 2) normative calculation and related alteration indices performed with the CONSONORM_LG method (Trépanier et al. 2015), a method derived from NORMAT (Piché and Jébrak 2004); and 3) Pearce Element Ratios (PER) diagrams (Stanley and Madeisky 1994).

Mass-balance calculations could only be performed on a part of the samples for which a precursor was available, and reveal important K-gains, local Si-gains, and Na-Ca-losses. Normative calculations enable a precise estimate of carbonatisation, even though CO₂ had not been analysed, and reveal that most white mica and chlorite observed in the field may have form as a result of carbonisation. The PER diagram method enable a verification of several hypothesis and a quantification of K-gains for the bulk of historical analyses.

Combining these methods enable the documentation of intense K-feldspar alteration, silicification, and Na-Ca-leaching in the vicinity of gold mineralisation, as well as distal carbonatisation (Fig. 1). Possibly, mobilisation of alkali and silica are consequences of the predominant process related to carbonisation. The Beattie Syenite is an example where several methods are combined to successfully quantify alteration in a complex setting (i.e. alkaline precursor).
3 The Coulon deposit, La Grande Subprovince, Baie-James, Canada

The Coulon deposit is a volcanogenic massive sulphide (VMS) deposit that was metamorphosed to amphibolite-facies conditions. It occurs within the ca. 2873 Ma Coulon greenstone belt of the La Grande Subprovince, Superior craton (David et al. 2009). The data documenting the alteration halo correspond to: 1) 5583 chemical analyses provided by Osisko Ltd.; and 2) field and petrological observations by R.A. Bouchard (MSc. In progress, see Mathieu et al. 2016b).

The quantification of alteration, in this context, is complicated by high grade metamorphism. Metamorphism is not an isochemical process, especially for volatiles, but the chemical changes induced by this process are minor in comparison to the modifications induced by hydrothermal alteration. For this reason, mass-balance calculation can be performed on metamorphosed rocks. However, such calculations generally necessitate the documentation of a precursor, the identification of which is not straightforward where units have been intensely deformed and metamorphosed.

Precursors can also be modelled using the Trépanier method (Trépanier et al. 2016), which has two requirements: 1) the precursor must be a magmatic rock, or its metamorphic equivalent; and 2) immobile trace elements must be analysed (at least Zr, and Y, Cr, Nb, and Th if possible). The application of the Trépanier method enables a precise quantification of chloritisation, which concentrates in rhyolite units at Coulon (Fig. 2).

The alteration halo of Coulon is characterised by abundant cordierite, and the main assemblages are biotite-sillimanite, biotite-cordierite, and cordierite-anthophyllite.
Calculation of alteration indices using normative minerals calculated with the CONSONORM_HG method (Mathieu et al. 2016a) enabled an alternative quantification of chloritisation, and was used to relate mineral phases to the intensity of alteration quantified with mass-balance calculations.

Using these results, link could be established between the assemblages observed in the core shack and the intensity of alteration. The intensity of chloritisation, in the felsic volcanic unit, can be identified as followed: 1) rocks with (biotite+cordierite) < 20-30 vol% and biotite > cordierite are moderately chloritized; and 2) rocks with (biotite+cordierite) ~ 50 vol% and biotite < cordierite are intensely chloritized and are generally more proximal (Mathieu et al. 2016b).

Conclusion

Qualifying and quantifying hydrothermal alteration is an essential step in the targeting of gold and base metal deposits. Our comprehension of hydrothermal processes also necessitates precise and systematic documentation of alteration intensity. The chemical methods available, including those developed by the Consorem group, are now sufficiently performant and diversified to be applied in the various contexts encountered by exploration geologists.

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Laser spectroscopy: an emerging stable isotope technology with vector potential in epithermal deposits

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Abstract. Despite having utility as a tool for studying hydrothermal ore deposits, stable isotopes have historically been underutilised, due to high analytical cost. While isotope ratio mass spectrometers (IRMS) provide the most precise data, these instruments are expensive to maintain and require relatively lengthy measurement times (Barker et al. 2013). Commercially available laser spectroscopy units overcome these barriers (Barker et al. 2011; Barker et al. 2013). Herein, an overview is provided for utilising CO₂ and H₂O laser analysers to measure isotope ratios in epithermal Au-Ag deposits. With this instrumentation, it is possible to accurately assess isotopic signatures for carbon and oxygen in carbonates and hydrogen in hydrous minerals. Although the analytical target minerals differ for each instrument, comparable optics necessitate similar standardisation protocols. In the following, preliminary data is presented from the Waikato low sulfidation epithermal deposit within the Coromandel Volcanic Zone, North Island, New Zealand.

1 Stable isotopes in mineral exploration

Stable isotopes provide constraints on fluid flow, alteration, and temperature in hydrothermal systems. Historic isotope work has expanded the scope of knowledge on the origin of fluids, as well as the role of temperature and convective transport in ore formation (Taylor 1973; Criss et al. 1991; Cathles 1993; Nesbitt 1996; Criss et al. 2000; Barker et al. 2013). Taylor (1973) investigated isotopic alteration of host rock and ore in the Comstock Goldfields, Nevada, USA, and determined that fluids circulating through shallow epithermal systems are dominantly meteoric. Later, Criss et al. (1991) applied oxygen and hydrogen isotope ratios to make predictions on temperature and fluid flux in association with Eocene caldera ring structures at the margins of the Idaho Batholith. Evaluation of stable isotopes provides useful information on fluid δ¹⁸O, δD, and temperature. Identifying upflow can increase exploratory success, by providing constraints on where boiling and Au-Ag deposition would have occurred. Carbonates (e.g. calcite) and hydrous minerals (e.g. clays, micas) are important archives of fluid properties in hydrothermal systems.

2 Methods

Stable isotope data was collected at the University of Waikato using two Los Gatos Research (LGR) off-axis integrated cavity output spectroscopy (OA-ICOS) analysers, coupled with prototype autosampler systems. OA-ICOS analysers consist of a high finesse optical cavity in which a diode laser is pulsed through sample gas (Barker et al. 2011). The optical effect of analyte gas in the cavity influences the ringdown time, which is applied to calculate isotope values.

Online acid digestion and pyrolysis lines were constructed to liberate CO₂ from carbonates and H₂O from hydrous and hydroxyl containing minerals. Whole rock pulps were selected for stable isotope analyses.

2.1 CO₂ extraction from carbonates

Samples were reacted with 102% orthophosphoric acid in exetainer vials for a minimum of two hours prior to analysis. Acidification occurred at 72°C in a stainless steel heating block. Following acid reaction, CO₂ was collected by a robotic autosampler and passed through an ethanol-dry ice slush trap to remove water. The dry gas was then mixed with dry CO₂-free “zero” air in a batch tank. Mixing with zero air in the batch tank is necessary in order to achieve consistent gas pressure in the analyser cell.

The CO₂ analyser can effectively measure isotope ratios in gas samples over a range of concentrations, between 1,100 and 2,300 ppm. However, uncorrected data from the LGR system exhibits concentration dependency, where lower CO₂ concentrations record more negative calculated isotope delta ratios. This was corrected for by carrying out gas yield corrections using an in-house carbonate standard analysed incrementally between approximately 1,000 and 2,400 ppm CO₂. Nonlinear drift also occurred during runs, and was attributed to changing conditions in the ambient environment of the analytical lab. A CO₂ gas standard of known isotopic value was run at regular intervals to correct for drift. Four carbonate standards were run in order to translate isotope results to an international reference frame. Following each run, two standards were selected to generate a transfer function to correct unknown sample results. All results are reported in units per mil (‰) on the Vienna Pee Dee Belemnite (VPDB) scale for carbon isotopes, and the Vienna Standard Mean Ocean Water (VSMOW) scale for oxygen isotopes.

2.2 H₂O extraction

The water isotope preparation line features a high temperature quartz tube furnace, paired with a Costech zero blank autosampler in a setup developed from that described in Koehler and Wassenaar (2012). Mineral powders were dropped into the hot zone of the tube furnace, and advanced
to the optical cell via a dry air stream. Sample data is manifest as discreet pulses over a low background concentration (figure 1). The area under individual isotopologue peaks is determined and these values are compared to compute a delta (δ) value. As with the CO₂ analyser, δD values are concentration dependent. For this work, calibration spans concentrations from 5,000 to 15,000 ppm. Reference standards include liquid waters and IRMS verified hydrous minerals. All results are reported relative to VSMOW for δD.

Figure 1. Hydrogen isotope ratios were measured from pulses of water liberated from hydrous minerals in a 1000°C quartz reactor. Vapour pulses are manifest as discreet peaks. The background values are clipped out, and the area under each peak is integrated in a manner similar to CF-IRMS, following Koehler and Wassenaar (2012).

3 Epithermal case study

3.1 Geologic setting: Coromandel Volcanic Zone

The North Island of New Zealand is host to the worldclass Martha Mine at Waihi (figure 2), situated within the larger Coromandel Volcanic Zone (Christie et al. 2007). Historic production at the Martha Mine has yielded 6.4 million ounces of Au and 39.9 million ounces of Ag (Brathwaite and Faure, 2002). Au-Ag mineralization at Waihi, occurs in a series of andesite hosted quartz veins, dated to the late Miocene (Brathwaite and Faure 2002). Ore mineralization took place concurrently with the emplacement of volcanic host rock units, between 7 and 6 Ma (Booden et al. 2012; Christie et al. 2007). Veins containing electrum and acanthite occur with assemblages of pyrite, sphalerite, galena, and chalcopyrite (Christie et al. 2007). Quartz and calcite comprise the primary gangue minerals (Brathwaite and Faure 2002; Christie et al. 2007). To date, application of stable isotope data at Waihi has been relatively limited. Brathwaite and Faure (2002) report measurements on hydrothermal quartz and calcite as well as several fluid inclusions and host rock samples. Christie et al. (2007) report additional oxygen and carbon isotope measurements, as well as sulphur isotope analyses at Waihi. These papers indicate a meteoric origin of hydrothermal fluids, although Christie et al. (2007) suggest a small magmatic water component may have been incorporated into the system as well. Here, 57 measurements of carbonate are reported from 5 boreholes at Waihi. Hydrogen isotope analyses are ongoing.

Figure 2. Principal volcanic zones on the North Island of New Zealand. The active volcanic arc has migrated southwards time, with the Taupo Volcano Zone (TVZ) comprising the current locus of activity. From 18 to 2.9 Ma (Booden et al. 2012), the Coromandel Volcanic Zone was active. During this time, epithermal Au-Ag deposits were widely emplaced. Isotope data presented is from Waihi, site of the Martha Mine.

3.2 Results

Stable isotope measurements of carbonate δ¹⁸O and δ¹³C were collected from 5 drill holes at Waihi (figure 3). δ¹⁸Ocarbonate ranged from 0.7 to 10.7‰ VSMOW for all samples, with a mean value of 5.3‰ VSMOW (figure 3). The borehole exhibiting the widest isotopic range for oxygen is UW462, with values between 0.7 and 10.7‰ VSMOW. The borehole with the narrowest range of oxygen isotope values is UW320, with values between 3.8 to 6.0‰ VSMOW. In figure 2, the values of oxygen isotopes in the five boreholes assessed are compared to local meteoric water values, and the isotope measurements of carbonate, quartz, fluid inclusions, and host rock reported in Brathwaite and Faure (2002) for the Waihi system. The results collected in this study are similar to those observed by Brathwaite and Faure (2002). In measurements of 11 carbonate samples from two mineralised veins, they report average calcite δ¹⁸O of 5.0‰ VSMOW, with values ranging
from 2.9 to 9.4‰ VSMOW.

$\delta^{13}C_{\text{carbonate}}$ of individual samples ranged from -10.5 to -4.8‰ VPDB, with a mean value of -8.0‰ VPDB, which is similar to the average value reported by Brathwaite and Faure (2002) of -8.2‰. No statistically significant trends of covariation were observed when carbon and oxygen isotope records were evaluated relative to each other. This indicates that unique factors govern the partitioning of oxygen and carbon isotopes within the Waihi epithermal system.

$\delta D$ from three samples ranged from -42 to -56‰ VSMOW (Fig. 4). Although these values are more negative than that of local precipitation, they coincide with steam discharge values from some active systems in the Taupo Volcanic Zone to the south (Giggenbach and Stewart 1982).

**Figure 3.** Range of carbonate oxygen isotope values collected at Waihi. Stable isotope results from this study (blue) compared to values reported in Brathwaite and Faure (2002), and estimates for local meteoric water. The values reported here are similar to theoretical predictions for calcite precipitation from local meteoric fluids at 200°C.

### 3.3 Discussion

Two endmember models may be considered to explain the oxygen isotope variation in propylitic carbonates at Waihi. The reconstructed oxygen isotope composition of carbonates is related to the temperature of the system and the oxygen isotope value of hydrothermal fluid (Kim and O’Neil 1997). If a uniform temperature is assumed across the system, oxygen isotope variation would be wholly attributed to local variations in fluid composition. However, because temperature gradients are identified as a driving force in convection and upflow in modern epithermal systems, such as the Taupo Volcanic Zone, thermal influence on oxygen isotopes into carbonate minerals should be considered. The calcite-water thermometer can be used with medium confidence to determine the temperature of carbonate precipitation (Kim and O’Neil 1997).

**Figure 4.** Hydrogen isotope values (upper panel) and reconstructed temperature curve from the UW462 borehole (lower panel). In this work, the $\delta^{18}O_{\text{carbonate}}$ parameter is measured, but the $\delta^{18}O_{\text{water}}$ is estimated from modern meteoric values. With these two parameters it is possible to reconstruct mineralisation temperature with moderate confidence. The 462 borehole contains a clay mineral transition. This boundary also corresponds with a significant positive hydrogen isotope excursion. At lower temperatures, the fractionation between fluid and calcite mineral will be greater, and with consistent fluid $\delta^{18}O$, more positive $\delta^{18}O_{\text{calcite}}$ would be expected. Here, temperatures have been reconstructed from isotope data using modern mean meteoric water values (-5.5‰ VSMOW) as the input. Modern meteoric isotope values were extracted from the Online Isotopes in Precipitation Calculator (Bowen and Revenaugh 2003).

In figure 4, oxygen isotope values have been applied to calculate mineral formation temperature, with a uniform isotope value for mineral yielding fluid assumed, based upon modern local meteoric values (Bowen and Revenaugh 2003). Reconstructed temperature values in the UW462 correspond with clay mineral transitions across the same borehole (figure 4). The type of clay mineral alteration present is temperature sensitive. An illite-dominated zone along the first 400m of the UW462 corresponds with a lower $\delta^{18}O$ value in carbonates. From 491m onwards, clay XRD analyses indicate increasing presence of smectite, illite-smectite, and trace kaolinite, which form at lower temperatures than illite zones. Carbonate samples evaluated between 430 and 838.8m along the borehole display increasing $\delta^{18}O$ values. (figure 4).
value that is more positive than the local meteoric ratio if isotopic exchange of oxygen with host rock occurs, or primary magmatic water is incorporated. In fact, Christie et al. (2007) postulate that hydrothermal fluids at Waihi likely had $\delta^{18}O$ values ranging from -7 to +3.8‰ VSMOW based upon fluid inclusion temperature estimates. Nevertheless, the correspondence of increasing isotope values with an illite-smectite transition, moving along the length of the borehole suggests that carbonate $\delta^{18}O$ is reflecting primarily variations in fluid temperature.

4 Conclusions

LGR OA-ICOS technology provides new tools for isotopic assessment of carbonates and hydrous minerals in epithermal deposits. Here, increasing oxygen isotope values overlapping with clay mineral transition for illite to smectite indicate that temperature is exerting an influence upon the isotopic value of carbonate. If temperature can be unequivocally shown to exert the strongest influence upon oxygen isotope fractionation in Waihi-type volcanic hosted epithermal systems, rapid laser based assessment of alteration should provide means to model paleofluid temperatures, using known meteoric inputs, at epithermal ore bodies in other locales.

Acknowledgements

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Evaluation and validation of knowledge–driven mineral prospectively mapping of granite-related polymetallic mineralization in the Bushveld igneous complex, South Africa

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Abstract. The Bushveld Igneous Complex (BIC) is well-known for its PGE-Cr-V mineralization but it has also been a significant source of polymetallic Sn and F associated with the granites of the Lebowa Granite Suite. A continuum of polymetallic mineralization is recognized with a wide range of assemblages Sn-Mo-W-Cu-Pb-Zn-As-Au-Ag-Fe-F-U-REE, ranging from a higher to lower temperature magmatic hydrothermal mineralizing environment. A knowledge-driven approach was selected to assess the regional prospectivity of granite-related polymetallic mineralisation in the BIC. Regional soil geochemical data (1 sample /km²; n=106,877) and the 1:250 000 scale geological map were used in this study. The association of known mineral deposits with different classes of prospectivity model is evaluated by overlying the locations of known mineral deposits on a discretized model. The model predicted 72 % of the total deposits with 64 % of the deposits confined within at least 18 % of the high prospective area. The model has high success-prediction ratio of 3.5. This result indicates that other areas with high prospective values (fuzzy values) based on the model produced in this study can be used as targets for further exploration for polymetallic mineralization in the BIC.

1 Introduction

The Bushveld Igneous Complex (BIC) of South Africa was historically a significant source of granite-related Sn and F mineralization (Crocker et al. 1988, 2001) but declining prices and demand led to the closure of most of the mines and cessation of production. Mining for Sn mineralization was confined to several tin fields including: the Zaaiplaats, Union, Elands, Rooiberg, Olifants and Moloto (Fig. 1) (Crocker et al. 2001), and fluorite was mined from the Buffalo, Vergenoeg, Ruigetepoort, Vischagt, and Zwartkloof deposits. Numerous small deposits and occurrences can be found but the focus of mining was for the higher grade deposits (Crocker et al. 1988).

The BIC comprises the Rustenburg Layered Suite at the base, followed by the Lebowa Granite Suite (LGS), Rashaop Granophyre Suite and Rooiberg Group (Walraven et al. 1990). The overlying units, namely the Rooiberg Group and Rashaop Granophyre Suite, are commonly referred to as the roof rocks with respect to the LGS. The LGS comprises several granitic facies that can be identified by both color and texture at microscopic and macroscopic scales. Geochemically, the LGS show variable trends of fractionation (Walraven 1988; Labuschagne 2004). This is an important consideration in determining fluid focus within the cooling granite sheet. The apical granites, close to the roof rocks, are most-closely associated with polymetallic mineralization (Crocker et al. 2001). The LGS also exhibit variable geochemical signatures as a function of alteration and some local scale alterations are associated with mineralization (Pollard et al. 1991; McNaughton et al. 1993; Hunt, 2005).

2 Mineralization

The LGS and associated roof rocks are host to numerous small- to medium-sized polymetallic deposits and occurrences (Fig. 1) (Crocker et al. 1988, 2001; Bailie and Robb, 2004. The polymetallic mineralization exhibits various morphologies, although it is considered to represent a continuous, single mineralizing system from high temperature magmatic to low temperature hydrothermal mineralization (Freeman 1998, Robb et al. 2000). It comprises a Sn-Mo-W-Cu-Pb-Zn-As-Au-Ag-Fe-F-U-REE assemblage and can be subdivided into three stages of ore formation: high temperature (> 400 °C) Sn-(Mo-W) mineralization, intermediate temperature (400-200 °C) Cu-Pb-Zn-As-Au-Ag mineralization and low temperature (< 200 °C) hydrothermal Fe-F-U-REE (Freeman 1998; Robb et al. 2000).
3 Knowledge-driven model

A minerals system approach was adopted to develop a conceptual geological model that could be used to inform a knowledge Fuzzy Logic prospectivity model. Key to this was the identification of 1) sources of fluids, fluid focus mechanisms, 2) fluid pathways and barriers to flux and 3) trap zones (Kreuzer et al. 2008 and references therein; Hagermann et al. 2016).

The crystallization of the Bushveld granites was accompanied by a long-lived hydrothermal system involving high fluid circulation in granites and associated roof rocks (Walraven et al. 1990; Pollard et al. 1991; McNaughton et al. 1993). The known polymetallic mineralization is closely associated with the most highly differentiated granites and these granites are considered to be the most likely source of metal-rich fluids, and as such, areas closest to the apical portions of the granites were assigned a higher fuzzy membership of 1. This was combined with the Rb geochemical map, which was taken as indicative of the differentiation process and thus a proxy for fluid focus.

The fluid pathways could not be modeled directly using geological structures. But it was postulated that given the continuum of mineralization from higher temperature to lower temperature, the important structures could be mapped by various metal assemblages, inferring the fluid pathway. Principal Components were derived from the 23 individual soil geochemical element input raster maps. PC maps were obtained for the low temperature F-Fe-REE end-member (using PC4: Y-Th) and for the high temperature Sn end-member (using PC14: Sn-W). The two PC maps were rescaled into fuzzy membership.

A number of suitable trap-sites for polymetallic mineralization exist, including 1) endo-granitic mineralization in apical portions of the granites themselves; 2) exo-granitic mineralization in the roof-rocks including the Rooiberg Group volcanics, the Rashoop granophyres and the Transvaal sedimentary rocks. Each should be considered individually, but for the purposes of this study all were considered as having equivalent prospectivity.

A two-staged integration matrix was designed using suitable fuzzy operators to integrate the fuzzy evidential maps to produce the prospectivity map (Fig. 2): the first stage involving the generation of intermediate maps, and the second stage involving the combination of all intermediate maps to generate a mineral prospectivity map for Bushveld granite-related polymetallic Sn-F-(REE) mineralization. The fuzzy score of the mineral prospectivity map was classified into three classes: low, moderate and high prospectivity (Fig.3). The upper limits of the low and moderate classes were defined using box-whisker and histograms plots.
4 Validation of the models

After generation of the prospectivity model, known mineral deposits and occurrences from the South African Mineral Database were used to evaluate success rate of the model. The mineral deposit dataset was not used in generation of the model. The association of known mineral deposits with different classes of prospectivity model is evaluated by overlying the locations of known mineral deposits on a discretized model and produce predictive-area plot (Yousefi and Carranza 2015). Data used to plot success-predictive rate graph is illustrated in Table 1. The prospectivity model has good success rate and prediction rate and this is depicted by high gradient of the cumulative graph (Fig. 4). The model predicted 72% of the total deposits used to validate the model with 64% of the deposits confined within at least 18% of highly prospective area with a success-prediction ratio of 3.5 (Fig. 4). The smaller area (18%) is an ideal result, because it indicates high chance of finding a deposit. The remaining 8% of predicted mineral deposits are confined within moderately prospective areas which cover 54% of the area. This result indicates that areas designated as highly prospective based on the adopted model in this study can
be selected as targets for further exploration for polymetallic Sn-F-(REE) mineralization in the BIC.

Table 1. Data used to plot success-predictive rate graph.

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Figure 4. Predictive-success rate plots for knowledge-driven prospectivity map of granite-related polymetallic minerals.

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Automated gold grain counting: a quantum leap in drift exploration

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Abstract. Counting gold grains in glacial drift is a well-proven exploration technique. However, it is limited by the size of grains that can be recovered and observed, experiencing a recuperation collapse below 50 micrometres. Since ore petrography indicates the overwhelming abundance of very small gold grains, concentrating observation on the smaller fractions will improve accordingly the efficiency of the method. A dependable counting of very small particles is beyond the realm of human skill and requires automation. First, recovery must be conducted by methods which achieve constant concentration factors in the orders of 1:100,000 with constant recovery. Second the identification process requires the use of fully automated scanning techniques based on visible light image analysis and scanning electron microscope (SEM) interoperability. The technique here described enable recovery and counting of gold grains down to a few microns, plus the acquisition of high magnification images to characterize grain shape and EDS-SDD analyses. Results not only enable the detection of faint gold grains dispersion trains, but also characterized the grains in regard of their source rocks taking into account their chemical signature and morphology. A new classification of “pristine” grains in regard of their relation to host minerals is proposed.

1 Introduction

The counting of gold grains in glacial sediment remains one of the most efficient exploration tools in glaciated terrain. Glaciers erode ore bodies and the resulting gold grains are distributed through the deposited glacial till. The relative proximity of a gold ore body can be determined by the amount of gold grains counted in a till sample. Typically, heavy minerals are concentrated from 10 kg of till using a shaking table and/or panning. Gold grains are then counted and characterized by an operator using a stereomicroscope. Since 88% of gold grains in the original ore bodies are smaller than 50 micrometres (Figure 1) (Wood et al. 1986), small gold grains dominate in till samples.

Despite the historical success of this approach, two major areas of this protocol must be improved to enhance the quality of the signal for small particles: 1) on the shaking table, the successful recovery of gold grains collapses for grains smaller than 50 µm and their recovery is highly dependent on operator skills (Nichol 1986; Wang and Poling 1983)); and 2) the identification of gold grains using a stereomicroscope is difficult for small particles (<50 µm (DiLabio 1990) becoming nearly impossible for very fine grains (<20 µm) and again this is directly related to the operator skills. Despite some statistical treatments can be applied to geochemical data to estimate a realistic amount of gold grains within a till sample (Trepanier 2010), we propose a rethinking of till samples processing to improve recovery of very small grain sizes.

Figure 1. Size distribution of gold grains (N = 4316 gold grains) from hundreds of ore petrography reports published by IOS Services Géoscientifiques from Abitibi and James Bay mineral occurrences. Grey bars represent the relative abundance of a specific size fraction and the solid black line represents the cumulative abundance. As such, note that 88% of all gold grains within the sampled ore bodies are smaller than 50 µm.

2 ARTGold™

Since early 2016, IOS Services Géoscientifiques has commercialized an innovative approach for measuring gold grain abundance in tills using a proprietary gold grains concentration device similar to a fluidized bed. Known as the Advance Recovery Technique (ARTGold™), heavy minerals form a super-concentrate—about 150 milligrams—representing a concentration factor of 30,000 to 100,000x. The efficiency of this step is not much dependent on the technician’s skills. The super-concentrate is sieved at 50 µm. The >50 µm fraction is checked optically and the <50 µm fraction is sent to a SEM. The
optical count, which mimics the conventional technique, is done under an apochromatic stereomicroscope at a magnification up to 106x. Grains are extracted, photographed and their identification is confirmed under the SEM. The fine fraction (<50 µm) is dusted on a custom-made holder and checked under a Zeiss EVO MA15-HD SEM having a backscattered electron detector. The thoroughly automated routine, based on the Oxford Instruments’ Aztec platform, scans a mosaic of the grain holder surface in search of heavy minerals, acquires an EDS-SDD spectrum of detected grains and classifies the minerals. Finally, it acquires a high magnification image of the gold grains for shape classification and measurements that are presented in a certificate.

3 Recovery

Figure 2 compares the size distribution of gold grains recovered through the ARTGold™ approach (light grey) with that recovered using conventional method (dark grey). The abundance is normalized to a 10 kg sample to compare the average absolute abundance of gold grains in a standard till samples. The sampled tills were collected in the Abitibi and the James Bay area northern Québec. Given that grain sizes determined by the conventional method is estimated by a technician using a stereomicroscope, accurate measurements are not available and the size classes are broader than those of the ARTGold™ approach.

4 Identification

In our opinion, the best way to minimize errors in identifying fine particles is to automate the identification process. Despite the robustness and the efficiency of using a fully automated SEM routine, the technique is limited by its high operational costs and throughput. Automated detection of grains using optical imaging prior to SEM is needed to reduce operational time. This detection must be interoperating with the SEM to enable transfer of coordinates from an optical to electronic microscope.

Gold has a unique visible light reflectance spectrum characterized by a steep slope between 450 and 800 nm (Clark et al. 1990; Clark et al. 2007) that is not greatly affected by the silver content (Simard et al. in preparation). Therefore, spectral analysis is efficient for recognition of gold and this can be achieved by image analysis obtained from a petrographic microscope. Figure 3 summarizes the steps of the fine grain localization process from the super-concentrated heavy mineral phase to SEM.

4.1 Step 1: RGB localization

The super-concentrate mounted on a shuttle holder is fully
scanned under an optical binocular microscope using a motorized stage and high resolution RGB camera. By simple subtraction of the red and blue channels, pixels potentially representing a gold signature are detected and gold grain images are reconstructed. Location of every single grain is stored in an output file. This basic optical method can scan an average sample comprising about 2 million grains as small as 10 µm within 20 minutes. However, it also generates false positives (~60%) due to the spectral similarity with some silicates such as grossular garnet.

4.2 Step 2: Multi spectral confirmation

Each grain localized by the first optical step is then confirmed using a multispectral acquisition system. The shuttle holder is transferred to a laboratory microscope having a 500X magnification, a video stream multispectral camera based on 11 spectral pass bands from 475 nm to 650 nm (blue through red) and a motorized stage. The application software is applied to each grain, a multispectral image is acquired and the presence (or absence) of gold is then confirmed. The system produces five interpreted frames per second. The total scanning time depends on the number of grains identified in the previous step but typically lasts a few minutes. More than 95% of the gold grains are correctly identified. Identification errors occur if gold grains are coated by iron oxide or other coating material. High magnification images are also acquired for reporting purposes.

4.3 Step 3: SEM classification and measurements

Once gold grains are localized and confirmed the shuttle holder is transferred to a SEM for high magnification back scattered imagery and EDS-SDD acquisition. The fineness of gold (Ag %) is measured as well as contaminants and alloying metals such as Cu, Hg, Bi, Te, Pt, Pb, Sb, As and S down to a detection limit of about 0.2%. Precise measurements are made to extract the length, breadth, axis ratio, surface, perimeter and ECD of the grain. More complex parameters can also be calculated such as roughness and angularity.

Contaminant signature is used to discriminate diverse dispersion trains as well as to fingerprint the metallogenic environment. As examples, Hg-rich gold suggests a low-temperature orogenic system such as Hemlo; Cu-rich gold is related to porphyry or a mantos deposit such as Troilus; Pt- and Pd-rich gold grains are related to systems associated with ultramafics such as those from Sudbury area; and some other dispersion trains have been noted having distinctive Bi or Pb signatures. Silver content is highly variable, but its depletion is typically related to oxidation and the residence time of the sediments.

DiLabio (1990) proposed the classification of grain shapes based on the malleability of gold grains to estimate the distance of transport. The grains are considered “pristine” when the shape is minimally modified by transport thereby suggesting a proximal source. Inversely, grains that are “modified” or “reshaped” with increasing deformation, are interpreted to be related to longer transport distances. The shapes of gold grains from the conventional methods are dominated by “reshaped” or “modified” morphology. Figure 4 presents a compilation of the size distribution of gold grains measured using ARTGold™ according to shape. “Pristine” grains clearly dominate the small size fraction, a character that “does not appear until they are viewed at high magnification (~1000x)” (DiLabio (1990)). The systematic use of SEM images considerably reduces misclassification of minute grains. Moreover, smaller grains have a lower probability of being deformed during transport, an aspect that can explain the abundance of “pristine” gold grains.

Figure 4. Size distributions of gold grains in till processed through the ARTGold™ method classified by the gold grain shape (DiLabio 1990).

Considering the abundance of pristine gold grains, we propose a sub-classification based on the original morphology of the grain that reflects the type of relation to the adjacent minerals in the source rock:

- Remobilized grains (Fig. 5a) are gold flakes that filled cracks in other minerals. These grains are typically very delicate and their shape is rapidly altered into “reshaped”.
- Crystalline grains (Fig. 5b) are gold grains that developed their own crystalline form according to gold cubic crystalline structure. This means that these gold grains had a stronger crystallization strength than the host minerals. These grains are either small or more-or-less stubby or grown as dendrites. They were likely originally embedded in quartz.
- Mutual grains (Fig. 5c) are gold grains that grew within sulfides developing a mutual relationship, in which the gold and their host minerals had similar crystallization strength. They are characterized by curvy and typically
convex shapes. Such grains are typically small and minimally modified.

- Intergranular grain shapes (Fig. 5d) are gold grains having irregular and complex shapes that mimic the boundaries of various other minerals, suggesting they filled intergranular boundaries.

- Spherules (Fig. 5e) are spherical gold grains. Their origin remains uncertain. DiLabio et al. (1988) suggested they may originate from in-situ chemical precipitation.

Figure 5. Pristine gold grains classification. a Remobilized, b Crystalline, c Mutual, d Intergranular and e Spherule.

Quantification of surface textures, morphology, angularity and sizing can reduce misclassification errors related to technician skills. As such, we have developed an artificial intelligence algorithm that is currently in a learning process in order to obtain a satisfactory level of recognition.

5 Conclusion

Gold, both in rocks and glacial sediments, is dominated by minute gold grains. Application of proper techniques to recover, count, image and analyze these gold grains have many advantages for exploration, both in terms of lower detection limits (hence, the use of smaller samples) and characterization of the source material. Recognition of the metallogenic context suggested by gold grains enables more efficient exploration targeting.

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The northwest-trending extension of the Lubin-Sieroszowice Cu-Ag deposit

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Abstract. The copper resources in Poland are confined mostly to the sediment-hosted stratiform Kupferschiefer-type deposits that occur at the Permian Zechstein/Rotliegend transition. Gradual depletion of shallow reserves results in exploration at deeper levels. Among the potential deposits, particular attention is directed to the prospects around mining areas. The highest prospectivity is expected in localities directly adjoining the Rote Fäule hematitic footwall alteration. The most interesting is the northwest-trending extension of the Lubin-Sieroszowice Cu-Ag deposit parallel to the eastern extend of the Zielona Góra Rote Fäule area. An extensive deep exploration drilling program is implemented to verify the resource potential within predicted copper belt.

1 Introduction

The PGI-NRI has conducted investigations of the Kupferschiefer series since 1957, when the giant sediment-hosted stratiform Cu-Ag ore deposit was discovered in the central part of the Fore-Sudetic Monocline. (Wyżykowski 1958). The documented reserves in the Lubin-Sieroszowice deposit still amount to 1 873 million tonnes of ore containing 34 Mt Cu and 102 thousand tonnes of silver, including both operated reserves and resources in undeveloped deposits adjacent to the mining area. This deposit closely rims the huge area where the lowermost Zechstein sediments are represented by the red-colored oxidized rocks (Rote Fäule) with no significant amounts of metal sulphides (Fig. 1).

The Polish Cu-Ag deposits occur within the contact zone between the Zechstein and Rotliegend strata and comprise the Kupferschiefer-related copper-bearing series (Fig. 2). Mineralized bed consists of Weissliegend sandstones (Ws), the Kupferschiefer shales (T1) and the Zechstein Limestone carbonate rocks (Ca1). Occasionally, small amounts of sulphides occur at the base of Lower Anhydrite (A1).

Since the ore bodies surround the oxidized Rote Fäule footwall alteration, determination of the range of oxidized zones is an extremely important exploration guide for the Kupferschiefer-type deposits (Rydzewski 1969, 1978). Detailed petrographic studies revealed the presence of the transition zone occurring between reduced and Rote Fäule oxidized rocks. This transition has features that intermediate between the oxidized and reduced zones with characteristic relict sulphide mineralization due to advanced alteration of primary mineralization (Rydzewski 1978; Speczik 1995; Oszczepalski and Rydzewski 1997; Oszczepalski 1999; Speczik et al 2007; Chmielewski et al. 2015). Over the last few years, thanks to systematic examination of the drill holes located throughout SW Poland, many prospective areas have been recognized and delineated (Oszczepalski and Speczik 2011; Speczik et al. 2013; Oszczepalski and Chmielewski 2015a; Oszczepalski et al. 2016). Based on the Regulation of the Minister of Environment issued in 2011, the following lower threshold values of parameters defining a mineral deposit and its boundaries are currently in use: 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 g/t Ag), minimum productivity – 35 kg/m². Consequently, the ranges of the prospective areas correspond to the 35 kg/m² contour of Cu eq productivity. Recently regions immediately adjacent to the documented Lubin-Sieroszowice deposit were qualified as the most prospective areas (Fig. 1). The greatest expectations shall be attributed to the eastern vicinity of the Zielona Góra oxidized area.

2 Relict mineralization in the Nowa Sól area

Due to the relatively shallow depths of the lowermost Zechstein, the Nowa Sól area has been subjected to numerous drilling projects since the discovery of the Lubin-Sieroszowice deposit. The first drill holes reaching the base of Zechstein (e.g. Broniszów IG-1, Bulin IG-1, Koźuchów IG-1, Mirosław IG-1, Słocina IG-1, Wschowa Geo6, Wschowa Geo7) were carried out over the period of 1958-1963 (Wyżykowski 1963). In the majority of drill holes only oxidized rocks were found without any considerable sulphide mineralization, except from Koźuchów IG-1 where the copper mineralization has been revealed (Rydzewski 1969). Taking into account this positive result and based on the regional metallogenic analysis (Rydzewski 1978) another 9 boreholes were drilled from 1978 until 1981 in the vicinity of Koźuchów IG-1 (e.g. Ciepielów K-4, Podbrzezie K-6, Koźuchów K-10, Zawada K-12). In turn, between 1974-1985, a number of drill holes in the eastern part of this area were done, documenting the western part of the Lubin-Sieroszowice deposit. Successively, in 1988 Borowiec 2 and quite recently 13 new boreholes in the area east of the Nowa Sól were drilled and were used to determine the extents of the Rote Fäule, both at the topmost Weissliegend and within
the shale-carbonate series (Fig. 1).

In Kożuchów IG-1 borehole the ores are confined to reduced sediments comprising only the middle part of the Zechstein Limestone (Fig. 2). They are represented by chalcocite, bornite, chalcopyrite, tetrahedrite, galena, sphalerite and pyrite. Rich copper mineralization in this profile is present within the favorable depth of 820.74-821.39m (2.49m above the Weissliegend top). This interval, 0.65m thick, is characterized by the average content of 1.43% Cu and the productivity Cu eq 34.59 kg/m². Unfortunately, the high grade copper mineralization is not present in the surrounding holes carried out in later years. Although, a significant unexplored area still exists (approximately 10 km²) around Kożuchów IG-1 drill hole, but the high position of sulphide mineralization in the profile (comparable to the sections typical for the western sides of the Lubin-Sieroszowice deposit) does not indicate the possibility of documenting significant prognostic resources in the Kożuchów area, larger than approx. 40 thousand Mg Cu. In other boreholes from the Nowa Sól area, rich copper mineralization was not found were only the top most parts locally contains relict sulphide mineralization typical for transition zone. Those remnants consist mostly of rare sulphides replaced by iron oxides (Fig. 3 A-D).

Reduced rocks with poor mineralization represented by minor chalcocite, chalcopyrite, bornite, digenite, galena, pyrite and sphalerite have been registered in Ciepielów K-4, Kożuchów K-10, Styraź K-13 and Stare Żabno 1 boreholes comprising the upper part of the Zechstein Limestone (Fig. 3 C-D). In several other boreholes (e.g. Wroclaw K-3, Ciepielów K-4, Nowe Żabno K-5, Podbrzezie K-6, Solniki K-11, Zawada K-12, Mirocin IG-1 and Lelechów 6), rare digenite, covellite, chalcocite, bornite, galena, pyrite and sphalerite (Fig. 3A) are dispersed at the base of the Lower Anhydrite (Fig. 2). A very interesting ore mineralization was found in Kiełcz K-1, Otyń 2, Borowiec 2, S-482 and S-483 drill holes. In Kiełcz 1 borehole, six thin intervals with relict mineralization and copper contents ranging between 0.10 and 1.65% occur. Similarly, in Otyń 2 borehole five intervals with relict mineralization (0.1 to 0.2% Cu) have been identified, separated by extensively oxidized rocks. In this borehole only the base of the Lower Anhydrite represents reduced rocks mineralized slightly with digenite, covellite, chalcocite and pyrite, while the contact of the Lower Anhydrite with the Zechstein Limestone exhibits features characteristic for the transition zone with minor copper sulfides (covelite, digenite and chalcocite) accompanied by hematite. In turn, in Borowiec 2 borehole, the reduced horizon is observed in the upper part of the Kupferschiefer (containing 5.02% Cu) over the oxidized lowermost part of the Kupferschiefer (Fig. 2). However, the overlying Zechstein Limestone contains only relict copper mineralization (covelite, digenite and chalcocite) associated with hematite, whereas the upper part of Ca1 and the lowermost part of A1 are reduced and mineralized (chalcocite, bornite and digenite), containing 0.46 to 1.51% Cu as well as up to 0.63% Pb 0.33% Zn.

The oxidized rocks are usually enriched in Au, Pt and Pd, up to 1,990 ppb Au, 391 ppb Pt and 736 ppb Pd (in the richest samples of the Kupferschiefer). Some Pd and Pt minerals and their carriers have been identified, such as: soberovskite, maslovite and tiny inclusions of Pt-Pd alloys in digenite and covellite. Generally, in the central parts of the oxidized areas, PGE (particularly Pd) tend to dominate over Au, while towards the external parts of the oxidized areas the Au content increases relative to Pt concentration (Oszczepalski and Chmielewski 2015).

Figure 1. Cu-Ag prospects in relation to Rote Fäule areas in the Kupferschiefer series of Nowa Sól-Grochowice area.

Figure 2. Correlation of the selected profiles of the Kupferschiefer series across the Nowa Sól-Grochowice area (depth in MBGL).

Barite-calcite (Kożuchów IG-2) or calcite-gypsum (Zatonie C3) veins cut locally oxidized profiles. Veins of second type are strongly mineralized with Co-Ni-Fe
arsenides (rammelsbergite, safflorite, nickeline) along with copper sulphides (digenite, chalcocite), silver amalgams and native silver and silver-bismuth composites (Fig. 4). Those veinlets were formed by low temperature hydrothermal fluids and are younger as compared to the oxidation of the host rocks (Krzemiński 2014).

3 Grochowice and Sława prospects

In the eastern part of studied area, exploration for copper deposits commenced with Sława IG-1 (1974) and Grochowice M-9 (1978) boreholes. Subsequently, another boreholes were drilled in later years (1977-1983), delineating the Lubin-Sieroszowice deposit from the north, and in the years 1980-1991 the oil industry made 28 further wells in Grochowice field.

Within areas with reduced facies, three prospective areas can be distinguished with the minimum productivity of 35 kg/m² Cu eq.; Grochowice I, Grochowice II and Sława areas (Table 1). In addition, the studied area extends to two other prospects: Wilcze and Kulów.

![Figure 3](image1.png)

**Figure 3.** Selected micrographs of sulphide relict mineralization from the oxidized rocks in the Nowa Sól area. A Anhydrite-replacing mineral assemblage consisting of bornite (Bn), digenite (Dg), galena (Gn) and sphalerite (Sph), locally rimmed by hematite (Hem). B Multi-mineral aggregate of bornite (Bn), chalcopyrite (Ccp) and covellite (Cv) vaguely replaced by hematite (Hem). C Remnant covellite (Cv) with tiny inclusion of electrum (Au-Ag) and hematite pigment (Hem). D Tiny grains of bornite (Bn) and native gold (Au) accompanied by irregular grains of chalcocite (Cc), galena (Gn) and dusty hematite (Hem).

![Figure 4](image2.png)

**Figure 4.** Selected micrographs of epigenetic veins cutting the oxidized rocks of the Zechstein Limestone in the Zatonie C3 drill hole. A The association of nickeline (Nk), rammelsbergite-safflorite (Ram-Saf), breithauptite (Brh) and digenite (Dg). B The rammelsbergite-safflorite intergrowths with nickeline (Nk) and silver (Ag) inclusions. C The rammelsbergite-safflorite (Ram-Saf) with inclusions of nickeline (Nk), native silver (Ag), native bismuth (Bi) and silver amalgams (Ag-Hg). D Native silver (Ag) and silver amalgams (Ag-Hg) accompanied with nickeline (Nk) and rammelsbergite-safflorite (Ram-Saf) composite.

### Table 1. Copper and silver prospective resources

<table>
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<th>Parameters</th>
<th>Grochowice I</th>
<th>Grochowice II</th>
<th>Sława</th>
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</thead>
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<tr>
<td>Area (km²)</td>
<td>15.80</td>
<td>2.35</td>
<td>9.48</td>
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<td>Depth range (MBGL)</td>
<td>1600-1700</td>
<td>1600-1700</td>
<td>1900-2000</td>
</tr>
<tr>
<td>Average thickness (m)</td>
<td>1.10</td>
<td>1.52</td>
<td>0.45</td>
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<tr>
<td>Average Cu grade (%)</td>
<td>2.59</td>
<td>1.60</td>
<td>1.92</td>
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<tr>
<td>Cu resources (Mt)</td>
<td>1.125</td>
<td>0.143</td>
<td>0.205</td>
</tr>
<tr>
<td>Average Ag content (ppm)</td>
<td>170</td>
<td>23</td>
<td>161</td>
</tr>
<tr>
<td>Ag resources (tonnes)</td>
<td>7386</td>
<td>205</td>
<td>1717</td>
</tr>
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</table>

Grochowice I prospect is adjacent to the north-western part of the documented Lubin-Sieroszowice deposit and it was delineated by four positive boreholes: Grochowice 28, Grochowice 35, S-483 and S-482. In these boreholes mineralization is present in Weissliegend and dominated by Cu-S sulphides (chalcocite, digenite, covellite) and bornite while the Kupferschiefer is mineralized with Cu-Fe-S sulphides (bornite, chalcopyrite) with minor tennantite, galena, sphalerite and pyrite. The maximum contents of copper were found in the Kupferschiefer samples (S-482 - 17.65%; Grochowice 35 - 7.17%) as well as in the Weissliegend specimens (Grochowice 35 - 2.84%; S-483 - 1.80%). The silver content is high, especially in the Kupferschiefer samples (up to 600 ppm in S-482 and up to 564 ppm in Grochowice 35), and in the uppermost part of the Weissliegend (e.g. 175 ppm in Grochowice 35 borehole). In the eastern part of the discussed area, the Kupferschiefer samples are characterized by distinctive increase in the concentration of Zn (up 3%) and Pb (to 1.5%). The Grochowice I area might contain approx. 1.125 Mt Cu and more than 7 thousands tonnes of Ag (Table 1). Other prospective areas: Grochowice II and Sława are smaller and contain polymetallic mineralization (chalcocite, bornite, galena, sphalerite, pyrite, chalcopyrite) located both in the shales and sandstones (Oszczepalski and Chmielewski 2015b).

New drill holes done between Grochowice I and Wilcze...
prospects revealed that mineralization is predominated by chalcocite, which is accompanied by bornite in the southeast and by galena and shalerite in eastern and northern parts of the investigated area.

4 Implications

The western part of studied area is dominated by oxidized rocks whereas eastern part represents reduced facies (Fig. 1). In the Nowa Sól area, with the exception of Kożuchów IG-1, the Zechstein rocks are intensively oxidized (Fig. 2). As a result, they contain only relics of sulphides partly replaced by hematite. Poor mineralization appears only in the highest part of the Zechstein Limestone or at the base of the Lower Anhydrite (Fig. 3). Typically, numerous oxidized profiles with several intervals containing relics of copper sulphides have been registered in the eastern side of the oxidized area. Alternations of totally oxidized intervals and intervals with relict sulphides clearly indicate that this type of complex mineralization is a result of advanced upward and lateral flow of mineralizing solutions that overlaps primary mineralization. Extremely pervasive oxidation in the Nowa Sól area denotes the extraordinary dynamics of the flow of mineralizing solutions during their passage outward from the centers of oxidative alteration.

At the reduced side of the redox front rich copper mineralization is found in several drill holes in the Grochowice area. Because the investigated drill holes in reduced areas are irregularly distributed with regard to oil and gas exploration, the boundaries of prospective areas, determined on the basis of geometric interpolation of irregularly distributed data, seem to be hypothetical. Previous studies of the Lubin-Sieroszowice copper district indicated that the ore bodies occur at proximal position to the redox boundary. On this basis, it is expected that - just as in the case of the western part of the Lubin-Sieroszowice deposit - the richest mineralization also in the studied area should appear in the nearest neighborhood of the Zielona Góra oxidized area, forming northwest-trending copper belt that rims the oxidized area. This predicted copper belt possibly extends from the Lubin-Sieroszowice deposit at least to the Wilcze prospective area (Fig. 1). Such suggestions have been earlier formulated (Oszczepalski and Rydzewski 1997; Oszczepalski and Speczik 2011; Krześniński and Speczik 2013; Oszczepalski and Chmielewski 2015; Oszczepalski et al. 2016). The recent drilling prospection conducted east of Nowa Sól by Miedzi Copper Corporation confirmed this possibility.

The position of the copper mineralization is moving down eastwards with the distance from the oxidized Zielona Góra area (Fig. 1 and 2). In the western part of the examined copper belt, the ore body is located within the Zechstein Limestone (over oxidized sandstones and shales), in the center - in the Zechstein Limestone and the Kupferschiefer over oxidized Weissliegend, and in the eastern part not only in carbonates and shales but also in sandstones similar to Rudna mine. However, current knowledge about character and distribution of mineralization is not adequate, because the range of copper mineralization is still not completely recognized by drilling, but ore body most likely continues in eastern and north-western directions.

Acknowledgements

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References

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Whole-rock $\delta^{18}O$ and $\delta^2H$ footprint of the Canadian Malartic gold deposit, Abitibi Subprovince, Québec, Canada

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Abstract. The O and H isotopic footprint to the Canadian Malartic gold deposit is the fossilized remnants to a hydrothermal system that has altered the host metasedimentary rocks and igneous intrusions. Mapping whole rock $\delta^{18}O$ and $\delta^2H$ outlines the hydrothermal footprint to the deposit up to 2 km outside of the open pit. The isotopic footprint consists of a decrease in whole rock $\delta^{18}O$ values, from $-59\%$ to $-91\%$, towards mineralization. In gabbro dykes, $\delta^{18}O$ values increase from $8.3\%$ to $9.1\%$ towards gold mineralization. Modelling of isotopic data suggests the isotopic footprint is the result of decreasing fluid/rock ratios away from mineralization at a temperature of 300°C.

1 Introduction

The Canadian Malartic gold deposit, Quebec, Canada, contains 10.8 Moz of gold in 314.2 Mt with an average grade of 1.07g/t (Gervais et al. 2014). The deposit is located in the Archean Superior province immediately south of the Cadillac-Larder Lake Tectonic Zone (CLLTZ) that marks the boundary between the Abitibi and Pontiac subprovinces. The deposit is dominantly hosted by the metasedimentary rocks of the Pontiac Group but mineralization also occurs in metavolcanic rocks of the Piché Group, dioritic porphyries, and gabbro dykes. Dating of detrital zircons and intrusions in the Pontiac Group constrain the age of the sedimentary rocks between 2685±3 Ma and 2682±1 Ma (Davis 2002). Porphyritic intrusions have been dated from 2677 to 2679 Ma (Helt et al. 2014; De Souza et al. 2015). Mineralization occurs dominantly south of the CLLTZ within envelops adjacent to the Sladen fault. Gold typically occurs as microscopic disseminations associated with pyrite or in quartz-carbonate veins parallel to the dominant S2 foliation. Re/Os dating of molybdenite from the mineralized area yields an age of 2664 Ma.

2 Results

2.1 Whole-rock geochemistry and isotopes

A total of 120 samples were collected over a 4 by 5 km area south of the Canadian Malartic deposit. These samples consist of both Pontiac greywacke ($n = 87$) and gabbro dykes ($n = 33$). Major element geochemistry for the greywackes is typical of this rock type in the geochemical classification of sedimentary rocks by Herron (1988). Similarly, data from meta-basic dykes plot mostly within the field of tholeitic gabbro of Wilson (2007)

$\delta^{18}O$ values of greywacke range from 7.8‰ to 11.9‰ and are normally distributed ($\bar{x} \pm 1\sigma = 8.4 \pm 1.3\%$). $\delta^2H$ values of greywacke are also normally distributed with values from -91‰ to -41‰ ($\bar{x} \pm 1\sigma = -59 \pm 8\%$). $\delta^{18}O$ values of gabbro dykes are also normally distributed with the exception of two outlying samples with high values of 11.6‰ and 12.2‰. With these outliers removed, the $\delta^{18}O$ values of gabbro dykes range from 6.8‰ to 9.8‰ ($\bar{x} \pm 1\sigma = 8.2 \pm 1.3\%$). The $\delta^2H$ values of gabbro dykes contain one outlying value of -105‰. Excluding this sample, the range of $\delta^2H$ is between -84‰ and -55‰ ($\bar{x} \pm 1\sigma = -71 \pm 7\%$).

Petrography of the outlying gabbro dyke samples indicates that the two samples with high $\delta^{18}O$ values contain a higher proportion of quartz and feldspar. The sample with a low $\delta^2H$ value contains relict feldspars that have been altered to fine grained phyllosilicates. These samples have been removed from subsequent geostatistical analysis.

2.2 Principal component analysis (PCA)

The PCA was performed using whole rock O and H isotopic values, and centred-log ratio (CLR) transformed geochemical data including: major element oxides, Au, C, H2O and S content for both rock types. The geochemical datasets have been CLR transformed in order to eliminate the effects of closure (Aitchison 1986). From the greywacke dataset, principal components 1 and 2 (PC1 and PC2) account for 54.05% and 13.15% respectively, of the variance exhibited by the data (Fig. 1a). Similarly from the gabbro dyke dataset, PC1 and PC2 capture 53.75% and 11.41% respectively of the total variance (Fig. 1b). Subsequent components capture less than 10% each and are not discussed.

PCA plots (Fig. 1) cluster together components that are positively correlated whereas components that are inversely correlated plot on opposite sides of the diagram. In both instances, PC1 indicates Au, C, S and $\delta^{18}O$ covary and are inversely related to major rock forming elements.
(SiO₂, Al₂O₃, MgO, and Fe₂O₃) and δ²H. PC2 is orthogonal to the first and reflect changes in alkali-bearing minerals and are attributed to potassic alteration.

The PCA of both greywackes and gabbro dykes indicate that carbonatization and sulfidation are linked to gold mineralization along with increasing δ¹⁸O and decreasing δ²H.

![PCA loading plots for the hostrocks of the Canadian Malartic deposit.](image)

**Figure 1.** PCA loading plots for the hostrocks of the Canadian Malartic deposit. a Greywacke and b gabbro dykes.

### 2.3 O and H isotopic footprint

Mapping the whole rock isotopic values of the host rocks to the Canadian Malartic deposit reveals an isotopic footprint that can be attributed to mineralization (Figs. 2 and 3). The regional trends in δ¹⁸O and δ²H values are derived from kriging based on variogram parameters. In greywacke, this footprint is best identified by a decrease in δ²H toward mineralization from values near -59‰ in regional background, 1 to 2 km outside of the pit, to values near -91‰ in the mineralization (Fig. 2b). δ¹⁸O values of greywackes show a subtle footprint delineated by the 9.9‰ isopleth S and SE of the deposit (Fig. 2a).

In gabbro dykes, the footprint is outlined by a decrease in δ¹⁸O from values greater than 9.0‰ in mineralization to background values near 8.3‰ up to 1 km outside of the pit. (Fig. 3a). The δ²H footprint in gabbro dykes highlights an area of δ²H lower than -73‰, up to 2 km S and SE of the deposit (Fig. 3b).

![Isotopic footprint using kriged δ¹⁸O and δ²H values in greywacke.](image)

**Figure 2.** Isotopic footprint using kriged δ¹⁸O and δ²H values in greywacke. a δ¹⁸O. b δ²H. Geologic map modified after Perrouty et al. (2017).
3 Discussion

3.1 Fluid O and H isotopic composition

The isotopic composition of water in equilibrium with the Pontiac Group metasediments at the greenschist-amphibolite transition can be approximated using the fractionation equations of Bottinga and Javoy (1975) and Matsuhisa et al. (1979). Assumptions used in this calculation include (1) the initial isotopic composition of the rock given by the average greywacke from outside of the -59‰ δ2H isopleth (δ18O<sub>Rock</sub> = 9.7‰, δ2H<sub>Rock</sub> = -53‰), (2) the mineralogy for greywacke simplified to 50 vol.% biotite and 50 vol.% quartz, and (3) a temperature of reaction of 475°C. This fluid has been calculated to have a δ18O value of 7.6‰ and a δ2H value of -12‰. These values are similar to the isotopic composition computed from vein biotite and quartz from the Canadian Malartic deposit (Beaudoin and Raskevicius 2014; Helt et al 2014) and to mineralizing fluids of nearby orogenic gold deposits (Beaudoin and Pitre 2005; Beaudoin and Chiaradia 2016). The O and H isotopic composition indicates a metamorphic fluid (Beaudoin and Raskevicius 2014) interpreted to be the primary source of mineralization for the Canadian Malartic deposit, and which is used for subsequent fluid/rock isotopic exchange models.

3.2 Modelling fluid/rock reactions

The computation of fluid/rock isotopic exchange models requires assumptions with respect to (1) the mineralogy and (2) the initial isotopic composition of the host rocks. For greywacke, the assumptions are outlined in section 3.1. For gabbro dykes, a simplified mineralogy of 45 vol.% hornblende, 45 vol.% biotite and 10 vol.% anorthite has been used, and the initial isotopic composition was approximated by the average dyke outside of the -69‰ δ2H isopleth (δ18O<sub>Rock</sub> = 7.3‰, δ2H<sub>Rock</sub> = -63‰). Using these assumptions, we compute the final rock compositions for both rock types using equations outlined by Taylor (1978) for fluid/rock ratios of 0 to 8 assuming open system conditions at temperatures of 350°C, 300°C and 250°C to span the geologically relevant temperatures of greenschist facies metamorphic rocks (Fig. 4).

Figure 3. Isotopic footprint in gabbro dykes. a Threshold δ18O values are outlined by the kriged 8.3‰ isopleth. b Threshold δ2H are outlined by the kriged -73‰ isopleth. Geologic map modified after Perrouty et al. (2017).

Figure 4. Plots of δ18O and δ2H values of a greywacke and b gabbro dykes. Ticks along fluid/rock exchange paths represent atomic fluid/rock ratios. Greywacke with >0.1ppm Au are shown as yellow points. Variance of δ18O in gabbro dykes may be ascribed to carbonate content in this rock.
ca. 300°C with the mineralizing fluid at atomic fluid/rock ratios up to 0.5. The greywacke data indicates that the system was rock-dominated and fluid/rock reaction has extensively altered greywacke δ²H values while leaving the δ¹⁸O values mostly unchanged.

In gabbro dykes, the footprint is characterized by an increase in δ¹⁸O proximal to mineralization. This shift may be caused by precipitation of epigenetic carbonates during mineralization. The PCA shows carbon to correlate with gold (Fig. 1 and 4B) and petrography shows carbonates to commonly occur in gabbro dykes proximal to mineralization. The preferential precipitation of carbonate minerals in gabbro dykes is most likely due to the chemical affinity for carbonate to complex with ferromagnesian minerals in the rock. Moreover, carbonates tend to have high δ¹⁸O values when precipitated from hydrothermal fluids (Δankerite-water = 6.2‰ at 300°C; Zheng, 1999).

The PCA of both greywackes and gabbros throughout the study area indicates δ⁲H is inversely correlated with Au, S, C and δ¹⁸O values. This is consistent with the lower δ²H values in greywackes proximal to mineralization and higher δ¹⁸O values in gabbro dykes observed in the isotopic footprint to the Canadian Malartic deposit.

Modelling suggest that the stable isotope data throughout the footprint is best explained using an initial fluid composition in equilibrium with Pontiac sediments at ca. 475°C. That interacted with the host rocks precipitate gold, carbonates and sulphides at a higher structural level at ca. 300°C, at lower W/R ratios away from the mineralized area.

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**References**


Tungsten-rich rutile as a potential indicator mineral in surficial till for Canadian Malartic-type gold deposits

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Abstract. It is challenging to trace detrital indicators in glacial sediments from gold deposits that are characterized by disseminated very fine gold particles. Other indicator minerals are needed. W-enriched rutile is associated with Au mineralization at Canadian Malartic and could be a useful indicator for gold deposits of this type. As a first test, 31 till samples were collected around the deposit and analysed for rutile content and matrix geochemistry. W-enriched rutile (> 0.40 WO3%) was recovered from the 0.125 to 0.500 mm fraction, the number of W-rutile grains was counted per sample site and mapped, and they were then compared to spatial distribution of W from the till matrix geochemistry. Overall, patterns are in agreement with the predicted net effect of recognized ice flow phases on the known extent of W-enriched rutile in bedrock. Future work will increase the density of control points, which should better constrain the patterns, source zones, and background levels. Finer fractions will also be analysed as they may contain more indicators specifically derived from Malartic than the coarser fractions. In summary, W-rich rutile is a promising candidate indicator mineral in till for Malartic-type gold deposits.

1 Introduction

As discoveries of high-grade gold deposits become increasingly rare and more difficult, there is demand for innovation in exploration techniques to discover large-tonnage, low-grade gold deposits.

The open-pit Canadian Malartic gold mine in Quebec is an example of such a deposit. There is no clear geophysical footprint at Malartic; instead, the potential for an open-pit mine was first realized as a result of targeted searching for key characteristics through a public geoscientific database (Wares and Burzynski 2011). We are using this deposit as a case study to develop new footprint and exploration techniques.

Drift prospecting is a well-established exploration technique for many deposit types, including gold deposits (McClenaghan 2005), in areas covered by glacial sediments. Detrital gold in glacial sediments (e.g., till) is an obvious indicator of gold mineralization from a source located up the ice flow direction, but standard gold grain picking techniques focus on sand-sized gold particles and are therefore less effective for tracing a deposit like Malartic, where gold particles rarely exceed 30 µm (Helt et al. 2014) in diameter. Furthermore, drift prospecting is more effective when a suite of indicators (e.g., as in kimberlites) can be used together to fingerprint a particular source that has distinct assemblages (e.g., diamondiferous kimberlite). It would therefore be useful to identify other indicator minerals for gold deposits, especially for more elusive high-tonnage low-grade deposits like Malartic.

Rutile (TiO₂) is a good candidate as an indicator mineral in till because it is physically resistant to weathering and can therefore survive glacial transport and post-glacial processes. More importantly, it often has anomalous tungsten (W) concentrations that vary in association with different ore deposit types (Clark and William-Jones 2004), including Malartic (Helt et al. 2014). An alternate potential source of W in till is scheelite (CaWO₄), but this mineral is poorly represented in the till in Malartic because it is present in relatively low quantities within the local bedrock.

2 Methodology

2.1 Fieldwork

Initial samples for this project collected in and around Malartic, QC consist of 18 surficial till and 13 Pionjar drill samples. The surficial samples were used both for picking grains and for matrix geochemistry, while the small volume drill samples were used only for matrix geochemistry.

Due to limited till coverage in the study area, the majority of the samples were first taken southwest of the Canadian Malartic deposit, which corresponds to one of the down-ice directions. This introduces a bias in the sampling, but was considered appropriate for the purpose of this preliminary study, which was to identify W-rutile in till. More samples have recently been collected to fill gaps and to better define background, but results from the second phase have yet to be fully evaluated.

2.2 Mineral separation

Heavy mineral concentrates (HMC) were prepared from the coarser fractions by using heavy liquid separation, ferromagnetic and paramagnetic separation. Rutile and
gold grains were hand-picked from the 125-250 μm and 250-500 μm HMC fractions using a binocular microscope. This is not the best size fraction for Malartic W-rich rutile, which is predominantly finer grained, but the use of a standard mineral separation approach was sufficient for a proof of concept, assuming that there is sufficient coarse W-rich rutile at Malartic or other mineralized zones in the vicinity along the Cadillac fault to produce a signal in the sand fraction of the till.

2.3 Electron probe microanalysis

Picked rutile grains were analyzed by wavelength dispersive X-ray emission spectrometry using a JEOL JXA-8900L electron probe microanalyzer using a focused beam, 20 keV accelerating voltage, 40 nA beam current, and ZAF correction. Counting time for W was 60s on the peak and 30s on each background. The lower limit of detection (3σ) for WO₃ is 0.04 wt%.

2.4 Q-Q plot

A Q-Q plot is a way to show deviation (z-score) from a normal distribution and is therefore a useful tool to identify anomalous values, potentially indicating association with an ore deposit (e.g., Grunsky 2010).

In this case, Q-Q plots were constructed for the measured WO₃ values in picked rutile grains, as well as for the W results from till geochemistry. Grain counts were normalized to 10g of HMC. Zoned grains were assigned their average WO₃ values. Anomalous WO₃ values were then determined from the graph by inspection, based on the location of a change in slope.

2.5 Geochemistry

Till matrix (<0.063 mm) was separated and analyzed for major and trace elements by ICP-MS following partial and total digestion, respectively. Partial digestion was achieved by digesting pulp in 8:1 ultrapure HNO₃:HCl for 1 hour at 95°C. Total digestion was achieved by heating pulp in ultrapure HF/HNO₃/HClO₄ until dry and then dissolving residue in dilute ultrapure HNO₃. The till matrix was also analyzed for gold following Pb fire assay pre-concentration. This allows tests of W alone as a geochemical pathfinder element acting as a proxy for W-rich rutile. Additionally, existing legacy geochemical data was levelled by Taves (2015) to be used in this context.

3 Results

3.1 Q-Q plot

Using the Q-Q plot method on this dataset, values of WO₃ ≥ 0.4 weight percent (wt%) were defined as anomalous.
3.3 Anomalous rutile

Based on our interpretation of the Q-Q plot, figure 4 shows the distribution of anomalous rutile grains (defined as ≥ 0.4 wt% WO₃) for the combined 125-250 μm and 250-500 μm size fractions.

Figure 4. Distribution of anomalous (≥ 0.4 wt% WO₃) rutile grains per 10g HMC for the combined 125-250 μm and 250-500 μm size fractions. The extent of the potential indicator dispersal fan is outlined by dashed lines.

3.4 Geochemistry

Figures 5a-b show Q-Q plots for W (ppm) and Au (ppb) values, respectively, based on till matrix geochemistry, and figures 6-7 illustrate the distribution of measured and anomalous W and Au values, respectively. Three out of four locations that show anomalous values for Au also show anomalous W values.

Figure 5. Q-Q plots showing the determination of anomalous values for a W and b Au in till matrix. Anomalous values were determined by visual inspection and are circled in blue. Detection limits are represented by a red dashed line.

4 Discussion

Till in the Malartic region is discontinuous and there is also extensive cover of glacial lake sediments, which together pose a challenge for drift prospecting, as they restrict where till samples can be taken. Despite this limited sampling, figures 3-4 show a potential dispersal fan from potential sources along the CLLDZ (i.e., East Amphi, and possibly Canadian Malartic). The patterns may result from the net effect of the southwest ice flow phase followed by an ice flow shift to the southeast. Erosional ice-flow indicators on outcrops within the study
area are mostly related to the SW ice flow phase, but the
till data suggest that the younger phases may also have had
influence on sediment transport and overall dispersal
patterns. Malartic may have contributed little as a source
of relatively coarse W-rutile, which may explain the
results and observed patterns.

Figures 6-7 show three coinciding Au and W
anomalies, all of which occur in till. Two of these are to the
south and SE of CM, and one appears to be associated with
East Amphi. These patterns are consistent with the
interpretation of the ice flow dynamics in the region,
namely the net effect of the southwest ice flow phase
followed by an ice flow shift to the southeast.

Overall, W-rich rutile grains occur in the till and appear
to be derived from sources along the CLLDZ. Results are
therefore encouraging for W-rich rutile as a potentially
useful indicator mineral for gold deposits such as Canadian
Malartic, that are associated with W-rich altered rocks
(Helt et al. 2014). Furthermore, the related occurrence of
anomalous values of W and Au suggest that W may be a
potentially useful geochemical pathfinder element on its
own.

5 Ongoing studies

Following up on this initial work additional surficial till
samples have been collected in and around Malartic in
order to fill in the distribution and geochemical mpA
patterns, and to help delineate potential indicator mineral
dispersal patterns. This larger set of samples will also
establish background (i.e., up-ice) measurement values for
the region.

Canadian Malartic is characterized by finer grained
gold and rutile than the East Amphi or other local sources;
the next phase of study will utilize rutile from the 75-125
µm size fraction to increase the likelihood of detecting an
indicator dispersal pattern from Canadian Malartic. Our
working hypothesis is that the smaller size fractions may
reveal different patterns, and possibly a stronger signal
from Canadian Malartic.

Similarly, geochemical analyses on till matrix are
underway on the additional samples, and will be integrated
into the overall interpretation of tungsten’s geochemical
pathfinder signal.

6 Conclusion

Till samples from the Malartic region have been analysed
for W-rich rutile as well as W and Au in till matrix.
Although the preliminary sparse sampling makes
interpretation challenging, there is evidence for a potential
dispersal fan in till down-ice from the Canadian Malartic
and adjacent ore deposits. More extensive data from
ongoing studies will help elucidate the dispersion pattern.
Overall, W-rich rutile is a promising indicator mineral in
till for Canadian Malartic-type gold deposits.

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White phyllosilicates geochemistry – vectoring porphyry ore deposits

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Abstract. Petrography, SWIR spectroscopy, electron microprobe, and LA-ICP-MS analyses could be used to identify anomalies and gradients in white phyllosilicate compositions from the phyllic alteration zone in porphyry ore deposits. Two different phyllic alteration styles were sampled from Copper Cliff deposit, Montana. An early phase characterized by pale green sericite, quartz, and specular hematite, pervasive and texturally destructive, and associated with hypogene chalcopyrite and bornite. A late phase characterized by sericite, quartz, and pyrite, structural controlled and texturally preserved, with no copper mineralization. Sericite from the early stage present higher Fe and Mg content, which is related to absorption features from 2203-2209 nm, in contrast with samples from the late phyllic alteration, with absorption features from 2198-2201 nm corresponding to higher Na content. Both stages can be differentiated via trace elements geochemistry. The vanadium and scandium concentrations are lower in the early stage compared with the late stage. Trace element geochemistry also allows identification of spatial variation relative to the porphyry center, giving indications of proximity to mineralization. B, Sc, V, Cs, and Ba increase in concentration with distance from the center of the system. By contrast, W display a maximum concentration associated with the mineralized center and decreases with distance.

1 Introduction

Traditional geochemical exploration tools, such as soil and rock geochemistry, have been successfully applied in the discovery of porphyry ore deposits with the recognition of hydrothermal alteration halos exposed at the surface. However, less attention has been focused on the development of geochemistry exploration tools that allow the discovery of poorly exposed or concealed ore bodies within a typically large volume of generally uneconomic phyllic alteration.

This work focuses on understanding possible vectors to porphyry ore deposits from geochemical variations present in white phyllosilicates from the phyllic alteration zone. The project has the general objective to study the geochemical signatures of white phyllosilicates from different phyllic events in porphyry systems in order to define lateral and vertical variations in the chemical compositions and generate a coherent geochemical hydrothermal zonation model. Of secondary interest is to develop a better understanding of the nature of the early pale green sericite alteration through the characterization of the mineralogical and geochemical signature, which has not been thoroughly documented before.

2 White phyllosilicates in porphyry ore deposits

White phyllosilicates are considered the most distinctive alteration minerals in the phyllic alteration. It is usually produced by the hydrolytic reaction in which K-feldspar and plagioclase alters to white phyllosilicate and quartz at temperatures below 550°C (Seedorf et al. 2005). The unit structure consist of one octahedral sheet between two opposing tetrahedral sheets, separated from adjacent non-hydrated interlayer cations, and bonded together by weak apical oxygen and anions to the tetrahedral sheet. This complex interplay allows several major and trace element substitutions in either the tetrahedral, octahedral or interlayer position (Deer et al. 2003). Now, considering that formation of the white phyllosilicates is controlled by the composition and pH of the fluid, and the bulk-rock chemistry (Hemley and Jones, 1964), subtle geochemical variations may provide important vectoring information to help focusing mineralized zones in hydrothermal systems.

3 Brief review of previous studies

Previous studies have identified variations in major and trace element geochemistry in white phyllosilicates from late D-type veins in porphyry systems (Cohen et al. 2011; Alva Jimenez et al. 2011; Dilles et al. 2014). In the Ann-Mason porphyry-Cu (Mo) deposit at the Yerington district, Nevada, a vertical zonation was observed with white phyllosilicates in the center of the system dominated by a muscovite composition (Na-Fe-Mg poor) and a 2200 nm infrared absorption feature, whereas in the upper part of the system a phengitic composition (Fe-, Mg rich) and Al-OH absorption at longer wavelengths (> 2205 nm) (Dilles et al. 2014). In addition, LA-ICP-MS analyses in white phyllosilicates reported enrichment in Tl, W, and Sn, from the potassic, phyllic, and shallow levels of the advanced argillic alteration zone, indicating the vertical pathway of magmatic fluid from the ore zone toward the paleosurface (Cohen et al. 2011).

Similar results were reported in the Highland Valley porphyry district district, southern British Columbia,
Canada. Analyses indicated that white phyllosilicates in the center of the system are sodium-bearing muscovites, whereas phengitic compositions dominated the distal parts of the system. Trace elements concentrations detected Rb, Cs, B and Tl to be increased with distance away from the center of the system, whereas Li, Sr, Ti, Sn and V decreased (Alva Jimenez et al. 2011).

All available data from these previous studies are consistent with the potential for developing vectors using mineral chemistry and SWIR spectroscopy in white phyllosilicates from late D-type veins. However, some aspects remain unclear, such as the chemical behaviors in systems with multiple events of phyllic alteration, e.g., deposits with the early phase of phyllic alteration characterized by pale green sericite, quartz, and iron-oxides (usually hematite). This type of alteration has been reported in just few deposits (Escondida Este, La Granja, Copper Cliff, Resolution, Chuquicamata, and Taca Taca; Maher, K., personal communication, April 2015), usually as pervasive and texturally destructive, centrally located and with associated copper mineralization comprising chalcopyrite and bornite (Slitoe, 2010).

## 4 Copper Cliff porphyry Cu deposit

Copper Cliff porphyry copper deposit is located 30 miles ESE from Missoula, in the state of Montana, USA. The deposit lies in the northeastern portion of the Garnet Range metal region (Elsworth, 1993). Deep drilling exploration programs conducted by Kennecott Exploration from 2006 to 2016 confirmed a block-cave mineable porphyry Cu-Au ore body at a depth of more than 1000m below surface, similar to a Resolution-style deposit (Fairbanks, 2009).

The deposit is hosted in a sequence of sedimentary rocks comprising quartzites and argillite from the late proterozoic belt supergroup, overlain by cambrian carbonates and shales from Silver Hill and Hasmark formations, and intruded by early eocene hypabyssal quartz latite plutons (Elsworth, 1993). Two stages of phyllic alteration are present: an early phase characterized by the mineral assemblage of pale green sericite, quartz, and hematite, with high-grade hypogene copper mineralization comprising mainly chalcopyrite and bornite. This alteration style is pervasive and textural destructive, and has been reported to be overprinting the potassic alteration at the center of the system. A late event of phyllic alteration characterized by white sericite replacing completely feldspar and mafic phenos. It is structurally controlled, forming halos of different scales along fractures, and associated with veinlets of pyrite overprinting potassic, and early green sericite alteration.

Besides from the potassic and early pale green sericite alteration that dominates the deepest part of the system, a well-developed shell of advanced argillic alteration is observed at shallow depths and extending downward directly into the early green sericite alteration. This alteration style comprises the assemblages of quartz-alunite and kaolinite-smectite-diaspore.

## 5 Methodology

Detailed core logging and sampling of Copper Cliff deposit was carried out from sixteen drill holes at the core facilities of Kennecott Exploration in Missoula. A total of 43 drill core samples were selected from both, the early and the late phyllic alteration style. Each drill core sample was analyzed by petrography, short-wave infrared spectroscopy (SWIR), electron microprobe, and laser ablation inductively couple plasma mass spectrometry (LA-ICP-MS).

The petrographic analysis allowed the basis for discrimination of the mineral assemblage and textures of the different phyllic alteration types, and also provided a foundation for selecting the representative mineral targets for an accurate mineral chemistry determination by electron microprobe.

Major element chemical analyses of the white phyllosilicates were obtained using a CAMECA SX-100 electron microprobe at New Mexico Tech. A total of 120 valid microprobe analyses were obtained. These analyses were used to calculate the structural formula of the white phyllosilicates, from which was possible to extract important petrogenetic information about the conditions of formation, as well as facilitate the corrections during reduction of LA-ICP-MS data.

Trace element concentrations in white phyllosilicates were analyzed by LA-ICP-MS at the Corman Center for Mass Spectrometry at Rensselaer Polytechnic Institute, using a LA-ICP-MS system consisting of a detachable Photon Machines Analyte.193 ultra-short pulse excimer laser ablation (LA) workstation and a Bruker 820-MS inductively coupled plasma mass spectrometer (ICP-MS). For consistency, analyses were performed on the same sample locations measured by electron microprobe, and using a spot diameter of 100 μm. A total of 81 valid LA-ICP-MS analyses were obtained, with 28 trace elements determined per ablation spot in order to evaluate their distribution and homogeneity.

The spectroscopic data was collected from the off cuts of the thin sections using the Analytical Spectral Device – OreXpress field portable short-wave infrared (SWIR) spectroscopic mineral analyzer at New Mexico Tech. Data was analyzed using the Spectral Geologist software.

## 6 Results

Petrographic analyses showed that the early phyllic alteration is typically comprised by the mineral assemblage of pale green sericite, quartz, and hematite, locally accompanied by chlorite, anhydrite, and calcite (Fig. 1a). Texturally, the pale green sericite is pervasive and destructive, occurring as irregular patches randomly
distributed within the rock. Iron oxides, as specular hematite occurs within the sericite patches (Fig. 1b). In some places, it seems like specular hematite is replacing previous mafic phenocrysts, associated with chlorite. Anhydrite and calcite is also observed within the sericite patches. Hypogene copper mineralization is related with this early phase of sericitic alteration. It is characterized by chalcopyrite, and bornite.

The late phase of phyllic alteration comprises the mineral assemblage of sericite, quartz, and pyrite (Fig. 1c). It is structural controlled, and the rock texture is preserved. All feldspars are completely replaced by fine-grained white sericite, whereas all mafic minerals are partially or fully altered to yellow colored sericite. The yellow color is produced by residual Ti-oxides such as rutile, which in some places is observed associated with relics of mafic phenocrysts. Pyrite commonly occurs as subhedral to euhedral cubic fine grains disseminated in the rock, associated to sericite replacing both feldspar and mafic minerals (Fig. 1d). No copper mineralization is associated with this late phase of phyllic alteration.

![Fig 1](image)

**Figure 1.** Early and late phyllic alteration in hand sample and thin sections. a Early phyllic alteration in hand sample. Obliterated texture of the rock by green sericite associated with bornite mineralization. b Early phyllic alteration in thin section. Pseudophenocryst replaced by sericite with specular hematite in a quartz-rich matrix. c Late phyllic alteration in hand sample. It is structurally restricted and represented by white and yellow sericite that completely replaces feldspar and mafic minerals respectively. d Late phyllic alteration in thin section. Preserved porphyritic texture, but replaced by sericite and associated with pyrite. Ba bornite, Ser sericite, Hem hematite, Py pyrite.

The analytical results from microprobe analyses of white phyllosilicates at both styles of alterations indicate a composition of muscovite, within the field of illite (Velde, 1985). The early phyllic alteration has the compositional range of (K$_{0.63-0.91}$ Na$_{0.02-0.07}$) (Fe$_{0.02-0.33}$ Mg$_{0.03-0.74}$ Al$_{1.34-1.99}$) Si$_{3.05-3.36}$ O$_{10}$ (OH)$_2$, whereas the late phyllic alteration has the compositional range of (K$_{0.47-0.93}$ Na$_{0.02-0.08}$) (Fe$_{0.02-0.27}$ Mg$_{0.03-0.67}$ Al$_{1.34-1.93}$) Si$_{3.05-3.36}$ Al$_{0.37-0.98}$ O$_{10}$ (OH)$_2$. The content of iron, magnesium, titanium and manganese in the octahedral site is higher in the early phyllic alteration than the late phyllic alteration. In contrast, silica, octahedral (Al VI) and tetrahedral (Al IV) aluminum are slightly higher in the late phyllic alteration.

The chemical variation of white phyllosilicates is reflected to some degree by the SWIR analysis. White phyllosilicates from the early phyllic alteration presented an absorption feature from 2200-2209 nm corresponding to higher Fe and Mg content, in contrast with samples from the late phyllic alteration which have an absorption feature near 2198-2201 nm corresponding to higher Na content. In addition, muscovites from the early phyllic alteration have an absorption feature near 2250 nm, which may be related to the presence of chlorite. Muscovite from the early phyllic alteration also shows medium to low crystallinity, whereas the late phyllic alteration shows high crystallinity.

The trace element geochemistry of muscovites from the early phyllic alteration indicated that the most abundant trace elements are Ba (average 673 ppm), Ti (average 586 ppm), Cl (average 407 ppm), P (average 304 ppm), Sr (average 145 ppm), and Rb (average 129 ppm). Average concentrations detected for Mn, Zn and Cr range between 100-400 ppm. V, Cu and B at average range of 20-40 ppm, and Ce and La at average range of 5 – 20 ppm. Li, Sc, Ti, Sn, and Y were detected at average concentrations between 2-5 ppm, and W, Cs, Co, and Cd at less than 2 ppm below detection limits within 2-σ interval.

In the late phyllic alteration the most abundant trace elements are Ba (average 1300 ppm), Ti (average 880 ppm), Cl (average 602 ppm), P (average 231 ppm), Rb (average 183 ppm), V (average 130 ppm). Average concentrations detected for Sr, Zn, Cu, and Cr range between 100-40 ppm. B and Mn at average range of 20-40 ppm, and Sc, Ce, Sn and La at average range of 5 – 20 ppm. Ti, Li, Cs, and Y are were detected at average concentrations between 2-5 ppm, and Cd, W and Co at less than 2 ppm below detection limits within 2-σ interval.

Vanadium and scandium concentrations from the early phyllic alteration are significant lower than the ones in the late phyllic alteration (Fig. 2). The concentration of scandium in the early phyllic alteration is lower than 9.27 ppm, and vanadium lower than 91 ppm, in contrast with the late phyllic alteration with scandium content up to 30 ppm, and vanadium up to 217 ppm. Thus, LA-ICP-MS data shows utility in differentiating them.

Lateral and vertical transverses plots were constructed in order to identify trace elements gradients in white phyllosilicates across Copper Cliff deposit. Trace element geochemistry in muscovites from the early phyllic alteration reported systematic spatial variation relative to the porphyry center, therefore giving indications of proximity to mineralization. The results show that B, Sc, V, Cs and Ba increase in concentration with increasing distance from the center of the system. By contrast, W displays a maximum concentration associated with the mineralized center and decreases with increasing distance. These variations are evident up to 1 km from the center of the system, which provides an excellent vectoring tool for exploration.
Figure 2. Trace element compositional variation of white phyllosilicates from early and late phyllic alteration at Copper Cliff. White phyllosilicates from the early phyllic alteration (EPA) have a range of Sc between 0.39 ppm and 9.17 ppm, and a range of V between 0.91 ppm and 100 ppm. White phyllosilicates from the late phyllic alteration (LPA) have a range of Sc from 9.19 ppm to 30 ppm, and a range of V between 91 ppm and 217 ppm.

7 Discussion and conclusions

Compositional variations of major and trace elements in white phyllosilicates of the early phyllic alteration in porphyry systems gave indications of proximity towards ore, similar to those identified by previous studies in the late phyllic alteration. The results of this research could be translated in a better constrain of the lateral and vertical footprint model of porphyry systems, which may prove useful where exploring under cover or in deeply buried systems. Petrographic analysis and SWIR spectroscopy, combined with electron microprobe, and LA-ICP-MS analysis could be used to identify anomalies and gradients in white phyllosilicate compositions and trace metal abundances during initial exploration activities.

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Chlorite and epidote chemistry of the Yandong Cu deposit, NW China: metallogenic and exploration implications for Paleozoic porphyry Cu systems in the Eastern Tianshan

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Abstract. Three periods and six alteration and mineralization stages were identified at the Yandong Cu deposit, i.e., Porphyry period (including Stage I: Propylitic alteration; II: Quartz-magnetite alteration; III: Phyllic alteration); Superimposed period (including Stage IV: Superimposed mineralization and V: Late vein) and Supergene period (Stage VI: Supergene mineralization). Stage IV chlorite contains lower SiO2, MgO, Cr, Ni, Co, B, Ca, Sr, but higher FeO, Al2O3, Sc, Ga, Sn, Ti, Zn and Mn than Stage I chlorite. Stage IV epidote contains lower Zr, Ba and Ti, but higher Sn, Y, Ga, Ag, U, and Sr than Stage I epidote. Concentrations of Ti, Zn, As, V, Sc and Cu are highest near the orebody for both Stage I and IV chlorite. Stage I epidote is geochemically similar to the Baguio porphyry and skarn deposits, but Stage IV epidote has higher Sn, Ga and U, but lower Zr, Ti and Ba than the latter.

1 Introduction

The Yandong Cu deposit, located in the Eastern Tianshan mountains (Fig. 1), Xinjiang, China, is the largest and economically most important porphyry Cu district in the province, containing ~500 million tons grading 0.46 percent Cu and 0.2 g/tonne Au, with significant amounts of Mo and Ag. The deposit is hosted in the Carboniferous Qi’eshan Group and tonalite porphyry (Han et al. 2006).

2 Alteration and mineralization

On the basis of megascopic and microscopic textural relationships and mineral assemblages, we have divided the hydrothermal alteration and mineralization of the Yandong Cu deposit into porphyry mineralization (including propylitic alteration, quartz-magnetite alteration and phyllic alteration stages), superimposed (including superimposed mineralization and late vein stages) and supergene periods (Xiao et al. 2016; Wang et al. 2016). Superimposed mineralization stage was the main Cu mineralization stage, which is characterized by the mineral assemblage of chalcopyrite + chlorite + anhydrite + calcite. Unlike typical porphyry Cu deposits, potassic alteration is not well developed at Yandong. Hypogene Cu mineralization occurred mainly at superimposed period and minor at porphyry mineralization period, during which Cu was deposited mainly as chalcopyrite with minor bornite.

3 Chlorite and epidote chemistry of the Yandong Cu deposit

Stage I chlorite (Chl-1) contains SiO2 = 26.75 – 31.91 wt.%, Al2O3 = 16.00 – 22.30 wt.%, FeO = 9.47 – 21.01 wt.% and MgO = 19.21 – 26.83 wt.%, with Fe/(Fe + Mg) = 0.17 – 0.37. Comparatively, Stage IV chlorite (Chl-2) contains lower SiO2 (22.41 – 29.65 wt.%) and MgO (7.78 – 20.51 wt.%), but higher FeO (16.71 – 34.57 wt.%), Al2O3 (15.89 – 24.36 wt.%) and Fe/(Fe + Mg) ratios (0.31 – 0.71). Chl-1 mainly falls in the pycnoclorite field. Chl-2 primarily plots in the ripidolite and pycnoclorite fields. In the correlation diagram of the main cations in chlorite, Chl-1 and Chl-2 both exhibit good linear Al vs. Si and Mg vs. Fe relationships. Epidote EMPA results show a wide range of compositions from the epidote end member [Ca2Al3Si3O12(OH)] to clinzoisite Ca2Al2Fe3+Si3O12(OH), with XFe values = 0.14 to 0.40. Stage I epidote (Ep-1) shows significant chemical variation, with SiO2 = 31.92 – 41.16 wt.%, Al2O3 = 18.43 – 28.19 wt.%, FeO = 6.36 – 17.54 wt.% and CaO = 16.75 – 23.70 wt.%, and Fe/(Fe + Al) = 0.14 – 0.40. Stage IV epidote (Ep-2) contains similar chemistry with Ep-1, with SiO2 = 28.99 – 39.84 wt.%, Al2O3 = 19.90 – 29.90 wt.%, FeO = 6.75 – 15.77 wt.% and CaO = 19.00 – 23.63 wt.%, and Fe/(Fe + Al) = 0.14 – 0.36.

The most abundant trace element in Chl-1 and Chl-2 are Mn (1000 – 10000 ppm). Most Chl-1 and Chl-2 have Zn, B, Na, K, Sc, V, Cr, Co, Ni, Cu, Ga, As, Sr, Rb, Ba and Ti contents ranging from ~1 to 1500 ppm, or 100 to 1000 times of their respective detection limits, whereas concentrations of other elements, e.g., Y, Zr, Nb, Mo, Ag, Sn, and REEs, are either close to or below the detection limits. Both Chl-1 and Chl-2 show positive Ga vs. V, Co vs. Ni, and Mn vs. Zn correlations, but negative Sn vs. As correlation. Compared with Chl-1, Chl-2 shows higher Sc, Ga, Sn, Ti, Zn and Mn, but lower Cr, Ni, Co, B, Ca and Sr.
Figure 1. **a** Tectonic subdivision of Eastern Tianshan. **b** Geologic map of the Tuwu-Yandong Porphyry Cu belt (Han et al., 2006)

Figure 2. Geochemical comparison among the Yandong chlorite (Chl-1 and Chl-2) and the Batu Hijau chlorite and metamorphic chlorite from two Proterozoic metamorphic terranes in Australia (Wilkinson et al. 2015), which suggest Chl-1 is geochemically similar to chlorite in propylitic alteration stage of porphyry deposits.

Figure 3. Geochemical comparison between the Yandong epidote (Ep-1 and Ep-2) and the Baguio epidote related to porphyry Cu deposit, which suggest Ep-1 is geochemically similar to epidote in propylitic alteration stage of porphyry deposits.

The most abundant trace elements in Ep-1 and Ep-2 are Mn and Sr (> 500 ppm). Ep-1 and Ep-2 have B, Na, K, Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, As, Y, Zr, Sn, Sb, Ba, Pb, Hf and REE contents ranging from ~1 to 2000 ppm, or 100 to 1000 times of their respective detection limits, whereas concentrations of Ag, Mo, Nb, Au, Tl, Bi, Th and U are low (< 1 ppm). Compared with Ep-1, Ep-2 contains higher Sn, Y, Ga, Ag, U, Cu and Sr, but lower B, Zr, Ba and Ti.
The Yandong Chl-1 geochemically resembles the Batu Hijau propylitic chlorite. However, the Yandong Chl-2 contains higher Fe, Al and As, but lower Mg and Sn than the Proterozoic metamorphic chlorite in Australia (Fig. 2, Wilkinson et al. 2015). We found that Chl-2 coexists with chalcopyrite, anhydrite and calcite in veins, which is clearly different from metamorphic chlorite, indicating another type of hydrothermal chlorite. Hence, chlorite chemistry can not only be used to distinguish porphyry mineralization-related propylitic chlorite from metamorphic chlorite, but also variable types of hydrothermal-related chlorite. Ep-1 is geochemically similar with the epidote from the porphyry and skarn deposits in the central Baguio district (Philippines) (Cooke et al. 2014). However, the Yandong Ep-2 contains higher Sn, Ga and U, but lower Zr, Ti and Ba than the Baguio epidote (Fig. 3), which also suggests hydrothermal system different from porphyry systems.

Table 1. Summary of composition and spatial variations for chlorite and epidote in the Yandong Cu deposit

<table>
<thead>
<tr>
<th>Elements</th>
<th>Distribution</th>
<th>Spatial variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti of Chl-1</td>
<td>14.87–607 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Ti of Chl-2</td>
<td>23.8–469 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>V of Chl-1</td>
<td>54.6–268 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>V of Chl-2</td>
<td>6.91–616 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Zn of Chl-1</td>
<td>142–919 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Zn of Chl-2</td>
<td>198–3860 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>As of Chl-1</td>
<td>0.47–6.47 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>As of Chl-2</td>
<td>0.34–19.2 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Sc of Chl-1</td>
<td>0.39–18.8 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Sc of Chl-2</td>
<td>0.74–22.0 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Cu of Chl-1</td>
<td>0.47–1670 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Cu of Chl-2</td>
<td>0.24–25529 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Sn of Chl-1</td>
<td>0.14–0.62 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Sn of Chl-2</td>
<td>0.12–5.99 ppm</td>
<td>not obvious</td>
</tr>
<tr>
<td>Ti of EP-1</td>
<td>95.0–886 ppm</td>
<td>most elevated near orebody</td>
</tr>
<tr>
<td>Sc of EP-1</td>
<td>1.04–267 ppm</td>
<td>lowest near orebody</td>
</tr>
<tr>
<td>Zr of EP-1</td>
<td>1.03–244 ppm</td>
<td>lowest near orebody</td>
</tr>
<tr>
<td>Sb of EP-1</td>
<td>0.33–391 ppm</td>
<td>lowest near orebody</td>
</tr>
</tbody>
</table>

Our new Yandong chlorite data show that most elements have similar spatial variation patterns, despite that Chl-1 and Chl-2 were formed at different stages, e.g., titanium contents are most elevated in both Chl-1 and Chl-2 near the orebody. Wilkinson et al. (2015) argued that temperature is the principal control of Ti concentration in chlorite, which increases with increasing temperature, indicating that the hydrothermal centers of both Stages I and IV are all close to the orebody, which is consistent with the presence of the ore-forming quartz albite porphyry and tonalite porphyry there. Although the granodiorite samples were collected far away from the orebody, the anomalous chlorite in granodiorite with high Ti contents may have been generated by the heat sourced from the granodiorite. Similar to the case of Batu Hijau, vanadium concentrations in both Chl-1 and Chl-2 are most elevated near the orebody. Zinc content of chlorite increases exponentially with increasing distance from the Batu Hijau orebody, while Zn in the Yandong Chl-1 and Chl-2 are the highest near the orebody. Besides, As, Sc and Cu in both Chl-1 and Chl-2 are most elevated near the orebody as well; Sn in Chl-2 are most elevated near the orebody and very low or below detection limits away from orebody; but these trends are not obvious in Chl-1; while Au, Sn, As, Sc and Cu contents of chlorite do not show obvious change patterns in Batu Hijau. Propylitic chlorite from Batu Hijau show that large ion lithophile element (LILE, such as K, Ca, Sr and Ba) concentrations increase with increasing distance from the orebody (Wilkinson et al. 2015), a trend not observed in the Yandong chlorite, which may have been related to LILEs remobilization, due to the late tectonic activities at Yandong Cu deposit. Therefore, LILEs should be used with caution for Paleozoic porphyry Cu exploration.

The Yandong Ep-1 shows the highest Ti and the lowest Sc and Zr contents near the orebody, which is different from the Baguio epidote. Antimony in Ep 1 are mostly low near the orebody, similar to the Baguio epidote (Fig. 4). However, these chemical variation patterns are not obvious in the Yandong Exploration Lines 7, 15, 16 and 55, which may have been related to the superimposed alteration. The spatial variation patterns of Cu, Mo, Au, Sn, As, Pb, Zn, Mn and REE in Baguio (Cooke et al. 2014) are not present at Yandong.

Acknowledgements

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References


S09 – Geometallurgy: risk reduction through communication, optimization and innovation

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COREM
The value of full project integration (Geomet)

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Abstract. Over the past ten years, the field of ‘geometallurgy’ has evolved from a linear ore-to-mill concept into a cyclical model involving project integration and cross-functional team building. Companies that are on board with geomet and can afford their own in-house capabilities still struggle with implementation and getting teams to commit. Companies without the resources to build in-house teams rely on external services that commonly skew perspective toward their own capabilities. As a field, geomet still has no one singular definition as to what it is. This is because of the overall broad dimensions and potential that are still being expanded and understood. Geomet is really only one component of the overarching transition underway in the minerals industry that includes sustainability and cyclical economies. This change is focused toward ultimate project financial gain through the inherent value in ore and process variability. The key elements are: understanding variability, responding flexibly, creating a smart deposit to drive the smart mine, and building internal and external cross-functional partnerships for stakeholder and market value.

1 The integrated value plan

2017 marks 10 years since the field of geometallurgy really took off. Prior to 2007, geomet consisted of some excellent communications (e.g. Williams and Richardson 2004; Dobby et al. 2004; Dunham and Vann 2007) and concepts that were not yet commonly known or largely put into practice. As far as can be determined, ‘geometallurgy’ was first mentioned in 1968 (McQuiston and Bechaud 1968) as the identification of the important link between geology and metallurgy. In later years, this space was occupied by the field of process mineralogy (e.g. Hausen and Park 1981) throughout the 1970s, 1980s and 1990s. The AMIRA GeM project was started in 2006 (AMIRA International 2006—2013) to address the need for better tests, tools and methods for improved operations in increasingly complex ores. A number of related developments occurred at about the same time, chief among which was the commercialization and wide distribution of quantitative mineralogical methods (eg QEMSCAN, MLA) that proliferated in service companies (SGS and Phelps Dodge, most abundantly). Geochemical and geological modelling methods also developed (Lawie 2015), enabling a platform for correlating the vast mineralogical and geochemical data coming out of operations and the possibility of making some statistical sense of it all. New tests developed by JKTech, SGS and others to quantify hardness, throughput and recovery linked to mineralogy and geochemistry finally provided quantitative inputs to metallurgists and miners to gain some understanding of the nature of geological variability and its impact on their process development (see for example Baumgartner et al 2013; and papers from geometallurgy conferences held by the AusIMM, Australia, and Gecamin, Chile and Peru 2011—2016).

Today, the old, linear view of geomet as an ore-to-process pipeline has transformed into a cyclical economical model with the inputs of ore variability and a circle of mining operations, flexible processing options, stakeholder impacts, and overall value gains throughout the cycle (Hoal 2008, 2016). Unfortunately, the human team-building side of the equation has been the downfall of many efforts in geomet. There has been ‘too much data’ and too few cross-functional workplaces for the true value of these initiatives to be gained, and many efforts have stalled or been entirely abandoned.

A few key concepts have clearly emerged as critical to the success of an integrated value plan (geomet). Chief among these is that the technical value chain of operations and data analytics must work in parallel with the team value chain, cross-functional team development and an understanding of the drivers of the stakeholders and market. These components are illustrated in Figure 1 and provide the framework for this presentation.

2 Technical value chain

2.1 Operations

Mining engineers, metallurgical engineers and operators have come to recognize that variations in throughput and recovery are directly linked to the nature of the ore feed in real time. Ore variability is a 3D spatial issue that translates into time-based scheduling, and the value factors of downtime, poor recovery, deleterious elements etc are well known to operators. Predicting ore-based challenges is a matter of linking geological models to financial models, so that the distribution of variable materials can be anticipated and scheduled, and shovels feed the plant with material that is anticipated. Integrating the tools of geological models, quantitative mineralogy, core scanning, and blast hole geochemistry in advance gives operators some comfort of being ahead of issues. Today, however, still too much emphasis is put on grade distributions over hardness and other metrics that may have more direct financial outcomes.

The key words for the technical side are variability and flexibility, by putting the knowledge of variability to work in a flexible mining process (Powell 2013); understanding that the value in variability can be positively gained from predicting the impact on operations. The unfortunate response from the mining side to highly refined geomet models is that the operators are unable to respond to change. They are constrained by
capital investments made into mill and plant equipment possibly at very early stages in planning, before the nature of the orebody was fully characterized. Quite often the plant is built for one type of ore but not optimized for later variability in ore. In order to anticipate and respond to variability, miners need more flexible tools. Fortunately there is a solution. More flexible, modular options are being developed that will help operators plan for anticipated ore streams far in advance. Possibilities include the flexible and modular mill options coming online (Powell 2013) and the online exchanges being developed for shared sale or trade of unused-unearning assets (e.g. Mangan 2017). For mining, this means that with notice of ore variability known well enough and in advance enough time, operators can plan years out for known and understood variability in ore materials.

2.2 Analytics

For some time, geomet meant confusion to many operators. Too much data, in too many dimensions, and not in any usable time frame. The increased applications of data analytics in the minerals industries has made for at least two significant mindset changes. Most people are aware of the growing robotic nature of mines and operations, most notably shown by Rio Tinto’s iron ore operations in Western Australia. Large companies with significant in-house capabilities and budget are able to move in this direction because of Internet of Things and other machine-to-machine linking data systems, leading to the development of the ‘smart mine’. Service companies and management consultants have jumped onto the data analytics in mining side as well, as one means of making mining certainly safer, and potentially more effective.

But data are not information, and there still is needed a means to help the smart mine actually mine smartly, and not simply automatically. This is the geomet world, where integrated orebody geological-mineralogical-grade-geochemical-structural models are brought together with risk factors such as hardness, deleterious mineralogy and elemental geochemistry, knowledge of unrecoverable resources, locking and liberation, etc. to develop the ‘smart deposit’, to inform and direct the smart mine.

3 Team value chain

3.1 Internal

Geomet as a linear process relied on external resources, experts and consultants, as a sort of one-man-band problem solver. The integrated process ends when the consultant goes away, if in-house personnel are not tasked to champion the broader geological-operational initiatives. As the field has matured, companies have developed internal capabilities that look at projects, operations and portfolios with consistent geomet protocols. In-house teams begin by bringing in diverse perspectives and operational viewpoints, but commonly end up as yet another distinct silo in the overall project or corporate structure. When isolated from other teams, these groups lose effectiveness and during cost crunches may be eliminated.

In the cyclical minerals model, geomet teams are integral to operations and are made up of individuals from across the company divisions. They are diverse, with diverse perspectives, but continuously focused on value as the key operative focal point. By being cross-functional, diverse, and value-focused, barriers to communications and cross-learning are lowered and new innovative ideas cross areas because of new insights. The ‘same old, same old’ cannot exist in an environment of new eyes and ideas.

3.2 External

With the one-man-band external expert role changed to an integrated in-house team, the opportunities for external team building is enabled through renewed and new partnerships. Partnerships with technical experts, labs with new and innovative resources that companies may not need to acquire internally, and financial assessments that have a broad understanding of all the technical risks being faced in a project. This means being able to convey and present the full understanding of the deposit and operations openly for review and analysis by the market, and by all the stakeholders, including shareholders and also community, regulatory, governmental, and financial stakeholders. The upside of full exposure, after full understanding is made internally, is in potentially new opportunities, a greater transparency, and improved visibility for the global public as well leading to new views for the industry.

4 Plan for value

The value of full project integration is in reduced uncertainty through greater understanding. This process allows for the ability to incorporate knowledge into new ways, by better data analytics and operational innovation leading to a smart deposit that directs the smart mine. In parallel and as essential, old mindsets and divisions transform into active cross-functional and diverse internal teams with external partners. From an academic perspective, this is what industry leaders tell us they need from graduates. Barriers and differences fall away when diverse activities are put in the context of value, instead of tons or ounces or minerals.

The current emphasis on sustainable development and the circular economy can provide new and exciting possibilities for the mining industry, if it is allowed to do so. Using flexible mills and reaching more value of unused capital assets are only two low-hanging-fruit examples of unrealized value gain. Ultimately, a spherical model will replace the circular economic model, as a web of interconnected impacts. Fully realized ore value will be the critical and central element to the truly smart deposit.
Acknowledgements

This work has evolved over many years and in response to conversations and collaborative work with many individuals. Key transformative leaders who have helped to develop and grow the value proposition for geometallurgy include Steve Williams, John Vann, Malcom Powell, Peter Amelunxen, Dave Lawie, Steve Walters, Graham Davis, John Thompson, Jean Richardson, Guillermo Turner, Regina Baumgartner, John Jackson, Alan Butcher and Jane Stammer Hearon. I thank them all and many others.

References


Figure 1. Simple organizational chart illustrating the key components of planning for value in an integrated process.
Towards a more automated mineralogy

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GeMMe, Université de Liège, Belgium

Abstract. Automated mineralogy has been around for more than thirty years as the reference technique to support process mineralogy and geometallurgical studies. Pioneering techniques such as the QEM-SEM have been further improved to benefit from the latest hardware developments in terms of stable, sensitive and efficient imaging. FEG sources, solid state x-ray detectors and almost real-time signal processing have made the most significant contributions in the last decade. A quick overview of existing technologies reveals that further improvement could be gained by merging different imaging modes and using more advanced classification algorithms such as those well known in machine learning and remote sensing. If such algorithms were complemented with hierarchical databases wherein only important economic minerals are listed with their associated probabilities of occurrences, significant improvements could be gained in automated mineral identification. This paper contributes to demonstrate that a real “mineral intelligence” of ores and materials is now within reach.

1 Introduction

Minerals are the essential building blocks of the rocks and ores we prospect and process. Therefore our capacity to describe any material in terms of constituent phases is of primary importance if we want to develop a prognostic characterisation of the behaviour of this material during mineral processing, extractive metallurgy or even recycling.

Quantitative approaches have been pioneered in the XIXth century and led to the incidental discovery of the first principle of stereology by a French mining engineer (Delesse 1848). In those times, hand-drawn contours of mineral grains were the basis of area fraction estimations \((A_x)\) whereas today the proportion of pixels in a digital image is a more straightforward procedure (Pirard and Sardini 2008) … given any pixel has previously been associated to a mineral species!

This critical step of properly assigning a mineralogical species to a pixel is at the heart of what is designated a bit abusively today as automated mineralogy (Sutherland et al. 1988). Indeed, the process of building a species identification protocol (SIP) before running any new analysis is a critical step still requiring a lot of manual editing and supervision by a skilled operator. A fully automated mineralogy will only be claimable once we reach a fully non-supervised classification. In this paper we explore some possible ways forward.

2 Mineral identification

2.1 Minerals from spectral signatures

Marcasite is a common mineral with a fixed composition \(\text{FeS}_2\) exactly similar to pyrite, but an orthorhombic crystal structure. With the exception of using micro-diffraction technologies, there is obviously no easy way to discriminate it from pyrite under the scanning electron microscope.

As evidenced by figure 1, the full reflectance spectrum from 400 to 1000 nm documented by Castroviejo et al. (2010) offers good perspectives in reflected light optical microscopy provided a suitable imaging technology is being used. A first possibility would be to take images in the very near infrared (700nm) and use a simple thresholding criteria to classify pixels as marcasite (< 50%) or pyrite (> 50%). An alternative technique is to stack together images taken at 500 nm but at different orientations of the polariser (Pirard et al., 2007) and make use of the variability of individual pixels as classification criteria (Fig. 2).

Figure 1. Specular reflectance spectra (400 nm – 1000nm) of bireflectant marcasite (red dotted lines) as compared to pyrite (green line). Data from Castroviejo et al. 2010.

2.2 Minerals from chemical composition

Modern Si-drift detectors have brought significant improvements to the capabilities of energy dispersive analysis of X-rays generated by e-beam excitation (SEM-EDX). It has been common practice until recently to identify mineral species by least square comparison of their raw spectrum with synthesized or experimental spectra collected in user-defined database. However, it is now possible to achieve almost real-time deconvolution of EDX spectra and identify minerals from their quantitative chemical composition.
3 Lessons learned

3.1 Multimodal imaging

Previous examples indicate that the combination of several imaging modes, what is known today as correlative microscopy, is the way forward to achieve an optimal phase recognition. Mineralogical imaging software should be able to stack together multispectral (different wavelengths) and/or multiradial (different orientations of the polariser) optical images, backscattered electrons images and EDX maps so as to almost perfectly discriminate the different domains existing in any material.

In order to improve image segmentation it is also strongly recommended to use multivariate classification and not just simple thresholding techniques. Basically, there are two families of multivariate classification techniques: the supervised and the non-supervised. The first ones require the operator to introduce a priori knowledge in terms of a list of minerals present in the scene, or alternatively to train the system by designating representative regions of the different minerals. Non-supervised techniques on the other hand, are fully autonomous and will identify clusters in the spectral signatures (feature space), which can then be checked automatically against a mineral database. The only problem with non-supervised techniques is that they need a stopping criterion such as for example the maximum number of clusters to be identified. Figure 3d illustrates how segmenting into six clusters instead of five reveals a chemical zonation in a hercynite crystal which would otherwise be considered as a single domain.

3.2 Mineral databases

There are plenty of databases compiling physical and chemical properties of minerals. Among the most well-known are WEBMINERAL with 4171 minerals searchable by composition or structure and RRUFF with 3527 minerals and their chemistry, X-ray diffraction patterns, Raman or Infrared reflectance spectra. Despite the commendable efforts made by the authors, these databases will remain of poor use in automated mineralogy as long as probabilities of occurrences and associations are not being introduced.

Considering applications in geometallurgy and process mineralogy, the selection of minerals can certainly be reduced to a few hundred species of economic interest. Moreover, within a given environment (orebody model), it is obvious that some minerals or some associations (parageneses) have to be ruled out or have very low probabilities of occurrence.

In addition to probabilities, a database could also include a hierarchical grouping of minerals into geometallurgical families as illustrated in figure 4. Geometallurgical families could be defined as groups of minerals with similar behaviour in a given process (ex. flotation) or containing the same valuable element.
3.3 Mixels

A classical problem in image segmentation is the appearance of mixels or pixels with a mixed signature. Mixels are very common in remote sensing as the spatial resolution is often so low that most pixels have to be interpreted as a mix of one or more pure mineralogical (or lithological) components. Algorithms such as pixel purity index have found interesting applications in mineral resources mapping (Caceres et al. 2008).

In automated mineralogy under the microscope, spatial resolution is usually higher than the smallest grain size. Hence, mixels are most often due to solid solutions or to transitions between two grains. In the first case, a mixel has to be interpreted correctly as a transition between two acceptable mineral species (ex. hübnerite and ferberite), whereas in the second case a mixel has to be replaced by either one or the other mineralogical species. Figure 4 illustrates how well identified mineralogical species can compete for a transition zone (mixels) using conditional dilation.

![Image of Figure 4](image)

**Figure 4.** Example of a hierarchical classification of sulphides and secondary Cu-bearing sulphides (chalcopyrite, bornite, covellite, digenite, chalcocite,…).

4 Conclusions

The proper identification of major ore minerals under the microscope is within reach of automated systems provided they use and combine all possible sources of information within one single classification procedure. So-called correlative microscopy should become a standard technology to seamlessly observe ore textures under different microscopy modes. Thanks to advanced classification algorithms (using for example hierarchical clustering), it will be possible to identify the purest signatures in a scene and check these with respect to a hierarchical database including probabilities of mineral occurrences. Remaining unclassified pixels should be further refined and checked against the possibility of being mixels of previously identified species. A propagation algorithm will make sure to reallocate all mixels to the corresponding mineral classes or eventually to a new term (solid-solution).

After classification, a cross-validation should always be performed between image analysis and chemical analysis (ICP-MS) or semi-quantitative mineralogy (XRD). Discrepancies should be identified and eventually lead to the decision to repeat the classification in case of major discrepancies in terms of identified minerals or mineral abundances.

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Mineralogy Database Online, available at [http://webmineral.com](http://webmineral.com)

RRUFF an integrated database of Raman spectra, X-ray diffraction and chemistry data for minerals, available online at http://rruff.info

Geometallurgical mapping of ore hardness

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Abstract. A method has been developed and tested on iron ore drill cores to predict the pinion energy measured by the SAG variability test (SVT) from the SAGDesign suite. The test requires the measurement of the specific power consumption of a roller crusher and its feed and product size distributions. Results using linear regression have shown that the power measurement and sieve analysis are sufficient to predict the pinion energy estimated by the SVT test ($R^2=0.71$). In order to determine the method’s robustness, a reference material was used periodically during the measurement process. The relative standard deviation in the grindability estimation of the reference material was 17%. This approach is suitable for variability mapping.

1 Introduction

Geometallurgy is recognized as a high-value activity for developing an understanding of ore characteristics. In turn, this information supports the design of more efficient machines, circuit, and process controls. Geometallurgy combines geological and metallurgical information to create spatially-based predictive models for mineral processing plants (Lamberg 2011). The spatial nature of geometallurgy should influence the selection of comminution tests for a campaign. Within this context, low cost and high variance tests (proxies) may be combined with more precise and expensive tests to generate the required data for informed decision making.

In the past, AMIRA developed a rapid and low-cost comminution test called GeM Comminution index (Kojovic 2010). The test was inserted into routine assay sample preparation and was based on constrained jaw crushing protocols with size distributions analysis. This comminution index was used to estimate the $Axb$ impact breakage parameter and the Bond ball mill work index. According to the authors, estimates of the $Axb$ showed a low level of correlation and required further research to improve the model. Limitations of the GeM comminution index also included problems with friable cores, high clay content, variable feeding, crusher closed size setting (CSS) drift, and large variation in shapes. To improve the accuracy of the different relationships, the authors mentioned investigating the use of a power meter to quantify energy consumed during crushing.

In order to overcome some of the limitations of the GeM comminution index, a new proxy test is suggested. The aim of this work is to develop a robust indicator that can be used to complement standard rock hardness variability tests.

The SAGDesign or SAG variability test (SVT) measures a combination of impact and abrasion breakage which may represent an advantage over the drop weight test because they replicate, at lab scale, the complex environment existing in an autogenous grinding (AG) or semi-autogenous grinding (SAG) mill and its mixture of breakage mechanisms (Starkey 2007). The new proxy test is based on power and size distribution measurements during routine metallurgical characterization preparation on a roller crusher.

The procedure was developed and tested on iron ore drill cores from Mont-Wright with the collaboration of ArcelorMittal Mines Canada (AMEM).

2 Methodology

2.1 Comminution index measurement

For the development of the test, approximately 600 drill core samples from ArcelorMittal were processed at COREM. These samples are used in a characterization program that requires crushing to minus 3.35 mm. An overview of the preparation and data acquisition for the measurement of the comminution index is presented in Figure 1. The drill cores were weighed, then coarsely crushed by a jaw crusher and split into two groups by sieving. The first part of the sample was used for SVT testing as a hardness reference. The other part was stage-crushed to a finer size. The product of the jaw crusher fed a roller crusher. The feed size distribution was measured. Then, the material was crushed down to 100% passing 2.8 mm with power consumption acquired using a power meter (Fluke 434, Fluke Electronics Canada LP) with an acquisition rate of 1 measurement per second. The product size distribution was measured. Overall, the new comminution index requires two size distribution measurements and a power measurement. Those tasks do not interrupt the normal assaying process, because power is passively monitored and sieving can be performed in parallel of the main operation.

Power measurement was achieved on more than 600 drill cores. A SVT was done on 39 of those drill cores for calibration. Crushing of those 39 samples was done within similar conditions, with measurement of the feed size distribution, product size distribution, and of the specific comminution energy at a CSS of 3.35 mm. Among them, 20 tests were repeated at a CSS of 2.8 mm.
Throughout the process, an internal reference material (MRI) was used to evaluate the repeatability of the measurements. First, analysis of the product size distribution was used to measure the system’s consistency to achieve identical results across multiple tests. Second, the statistical distribution of its grindability estimations provided an estimate of the precision of the test. Sixteen MRI were measured during the process.

### 2.2 SAG variability test

The SAGDesign test was invented to design AG-SAG/Ball mill circuits. The first part of the test measures the AG-SAG pinion energy to grind ore from 80% passing 152 mm to 80% passing 1.7 mm (Starkey 2006). The second stage of the test measures the Bond Ball Mill Work Index on SAG ground ore. SAGDesign ore feed is prepared from a minimum of 10 kg per sample of split or whole diamond drill core pieces by stage crushing the ore in a jaw crushe to 80% product passing 19 mm. The crushed ore is then ground in a SAGDesign SAG mill (26% total charge; 11% steel load, and rotation at 76% of critical speed). The SAG pinion energy is estimated to be within ±4.6% relative error (Starkey 2012). The SAG variability test is an abbreviated version of the complete SAGDesign test which allows predicting the SAG pinion energy within ~10% relative error.

### 2.3 Data processing

For every sample, the power measurement was integrated over time to provide a measurement of energy consumption. Specific energy was computed by dividing the energy by the mass of the samples. From this dataset, a linear model was developed around the crusher operating parameters using feed and product size distributions and specific energy to predict SVT grindability. Equation 1 shows the general form of the model.

\[ SVT = a \cdot P_{F0} + b \cdot P_{B0} + c \cdot P_{B0} E_{zp} \]  

### 3 Results

A linear model with interaction between the specific energy, feed and product size was investigated (Figure 2). Within this model, a CSS change within the range of 2.8 mm to 3.35 mm had nearly no effect on the predicted value of SVT grindability. Sixteen repetitions done on the reference material gave a relative standard deviation of 17% (Figure 3). Most of the duplicates gave the same prediction in kwh/t within the range of the standard deviation defined using the reference material (Figure 4).

**Figure 1.** Methodology for the sample preparation and data acquisition.

**Figure 2.** Calibration of the comminution index based on the feed size, product size and specific energy.

**Figure 3.** Prediction for the reference material.

**Figure 4.** Comparison of SVT predictions and measurements for two different crusher closed size settings. All duplicate predictions overlap within 1 standard deviation.
4 Discussion

The aim of this work was to develop a robust indicator that can be used to complement standard rock hardness variability tests and overcome some of the limitations of the GeM comminution index. The indicator is included in the process of producing material for the subsequent downstream concentrability testwork.

One of the first addressable limitations of the GeM comminution index (Table 1) is the variable feeding. The newly developed test was done on a roller crusher. During the preliminary tests, the roller crusher was more reliable than the jaw crusher for prediction. It is reasonable to suggest that a smaller feed with better controlled size and shape may be the main reason for the difference.

Another limitation of the test was the crusher CSS drift. By repeating tests with different CSS, it was shown that a CSS drift could generate important bias in the predicted grindability. Developing an indicator based on product size alone is very tempting because of its simplicity, but is very vulnerable to CSS drifts. The use of a reference material measured several times during the process could be enough to identify and potentially correct a CSS drift. Another solution, inspired by the laws of comminution, is to include feed size and specific energy consumption in the modeling process. Models including the feed size and specific energy provide some improvements over CSS variation.

Using a multiple linear model including feed size, product size and an interaction between energy and product has revealed to be a robust approach. The predicted SVT was higher when the product of energy and product size was high, corresponding to higher energy required to achieve a coarser product size.

The limitation related to predicting the A×b was addressed by selecting a different test. The SAG variability test was selected because it more closely replicates the complex environment existing in a SAG mill with its combination of abrasion and impact breakage. The problem of friable cores was not specifically addressed within this work, but the SVT allowed estimating grindability down to ~1 kwh/t from which some samples were in the friable category. Very hard ore is also expected to benefit from the selected test (Starkey 2010).

Geometallurgy, in the sense of measuring grinding hardness variability, is often unreliable because the grinding hardness data used today is too expensive and time consuming to relate to every block of ore in a mine model (Starkey 2010). The result may be a compromise in the spatial resolution achieved by grindability tests. In Figure 5, a 1D adimensional example can be seen for which the budget was for 4 SAG variability tests to capture the ore variability.

![Figure 5](image)

Figure 5. Example of 1D kriging using 4 points with relative error of 10%. The red line is the true variability of the ore. The black lines are the kriging model with 95% confidence interval.

![Figure 6](image)

Figure 6. Example of 1D kriging using 2 points (at position 0 and 1) with relative error of 10% and 20 points with 30% error.

If a proxy test is available for about 1 tenth of the cost, then another test pattern can be considered (Figure 6). Even though the relative error of each test is high, the quality may be offset by the quantity that can be achieved with the same resources.

<table>
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<th>GeM comminution index limitations</th>
<th>New comminution index solutions</th>
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<td>Feed size distribution is measured and included in the comminution index.</td>
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<td>Rock friability</td>
<td>SAGDesign tests can estimate grindability down to 1 kwh/t.</td>
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If a correlation can be found between assays, mineralogy, ore type and hardness, it may be possible to use this method to develop an enhanced geometallurgical model for the mine (Starkey 2010).

5 Conclusion

In conclusion, the aim of this work was to develop a robust indicator to complement standard ore hardness variability tests. It was shown that an indicator based on power and size distribution can be positively correlated with SVT measurements. The proxy is able to predict the pinion energy to grind ore from 80% passing 152 mm to 80% passing 1.7 mm with a relative error of 17% which must be added to the uncertainty of the SVT model versus the full SAG hardness measurement during the SAGDesign test. This level of error seems high, but the lower test cost offsets this limitation by providing 10 times the amount of tests, and therefore a better spatial resolution for the same amount of money.

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Gold deportment in mills: Insights from exploration techniques

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Abstract. Gold erratic distribution and low abundance makes evaluating its deportment in mill difficult. Gold grains are rare and thus statistical representativeness is difficult to reach. Therefore establishing where it stands in regards of other phases can be challenging. Gold is present in parts per million in the ore, and parts per billion in the tails. Conventional techniques such as MLA are of no match with statistics, and extreme preconcentration is required to obtain a sufficient abundance of gold grains to be meaningful.

Preconcentration of gold grains for counting is routine technique in glacial drift exploration. Insight from the latest technologies enabling recovery of very fine grains can be used for assessing gold deportment in metallurgical processes. Free gold grains larger than 20 μm can be reliably recovered with fluidized beds and counted with the use of automated SEM. Grains smaller than 20 μm can be concentrated by centrifuging the sample in heavy liquids at a density of 4 or higher, and counted with automated SEM at high magnification. Non-liberated gold grains hosted in particles larger than 20 μm are concentrated with heavy liquids at a density of 4, and mineral proportion evaluated with MLA type routine.

1 Introduction

Even if most gold mining operation achieves recoveries in excess of 90%, this still means that about 300 tons of gold is lost in tailings per year, for a value of about 12 b$. Even for a single mid-size mine, such as Canadian Malartic Mine in Abitibi or Goldcorp's Eleonore in Northern Québec, this represents about 30,000 to 60,000 ounces per year!

Maintaining good recovery is a daily challenge in a process plant, and gold is no exception. One of the difficulties remains in establishing where does the non-recoverable gold reside? This information is critical in mill adjustment, just as for any other minerals. This difficulty originates from the very low abundance of gold in tailings, typically below one tenth of a gram per ton, or <0.1ppm and the nugget effect (Goodall 2008). It means that, if gold is present solely as native metal, about one gold grain is found per 10 million particles. This low abundance renders conventional quantitative mineralogy techniques to measure deportment, such as MLA (Gu 2003) or QEMSCAN (Butcher et al. 2000), inefficient. A typical epoxy grain mount contains up to a maximum of 100,000 grains. To find a single gold grain would require to scan about 100 mounts, and at the least ten particles are required to achieve a minimal statistical representativeness, and about 100 particles for the coarse fraction. Even using bright phase recognition based on back scattered electron imaging, the challenge is unrealistic and extreme preconcentration is needed.

2 Gold deportment

The characterization of gold deportment is crucial to increase the efficiency of gold extraction. Reasons that gold can’t be recovered in milling process depend mostly on how the gold is set. This section attempt to summarize, depend on the gold habits, the gold recovery and the method used to characterize gold deportment.

2.1 Native gold

Bulk of the gold in most deposits is present as native gold, more or less alloyed with silver (Hough et al. 2009). Size of thousands of gold grains unmodified by comminution down to the optical resolution of 1 μm were measured in-situ by ore petrography conducted on hundreds of samples from various mines of the Abitibi and James Bay (Fig. 1 and 2). A grain size distribution curve indicates that about 80% of the gold grains are smaller than 20 μm (long axis), regardless of the host minerals. Such grains are not recovered by the gravimetric circuit in mills, but expected to be recovered by the cyanide or flotation circuits (Soto et al. 1996). However, mass being a cubic function of the diameter, grains larger than 20 μm still represents about 90% of the metallurgical balance, explaining the high recoveries despite the loss of small grains. Usually, native gold deportment as characterized by automated mineralogical techniques using SEM (Henley 1992, Hall 1977). As an example, 80% of the grains are smaller than 20 μm, not recoverable by gravity circuit in mills, and accounts for 10% of the gold by weight.
Figure 1. Gold grain’s size distribution (N = 4316 gold grains) from hundreds of ore petrography reports from Abitibi and James Bay mineral occurrences by IOS Services Géoscientifiques. The upper curve represents cumulative proportion of grains according to grain size, while the lower curve represents their cumulative contribution in regard of mass balance.

Figure 2. Gold grains from Cheechoo occurrence, James Bay, Québec, as seen under the optical microscope at 1000x. Notice the overwhelming abundance of micron size grains.

2.2 Gold minerals

Gold forms few minerals by itself, which are rare in most deposits and has minimal contribution to metallurgical balance. Calaverite AuTe2, maldonite Au2Bi, aurostibine AuSb2, are the most common (Marsden and House, 2006). These minerals can be recovered either by gravity or flotation along with other sulfides. Estimating their proportion require concentration just as for gold grains and faces the same challenge to be representative (Goodall 2007).

Gold can also be present as an alloy with other metals, such as electrum (Ag,Au), amalgam (Hg,Au) and various platinoid (dominantly Pt, Pd and Ir). These are expected to behave as native gold in metallurgical circuit. Estimation of their abundance require the same approach as estimating gold grains.

2.3 Non-liberated gold

Gold attached to its gangue minerals, either sulfides or silicates, is either non-liberated or encapsulated, depending on whether one face of the grain is exposed. Encapsulated gold is not available for cyanide leaching and significant contribution to losses.

Concentrating non-liberated or encapsulated gold grain cannot be achieved efficiently by conventional gravity methods (shaking table, Knelson concentrator, etc). The density of the composite particle is dependent on the nature of the host mineral and the volumetric proportion of the gold grain. Using heavy liquids, density shall be selected carefully to optimize recovery, while not generating concentrate which are too large to be efficiently scanned with the SEM (Goodall 2008). Counting of non-liberated and encapsulated gold grain can be accomplished with conventional MLA, but require working with polished epoxy mounts to expose them, and upon a sufficient number of mounts to obtain representativeness.

2.4 Gold as substitutions in other minerals

Gold benefits from being overwhelmingly present as native metal, and not present in significant proportions as a chemical contaminant in other minerals. Gold as substituted in sulfides can be measured in-situ by LA-ICP-MS, SIMS or fLA-ICP-TOFMS, with a typical abundance of 10 to 20 ppm. There are abundant studies reporting abundance of gold in various sulfides for academic purpose, typically 10-20 ppm. Bulk abundance can be measured by assaying of sulfide concentrates. Assessing the abundance of sulphides can easily achieve with conventional MLA.

Gold abundance as chemical substitutions in silicate mineral is poorly documented, and usually considered as negligible. However, although present at ppb levels, it can contribute to a significant proportion of deported gold in tailings.

2.5 Unrecovered cyanide leach liquor.

Gold from the cyanide leach liquor can be almost totally recovered by activated carbon, as long as this liquor is thoroughly rinsed from the pulp. Minute amount of dissolved gold is expected to remain in the moisture of the paste.
3 Technologies from exploration

Gold grain counting in glacial sediments is a well-proven exploration technique since more than 40 years (Hallbauer and Utter 1977). It is based on recovering and counting grains, from samples typically 10 kilograms in size. Gold grains are concentrated using various gravimetric methods, usually tabling and panning, up to a super concentrate weighting a fraction of a gram, which is then examined underneath a binocular microscope. The conventional method is, however, plagued by non-constant recoveries, and limitations in regard of grain size. It is labour intensive technique, requiring skill and practice for the operator, and therefore not parameterized and hard to automate. Typically, with proper care, a recovery of about 60% of the gold particles is achievable down to a grain size of 50 μm, below which recovery collapse. Grains larger than such threshold represent less than 10-12% of the population or 50-60% by weight, and are plagued by erratic distribution (Fig. 1).

In the last few years, number of improvements on the gold grain counting technique has been introduced, both as more reliable gravimetric concentrator, salt-based heavy liquids and SEM grain counting. The method uses a “fluidized bed” technology to concentrate the gold particles down to a few micrometres. The concentrate, produced from 10-20 kilograms of pulp, is about 100 milligrams in size, containing about 2 million particles. Commercialized as ARTGold™ (Néron et al. SGA, 2017), the method enables counting of gold particles with a recovery in excess of 90% down to a grain size lesser than 20 μm. Recoveries have been monitored for months, and constantly demonstrated. The concentrate is spread on a specifically designed sample holder, and scanned with the SEM, using Oxford-Instrument Aztec-Feature software (Fig. 3). This software enable cataloguing particles based on a classification algorithm involving BSD phase recognition and fully deconvoluted EDS analyses on selected particles. Dense particles such as gold grains, are detected, counted, indexed, imaged with high resolution BSD, and analyzed by EDS-SDD. An atlas of grain is produced with proprietary software, each classified in terms of shape with the use of artificial intelligence (Fig. 4). Scanning and classification of a sample is achieved in less than an hour. Volume, hence mass, of the grain is estimated using Corey shape factor (Corey, 1963), accorded to the shape of the grain. The procedure allows fast and accurate measurement of the coarse gold in the tails. Optical sorting technology, using similar procedure as SEM-based, are currently being developed, which would enable multiplication of the counting capabilities.

Concomitantly, technologies are currently being developed to further reduce grain size recovery, down to a few micrometres. The exploration goal is to improve “detection limits”, in order to maintain representativeness while reducing sample size and thus sampling costs. SEM based grain counting techniques are demonstrated to work down to the micrometer. However, the challenge is the concentration of the clay size gold dust, which is not achievable by conventional gravimetric methods in water. Rheology calculations indicate that settling time for such particles is too long, and therefore concentration of such dusts is not possible using conventional methods.
small grain far exceeds residence time in a concentrator. A two-step technique involving separation by heavy liquids has been developed. First, the material (1 kg) from the tails is sieved at 20 μm with ultrasonic sieves. Heavy minerals from the clay fraction <20 μm are separated by a proprietary heavy liquid in a centrifuge at a density of 4 g/cm³. Only a few grams of material are required to achieve statistical representativeness. Thus, the separation is conducted in small test tubes. The heavy mineral is dusted on a custom sample holder, and scanned at high magnification with the SEM, in a manner similar to ARTGold™. Grain counts can be converted into volume and mass, providing the deportment of free gold not recoverable by gravimetric circuit.

The >20 μm material separated by ultrasonic sieving is expected to contain the particles with non-liberated gold. These are separated in lithium sodium polytungstate liquor (Fast-Float LST™) at a density of 2.85 g/cm³ in large 2 litres funnels and allowed to settle for days. The heavy mineral concentrate is then reprocessed with a higher density liquor, either LST up to 3.5 to 4 g/cm³, or proprietary liquor up to 5.5-6.0 g/cm³. Density is adjusted depending on the required phases to be recovered, either searching for gold grains attached to silicate or sulfides. The heavy concentrate is then mounted on epoxy, polished and processed with conventional SEM techniques. Abundance of sulfides is measured along. This manipulation enables measuring the abundance of non-liberated or encapsulated gold, as well as of sulfides or any other heavy mineral phase.

4 Conclusion

Most gold mill achieves recoveries in excess of 90%, but still each percent of recovery improvement represent significant income for the mine. Improving recovery require that gold deportment being measured, which is challenging due to its low abundance. The proposed technique, developed for exploration purpose, has been adapted to measure efficiently the abundance of minute gold particles, silt and even clay size, particles, and thus enabling the quantification of gold deportment between native gold, micronized gold, gold bearing minerals and sulphide abundance. The concentration procedure enables to obtain representativeness without having to multiply the number of mounts in the SEM. Currently close to be commercialized, the technique promises to be cost effective, dependable and accurate. Although complex, the technique can be implemented with a fast turnaround by commercial or operator’s laboratory.

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References


Abstract. X-ray computed tomography is a powerful technique to explore in 3D the distribution of pores and mineral phases in natural and synthetic samples. The present contribution illustrates its application across a range of scale to characterise and quantify in 3D iron-ores.

1 Introduction

Almost 1 billion tonnes of iron ores (A$60b) were produced in Australia in 2016 with approximately 96% of the iron ore exports mined from deposits located in the Hamersley province of Western Australia. Iron Ore exports dominate the industry in term of volume and price and represent respectively 91% in volume and 56% in value of total mineral export for the Australian economy.

The quality of an iron ore deposit is directly related to its Fe content and to its geometallurgical properties. In a nutshell, high Fe content and good geometallurgical properties will lead to higher selling price. Ultimately, geometallurgical properties are controlled by mineralogical, chemical and textural (3D distribution of pores and minerals and their shape/association characteristics) parameters. Optical and scanning electron-based microscopy techniques (SEM, MLA and QemSCAN) are the most commonly used for iron-ores (Donskoi et al. 2015 and Tonzetic 2015).

The present contribution presents some recent advances in 3D characterization of iron ores using X-ray computed tomography combined with 3D image analysis and quantification.

2 Methodology

2.1 X-ray computed tomography

X-ray computed tomography (XCT) is a non-destructive technique used to explore in 3D the distribution of pores and mineral phases in natural and synthetic samples, leaving the samples intact for further characterization (Fonteneau et al 2013; Godel 2013 and references therein). XCT is now commonly applied to a wide variety of rocks and ore materials across a range of scale (from 100’s of centimetres down to 100’s of metres of drill-cores). Although, the data acquisition is rapid (few metres per hour), the spatial resolution achievable limit the ability to differentiate complex mineral assemblage and textures. As such low resolution XCT is best used to quantify parameters that will complement logging (i.e. density logs, fracture networks, layering, large scale heterogeneities etc).

In contrast, high-resolution XCT (HRXCT) has the ability to generate multi-scale data (~25 micrometres down to a few hundreds nanometres) that can be used for quantitative measurements.

2.2 3D image analysis and quantification

After reconstruction, the dataset represents a regular volumetric grid, where each voxel has a unique gray-scale value. Dedicated image processing procedures allow not only the visualization of the three-dimensional volumes but also to the extraction of a number of three-dimensional microtextural parameters such as size, shape factor and morphology, textural relationships.

3 Example of application to Australian iron ore

3.1 3D characterization at the core scale

A decimetre-scale sample of banded iron formation (BIF) was scanned using low resolution XCT to highlight Fe-oxides micro-bands present across the sample (Figure 1A). The XCT data were notably used to provide direct measurement of density variation across the sample at ~500 µm resolution (Figure 1B).
Figure 1. Example of the application of low resolution X-ray computed tomography. (A) 3D volume rendering of a sample of Banded Iron Formation showing microbands of Fe-oxides in orange to yellow colors whereas quartz, minnesotaite, riebeckite, calcite and stilpnomelane are rendered as a shade of red colors; (B) Variation in average density calculated (for each XCT slice) across the entire sample based of X-ray attenuation. The XCT data was acquired at a 100 µm voxel size.

3.2 3D characterization at high-resolution

An iron ore lump (martite-goethite ore) was scanned at 3.35 µm voxel size to illustrate the utility of HRXCT in quantifying iron ore textures in 3D (Figures 2 and 3). The data were segmented to quantify pores, martite, vitreous goethite and ochreous goethite (Figure 3). The pore network topology and pore characteristics (open versus closed pores, pore size distribution and pore morphologies, degree of connectivity of the pore network and its tortuosity) have been quantified (Figure 2D). In addition, the presentation will illustrate other examples of mineral quantifications such 3D textural relationship, size distribution, degree of heterogeneity across the sample.)

Figure 2. Example of the application of high-resolution X-ray computed tomography. (A) volume rendering of the martite-goethite ore showing the overall lump texture; (B) and (C) 2D slice cut in the xy plane shown in A; and (D) pore network rendered in 3-D with light blue colour representing an interconnected pore-space network and red, yellow, green and dark blue colours representing closed pores of various size ranges.
Conclusion

Geometallurgical properties are controlled by mineralogical, chemical and textural (3D distribution of pores and minerals and their shape/association characteristics) parameters. X-ray CT is a powerful technique to characterize iron-ore and quantify its 3D textures. Future work will focus on the development of techniques to increase samples throughput to several hundreds of samples.

References


**SEMs, mines and mineralogy – On-site automated mineralogy delivering an operational mineralogy approach for mine management**

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**Abstract.** Automated mineralogy has had a long and successful history in delivering value to mines through its application within an integrated process mineralogy approach. Over recent years, technological developments have led to the introduction of automated mineralogy solutions (MinSCAN) onto the mine site itself. The deployment of such technology has enabled the evolution of process mineralogy towards operational mineralogy. By deploying such technology onto the mine site, mines are able to carry out routine mineralogical characterization of material passing through the plant. Through employing routine mineralogical assessments and utilizing a big data approach, these onsite solutions are delivering actionable data that can be used to optimize processing circuit and produce a more consistent operation. This talk will introduce the concept of operational mineralogy and highlight how onsite and routine mineral analysis can deliver value.

**1 Introduction**

Process mineralogy is an integrated and multidisciplinary practice that has developed over the years to deliver unquestionable value to mining operations around the world. The driver behind process mineralogy is to understand the connection between mineralogy and metallurgical performance in the plant. A modern process mineralogy approach is built around 5 key pillars; representative sampling, understanding geometallurgical domains; strategy for mineralogical measurement; quantitative/automated mineralogy and metallurgical test work (Lotter et al. 2011). At the core of these integrated studies is a thorough and robust characterization of the mineralogy. The mineralogical characterization is typically carried out during the feasibility and process development phase of the project and at intermittent periods through the life cycle of the operation.

Typically, techniques such as automated mineralogy (AM), electron microprobe (EMPA) and XRD are used. AM, using a SEM-EDS based approach is able to provide high resolutions and high throughput characterization of the mineralogy, liberation, grain size, elemental deportment, associations and locking characteristics. The application of automated mineralogy to provide this level of data revolutionised the industry through the data and the understanding it was able to provide.

In recent times, the importance of delivering a robust and reliable mineralogical characterization and understanding the effects the mineralogy has on the metallurgical productivity has grown in importance. This has largely been a result of challenging industrial trends such as the increased extraction of complex and mineralogically variable ores with a finer grain size and increased amount of deleterious minerals/elements (Baum, 2014; McKeith et al. 2013; Mudd et al. 2013). In addition, rising OPEX costs such as the increased price of water, fuel and electricity and the rising ore deposit discovery costs all impact on the profitability of the operation (McKeith et al. 2013).

These current trends outline how the current operating mines face a more challenging environment than ever before. As such, it is clear that there is a greater need for routine mineralogical characterization and understanding to ensure the plant is optimized, consistent and performing as expected. The development of the MinSCAN enables an operational mineralogy approach, and is proposed as part of the solution in addressing these challenges. Such integration of on-site automated mineralogy allows for better decision making through providing a greater understating of the resource base, metallurgical accounting, big data analysis and the ability to actively troubleshoot on-site with a 48 hour turnaround time for producing actionable data.

**2 Mine site approach – Operational mineralogy & MinSCAN**

**2.1 Operational mineralogy**

Operational mineralogy is newly developing branch of process mineralogy which focuses on providing routine daily mineralogical data to mine sites (Strongman et al. 2017). This represents a step change in how the industry is able to perform process mineralogy studies. Historically samples – usually monthly composites - were collected and sent to central laboratories for project specific studies or a regular plant audits. This was largely a result of the nature of the automated mineralogy systems (SEM-EDS) and the location of the equipment and the skilled operators. As such, the time from sampling to receiving data is often week to months.

By delivering a ruggedized, mine site ready and turnkey solution, operations are now able to run routine daily samples. The goals behind setting up an on-site operational mineralogy approach is to (Strongman et al. 2017):
Integrate key mineralogical information in daily reporting for decision making
2) Relate positive and negative changes in performance to mineralogical drives
3) Understand in more detail the impact of changing ore types
4) Provide the capabilities to run continuous improvement projects
5) Deeper understanding of the geology and the geometallurgical domains to develop a proactive/predictive operation as opposed to a reactive operation

The core principle in operational mineralogy is to focus on trends and establishing a benchmark for what is a “good operation” for each specific ore type. Once this benchmark is set and understood, the focus then switches to establish a sampling programme where daily samples are taken from the feed, concentrates, tailings and key/focused parts of the plant. These samples are split into the required size fractions for analysis.

Each analysis on a per sample basis is specific and tailored to extracting the information needed in the most time efficient manner. As such, analyses on certain samples can take as little as 20 minutes to produce the required data. This high resolution of sampling enables an almost live time mineralogical understanding and control on the operational performance. A key advantage of working with daily samples is the resolution it is able to provide that results in less smoothing of critical events and trends. This level of information maybe lost when resorting to a weekly or monthly samples regimes.

2.2 MinSCAN & Mineralogic
The ability to perform this level of analysis on site is a direct result of the ability to deploy a ruggedized mine site ready automated mineralogy solution. The MinSCAN, equipped with Mineralogic software has a proven track record of operating in challenging environments (Kalichini et al. 2017). The SEM platform was developed originally for military grade applications and to service particle analysis applications for jet engines (JetSCAN). Following this development, the SEM platform was applied to oil and gas applications (RoqSCAN) providing mineralogical data on drill chippings to understand depth in the strata of the drill bit, frackability and also applied to understand geo-steering and well spacing (Pfau and Oliver, 2011; Ashton et al. 2013).

With the successful implementation of the JetSCAN and RoqSCAN, the ruggedized SEM platform was then equipped with Mineralogic (automated mineralogy) and multiples EDS detectors for chemical analysis and fully quantitated spectrum quantification and mineral classification (Graham et al. 2015).

A key part of the successful implementation of the MinSCAN and thus the development of Operational Mineralogy is the ability to deploy the instrument into locations that are unfavourable and extreme for laboratory based SEMs and also the flexibility and ease of use of Mineralogic (Kalichini et al. 2017)

3 Operation mineralogy at Kansanshi – Proof of concept of on-site routine process mineralogy
Kansanshi is a Cu-Au deposit composed of a complex mixture of sulphide and oxides Cu bearing minerals. The deposit is located in the Zambian copper belt and is vein hosted as opposed to the stratiform hosted deposits associated within this region. The mine is an open pit operation with 3 main processing circuits to deal with the complex and variable ore. These streams are split into a sulphide circuit, oxide circuit and a mixed circuit.

A key challenge at Kansanshi and one of the main focuses of the operational approach and utilization of the MinSCAN was to produce data and understand the viability of ore minerals reporting to each circuit (Kalichini et al. 2017). As a result of the integration of an operation mineralogy approach and the utilization of the MinSCAN various recovery improvement opportunities and grade improvement opportunities were identified. Recovery improvements of Cu in the +150 µm size fraction have been possible. The identification of recoverable Cu sulphides and secondary Cu sulphides in the -38 µm size fraction also provided Kansanshi with another improvement opportunity. In addition, grade improvements opportunities has been identified through the rejection of liberated pyrite from the concentrate (Kalichini et al. 2017). 60% of all pyrite that was found in the concentrate streams was fully liberated and thus easily suppressed/rejected (Kalichini et al. 2017).

Through the acquisition of high resolution, on site data that was used to build a comprehensive understanding of the ore and the circuit performance, key opportunities for optimization and increased profitability of the operation were identified.

4 Discussion and summary
The value of understanding the mineralogy of a deposit and understanding the impact ore variability has on operation performance and profitability are not new. However the work carried out by Kansanshi (Kalichini et al. 2017) and the method developed behind Operational Mineralogy (Strongman et al., 2017) deliver a new capability and a new level of mineralogical understanding to operations. This data allows for a greater operational management and optimization to increase recovery and ultimately profitability. As the mining landscape continues to provide economic challengers and we continue to mine more unfavourable deposits, the importance and value generating potential from understanding the resources and
its variability is higher than ever. The successful implementation of sampling, benching marking, big data trending and plant optimization at Kansanshi has shown the application of routine mineralogical assessment on site is possible and can deliver value to the operation. Independent reports has tried to understand and assess the value at stake for the mining industry, and it is estimated $250 billion of value generation is available through greater operations management and continuous improvement (McKinsey, 2015).

Key aspects of operations management focus on a deeper understanding of the resource base, optimization of material flow and improved monitoring of real-time performance vs planned performance. Whilst mineralogy is not the only answer to these aspects of operations management, on-site mineralogy can be an important and valuable tool in empowering mine sites with the capability and data needed increase productivity, efficiency and ultimately profit.

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Geometallurgical applications of process mineralogy for the recovery of critical elements

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Abstract. Most ore deposits display a high degree of variability that arise from geological and mineralogical complexities that can have serious implications in metallurgical processing. While the application of process mineralogy for base and precious metals geometallurgy has been documented, little has been done for rare or critical elements. As with the former, the proper characterization of the ore and gangue minerals requires a multi-disciplinary approach combining geology, mineralogy, geochemistry and processing. However, mineralogy to a large extent dictates the metallurgical process. SGS has implemented automated mineralogy as a practical tool for this purpose, using QEMSCAN and other methods, throughout the mining chain from advanced exploration through to production. In this paper, we discuss actual case histories where automated mineralogy has been applied in a geometallurgical framework at a pre-feasibility to feasibility level. We will present examples from rare earth element, lithium and niobium deposits.

1 Introduction

Critical elements have become important in the development of new technologies such as smart phones that are now central to modern lifestyles, in addition to industrial, military and green applications such as electric or hybrid vehicles and windmills (Verplanck and Hitzman 2016). Industrial use of these elements has generally been low in the past but may have spiked significantly due to an increase in demand from the application in new technologies. Examples include use of rare earth elements in hybrid vehicles, lithium in lithium ion batteries or niobium in superconducting alloys. Subsequently, these surges in demand have led to increased exploration and development of new deposits to satisfy this marketplace. This in turn, has put pressure on metallurgical labs to rapidly come up with new flow sheets for the metal recovery.

Metallurgists have been aided in this by the availability of new tools and concepts in process mineralogy (Grammatikopoulos et al. 2013, Jordens et al. 2016) that allow fast and thorough characterization of the ores that can help define the metallurgical process. These tools reduce considerably the need for the traditional trial and error process using bench testing for flowsheet development, resulting in savings of time and money.

The concept of geometallurgy (e.g., Lund and Lamberg 2014) has developed over the past 20 years to deal with the variability in metal recovery encountered in large tonnage base metal deposits. Examples of these are copper porphyries in countries like Chile where they use the results to interpret variations in hardness that affect grinding or the presence of clays that impact flotation processing.

Both can be predicted by mineralogy which in turn can forecast throughput and grade controls. These same geometallurgical concepts can be applied to smaller deposits that host critical elements, many of which display a greater degree of variability within the orebody.

This presentation discusses the instrumentation used for, and the interpretation of mineralogical data for process mineralogy, as applied to geometallurgy. Case histories from well known critical elements illustrate how the mineralogical data can predict the metallurgical outcome.

2 Methodology

Quantitative automated mineralogy using SEM based instrumentation such as QEMSCAN, MLA, TIMA, Zeiss is now routinely applied to the study of ore deposits for mineral processing. Automated mineralogy, coupled with geological, geochemical, mineral chemistry and data analysis, are used to solve specific problems for mining and processing (e.g. Baum 2014).

Data from analytical techniques such as electron probe micro analysis (EPMA), Laser Ablation ICP-MS (LA-ICP-MS), ToF-SIMS or D-SIMS, Raman spectroscopy can be integrated to further link the automated mineralogy to geology, mining and processing.

Quantification of mineralogical parameters for a variety of ores including critical elements such as REE, Li, Nb-Ta can be applied to exploration (Mackay et al. 2016), or lead to the identification of distinct zones with specific metallurgical properties to domain the deposit (e.g., Grammatikopoulos et al. 2013). This in turn is used to predict metallurgical response. For example, domains can be defined based on the heavy (HREE) or light rare earth element (LREE) mineral carriers, or Nb-phases (e.g., pyrochlore, columbite or Nb-bearing Fe-Ti-oxides) and Li-carriers (e.g., spodumene, petalite and Li-bearing micas). Not only is this important to understand the mining geology and design a mine plan because minerals will carry different concentrations of the element of interest and will affect both grade and recovery, but this elemental deportment becomes essential to the resource evaluation of an orebody as each mineral may have a different economic value.

Furthermore, grain size, exposure, liberation and association, mass distribution by size, of critical element...
and associated gangue minerals can indicate: the optimum liberation size and possible grinding effects; potential recovery methods flotation using the exposure of the minerals, or gravity upgrading using the specific gravity characteristics of the minerals. Mineral speciation (e.g., monazite, xenotime, Zr-REE silicates) can dictate the recovery process i.e., flotation, gravity, magnetic separation or a combination of the above, and inform on leaching potential of such phases.

Therefore, the mineralogical information can delineate the deposits based on specific inherent mineralogical features and be linked to different metallurgical responses, rather than be used purely to describe geological features.

3 Case studies

3.1 REE deposits

REE deposits occur predominantly in carbonatites, peralkaline intrusions or ionic absorption clays. They are characterized by a significant number of minerals which in turn display a wide variation in major and trace element composition (e.g., Th in monazite, Ce, La, Y in Zr-silicates). Although geochemical analyses can illustrate HREE/LREE distributions, they are not adequate to determine the mineralogy or the mineralogical attributes of the rocks. Simple mineralogical examinations of polished thin sections will provide false indications with regards to the mineral mass and their liberation. REE deposits are considered and should be treated as multi-mineral and multi-element systems. QEMSCAN analyses have determined the variability and occurrence of the minerals in REE deposits (e.g., Grammatikopoulos et al. 2013) and domain the ore based on its potential metallurgical response. It can resolve the mineralogical characteristics of single minerals, e.g., monazite (a phosphate) and allanite (a silicate) that could be responding differently during flotation. When the data are coupled with mineral chemistry (EMPA), then the distribution of the REE can be mapped out. Minerals such as titanite or apatite normally are monazite grains with Liberation increases below 106 μm. Therefore, fine grinding would be required to improve liberation and further recover monazite. Data for other minerals can be derived from the same mineralogical analysis to provide a road map to processing.

REE grade and recovery relationships will be difficult to understand without the mineralogical characterization of the various metallurgical products. Figure 2 illustrates a mass balance of minerals and REE oxides. It is apparent that significant Ce and La are lost to the tails. Given the complexity of the mineral chemistry, it is impossible to determine the mineral(s) lost to the tailings and the liberation attributes. The QEMSCAN analysis identified that allanite and monazite accounted for the majority of the LREE losses. Adjustments were then made to the metallurgical flowsheet so that these minerals could be recovered.

![Figure 1. Liberation of monazite by size fraction](image1)

![Figure 2. Mass and oxide balance from metallurgical testwork](image2)

3.2 Li deposits

Hard rock lithium deposits are typically observed in shield areas present in several countries such as Canada, USA, Australia, Brazil, Zimbabwe and elsewhere. The main Li-minerals are spodumene, petalite, Li-bearing micas, and amblygonite. Granitic pegmatite deposits can have significant internal variability and multiple minerals hosting Li that reflect the original zoning or alteration of the ore. QEMSCAN analysis was conducted on nine composite samples reflecting different zones and field characteristics of the pegmatite. The data included the mineral mass and liberation of individual Li-bearing minerals for processing purposes. The mineral mass and liberation are critical due to the complex separation required to reject i.e., quartz and feldspars from petalite.
The liberation attributes for the main minerals (micas and petalite) show similar characteristics in each sample but significant variations between different samples with regards to mineral associations (Figure 3). Essentially, two concentrates could be produced: a petalite concentrate and a Li-mica concentrate.

Note that electron microscopes and microprobes cannot detect Li. Therefore, LA-ICP-MS was conducted on the Li-bearing minerals to determine the Li concentration because it is not always fixed especially in micas, topaz, and ambygonite. The LA-ICP-MS showed a wide variation of Li concentration in the micas. The results coupled with the QEMSCAN data were used to calculate the Li distribution among minerals and composites (Figure 4). This distribution reflects both the mineral mass and Li concentration.

Li recovery will vary in the mica concentrates reflecting the Li concentration in the mineral. A rougher concentrate (micas and petalite) will reflect the liberation of the minerals and the chemistry of the micas because the Li is distributed mainly between petalite and micas. Further studies of the tails indicated Li losses were mainly due to rejection of the topaz and montebrasite which will decrease the available recoverable Li by more than 10% in some of the samples.

3.3 Nb deposits

Mineralogical analysis of large sample set from a Nb-deposit was conducted to determine the Nb-minerals and their liberation. The results reveal that the main Nb-phase is pyrochlore. However, the composition of the pyrochlore varies from Ba-rich to Ba-poor, while Fe, U and Th vary significantly between samples. Theoretical grade-recoveries generated from the QEMSCAN analysis were compared to the actual metallurgical values.

The metallurgical recoveries fall between 60 and 80% of the total Nb in the samples. In cases, where the predicted Nb₂O₅ grade is higher, than the one achieved, (Figure 5) is attributed to both mineralogical and process related parameters (i.e., flotation reagents). For example, pyrochlore is fine-grained (<20 µm) and is lost as entrainment into the tailings. Coarser particles with both poor and good exposure are also lost. The theoretical
grade-recovery calculations assume that every single grain, regardless of size, could be recovered. Furthermore, changes must be implemented to recover the fine particles, and re-grind the coarser middling particles to increase liberation and surface exposure for flotation.

On the other hand, many samples have harmonic relations between the theoretical and metallurgical grades and recoveries. Figure 5 shows that the maximum metallurgical grades are achieved as they plateau those from the QEMSCAN, although the latter shows a range of recovery values. The grain size of pyrochlore is about 10-20 μm coarser than that in the previous sample, and middling particles contain pyrochlore with higher surface exposure. Thus, they are better recovered from those in the previous sample.

The grade-recovery curves for Nb2O5 (essentially pyrochlore) as a function of sizes (here are conventionally set every 10 μm) for a metallurgical sample are shown in Figure 6.

The graph shows the potential to recover pyrochlore from different size classes from this sample. Pyrochlore appears to be contained in particles of varied size distribution ranging from >10 to 100 μm. Pyrochlore is lost in the +100 μm fraction (no free particles occur in this class), but most of the free and liberated particles are between 10 and 70 μm. That is why the best potential to recover the pyrochlore in this sample is expressed by the various curves <70 μm. This is certainly a function of the absolute pyrochlore mass and its liberation degree in the samples.

4 Conclusions

Quantitative automated mineralogy is increasingly playing a significant role in geology, mining and mineral processing. There are numerous applications of data in daily process, from variability studies, support metallurgical test work and plant optimization. It is important in the evaluation of critical element deposits (REE, Li, Nb) deposits because it can quantify multiple mineralogical parameters (liberation, exposure, grain size) that cannot be determined with other methods. The three examples presented here merely illustrate how quantitative mineralogy conducted on a systematic base, and coupled with other data, can provide a road map and direction for both geology and mining.

These analyses belong to the emerging discipline of geometallurgy that is now accepted as a discrete and high value activity aimed at a more effective integration of exploration, mine development and process optimization. Automated and quantitative mineralogy constitutes an integral part of the geometallurgical framework.

Figure 6. Grade-recovery curves of Nb2O5 by size class calculated using the QEMSCAN data

Figure 7. Nb2O5 recovery between cleaner and rougher concentrates using the QEMSCAN data

Acknowledgements

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References

Geometallurgical grain size assessment using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) line scan analysis

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Abstract. In order to assess the liberation and recovery response of a rock mass, geometallurgical models require grain size data as an input. Grain size assessment is traditionally completed by scanning electron microscopy (SEM). While this method is suitable for grain size assessment, it requires coating the sample and completing analysis across the entire sample surface. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can be completed on any clean, flat surface and allows for the identification of mineral grains based on major and trace element chemistry. Using this technique, multiple line scans covering only a portion of the sample can be used to determine grain size by calculating the changes in chemical composition along the analysis line.

A pilot study is currently being undertaken to evaluate the application of LA-ICP-MS to effectively detect copper sulfide and gold grains using a series of line scan analyses. Samples representing both low- and high-grade copper mineralization from a copper-gold porphyry deposit were analysed. The preliminary results of this study illustrate the potential application of LA-ICP-MS analysis to assess grain size for geometallurgical studies.

1 Introduction

There is a strong correlation between grain size and the liberation and recovery of economic minerals present in ore (Hunt et al. 2011). This relationship dictates that predictive, geometallurgical models will require quantified grain size data. Grain size assessment is traditionally completed by reflected light microscopy or scanning electron microscopy (SEM) in conjunction with advanced mineralogical interpretation software packages (Gu 2003; Fandrich et al. 2007; Goodall and Butcher 2012). These methods have proven reliable for grain size assessment, but they require preparation of a highly polished surface and can be very time consuming for the quantification of sub-micron particles. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technology is capable of precise trace elemental analysis of rock samples in spot, line, or rastering analytical modes. The advantage of the LA-ICP-MS system is that a large range (up to six orders of magnitude) of concentration can be analysed and may allow for the simultaneous detection and quantification of micron to sub-micron mineral grains at the same time as much larger grains on unpolished rock samples.

In order to evaluate the potential application of LA-ICP-MS line scan analysis to grain size assessment, an initial pilot study is currently being undertaken. This paper discusses the methodology, preliminary results, and future work required to assess LA-ICP-MS line scan analysis for grain size assessment in a geometallurgical context.

2 Traditional grain size assessment

Prior to the development of advanced mineralogical interpretation software packages, grain size was measured manually using reflected light microscopy. More modern reflected light microscopy techniques rely on image analysis software to identify mineral phases of interest in a reflected light image (Hunt et al. 2011; Berry 2008). While both manual and automated reflected light microscopy techniques produce robust grain size measurements, both techniques require a mounted, polished sample and, traditionally, analysis across the entire sample surface.

Automated SEM systems equipped with advanced mineral identification software, such as the mineral liberation analyser (MLA) and the quantitative evaluation of mineral by scanning electron microscopy (QEMSCAN), are now commonly implemented in grain size assessment (Coetzee et al. 2011; Lamberg 2011; Goodall and Butcher 2012; Fandrich et al. 2007; Gu 2003). Fundamentally, these grain size assessment methods identify minerals of interest, define the boundaries of the interested minerals, and then calculate the grain size of each mineral phase. While SEM-based systems are effective, this method requires polished, carbon coated and mounted samples prior to analysis. Additionally, these systems scan the entire sample surface, which is expensive and time consuming.

3 Considerations for grain size assessment

Previous authors have noted that the estimation of grain size is inherently biased by the effects of cutting a random section through a particular grain of unknown orientation and geometry (Sutherland 2007; Higgins 2006). To address this, line scan analysis can be used to define an intercept length of a specific mineral phase by determining the transition from one mineral to the next along the analysis line. Using the mean intercept length (L), the mineral surface area can then be estimated by the phase specific surface area (PSSA) equation:

\[ \text{PSSA} = \frac{4}{L} \]  
(Sutherland 2007).

By assuming a spherical shape for grains, the grain size
estimation for diameter (\(D_{\text{PSSA}}\)) can be calculated by:

\[
D_{\text{PSSA}} = \frac{6}{\text{PSSA}} \quad \text{(Sutherland 2007)}.
\]

4 LA-ICP-MS technology

In LA-ICP-MS analysis, major and trace element concentrations are measured \textit{in situ} by a process involving laser ablation, ionization in a plasma, and, finally, mass spectrometry. This technique requires that the sample surface be relatively flat and clean and results in minimal surface damage to the sample. While many sulfide studies use either targeted spot analyses or sample imaging by spot rastering, the LA-ICP-MS system is also capable of line scan analysis. In line scan mode, the LA-ICP-MS system continually fires the laser at a set repetition rate while moving the sample stage at a constant rate. The mass spectrometer measures the elements sequentially every 0.22 seconds along the length of the analysis line.

5 LA-ICP-MS line scan pilot study

The goal of this study is to investigate if LA-ICP-MS analysis can be used to effectively detect and assess chalcopyrite, bornite, and covellite (collectively, copper sulfides) and gold grain sizes using a series of line scans.

5.1 Experimental conditions

Drill core samples from the ore zone of a copper-gold porphyry deposit (representing both high- and low-grade mineralization) were cut into 3 cm by 3 cm tiles and rough polished to ensure the surfaces were relatively flat. These samples were then analysed by LA-ICP-MS using a Resolution S155 laser ablation cell coupled to a 193 nm Coherent Geolas excimer laser and Agilent 7500a quadrupole ICP-MS system at CODES, University of Tasmania, Australia. A series of 20 lines (each 23 mm long), spaced approximately 1.4 mm apart were completed across each sample. The line scan analyses were completed using a laser fluence of 3 J cm\(^{-2}\) at 20 Hz, and a 34 µm\(^2\) square beam moving at 300 µm per second. A pre-ablation sequence of the analysis line was completed before each analysis pass. Initial analysis and reduction of the raw data was completed using the methodology outlined in Danyushevsky et al. (2011). Further data processing was performed to correct for mineral specific laser ablation effects using algorithms developed at the University of Tasmania.

5.2 Copper sulfide grain assessment

Using the concentrations of copper, iron, and sulfur, chalcopyrite, bornite, and covellite can be identified in the LA-ICP-MS line scan data. For grains larger than the 34 µm spot size, threshold values for each element are applied to automatically detect and speciate copper sulfides along a line scan (Table 1). The intercept length for each species is then calculated by measuring the distance along the line that meets the threshold values, and these intercept lengths can be used to calculate the grain size using the \(D_{\text{PSSA}}\). For grains less than 34 µm, the relative proportions of copper, iron, and sulfur are used to identify copper sulfide species (Table 2). The elemental concentrations are then compared to the ablation volume to estimate the size of the grain encountered.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Mineral} & \text{Element} & \text{Expected Value (\%)} & \text{Upper Threshold (\%)} & \text{Lower Threshold (\%)} \\
\hline
\text{Chalcopyrite} & \text{Cu} & 34.63 & 44.63 & 24.63 \\
& \text{Fe} & 30.43 & 40.43 & 20.43 \\
& \text{S} & 34.94 & 44.94 & 24.94 \\
\hline
\text{Bornite} & \text{Cu} & 63.31 & 73.31 & 53.31 \\
& \text{Fe} & 11.13 & 21.13 & 1.13 \\
& \text{S} & 25.56 & 35.56 & 15.56 \\
\hline
\text{Covellite} & \text{Cu} & 66.46 & 76.46 & 56.46 \\
& \text{S} & 33.54 & 43.54 & 23.54 \\
\hline
\end{array}
\]

\text{Table 1. Threshold values for copper sulfide minerals used when grains are greater than the 34 µm spot size.}

5.3 Grain size vs spot size

The LA-ICP-MS results represent the chemical composition of the total volume ablated by the laser in a given spot. The analysis was completed using a 34 µm spot size, meaning that any grains encountered that are larger than 34 µm would produce concentrations equal to those of pure gold or pure copper sulfide minerals. If grains less than the 34 µm spot size are encountered, other minerals are ablated in that spot volume. This decreases the overall concentrations of copper, iron, sulfur, and gold in the LA-ICP-MS data. In the case of copper sulfides, the concentration values will be decreased, but the proportions of elements will remain the same, depending on the copper species present. Using the proportion of quantified copper, iron, and sulfur values relative to the volume of ablated material along the line, the size of grains less than 34 µm can be estimated. Similarly, the size of gold grains can be estimated by comparing the gold concentration to the ablation volume. In the case of both copper sulfides and gold, this estimation can be used to identify micron to sub-micron grains.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Approximate Element Ratio (Cu:Fe:S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcopyrite</td>
<td>1:1:1</td>
</tr>
<tr>
<td>Bornite</td>
<td>6:1:3</td>
</tr>
<tr>
<td>Covellite</td>
<td>2:0:1</td>
</tr>
</tbody>
</table>

**Table 2.** Elemental ratios of copper, iron, and sulfur used to identify copper sulfide minerals when grains are less than the 34 µm spot size.

Assessment of the LA-ICP-MS data collected shows that the elemental concentrations of copper, iron, and sulfur can be used to indicate the intercept length of copper sulfide grains along an analysis line (Fig. 1). When copper sulfide grains greater than the 34 µm spot size are encountered in the line scan, the elemental concentrations for copper, iron, and sulfur match the expected values for the mineral (Fig. 1A). When a grain less than 34 µm in diameter is encountered, the concentrations of copper, iron, and sulfur are lower than the expected values, but are still proportional based on the expected elemental ratios (Fig. 1B).

### 5.4 Gold grain assessment

Assessment of the LA-ICP-MS gold data suggests that the concentrations of gold can be used to identify gold and estimate grain sizes along an analysis line (Fig. 2). Since LA-ICP-MS is highly sensitive, detected gold likely represents gold grains or gold in solid solution in minerals such as pyrite and chalcopyrite. By comparing the gold concentrations and the concentration of other elements hosted in gold grains to the ablation volume, a grain size estimate can be calculated.

**Figure 1.** Example of LA-ICP-MS results of a single analysis line from a high-grade copper pilot study sample. **a** Corresponding peaks in copper, iron and sulfur (each approximately 30%) show the location and intercept length of a chalcopyrite grain. **b** Example of proportionally correct Cu:Fe:S ratios for a bornite grain less than 34 µm in size.
6 Preliminary conclusions and future work

While this work is ongoing, a preliminary analysis of the pilot study results show that copper-sulfide and gold grains can be successfully detected along the LA-ICP-MS analysis lines by identifying the location of copper, iron, sulfur, and gold peaks. For grains larger than the 34 µm spot size, the intercept length of grains encountered can be used to estimate the grain size for each grain encountered. For grains smaller than 34 µm, the proportions of copper, iron, and sulfur are used to identify the species of copper sulfide. The concentrations of copper, iron, sulfur, and gold are then compared to the ablation volume to estimate the grain size. This method allows for the identification of micron to sub-micron grains.

If successful, this type of analysis could be used to rapidly assess grain size for liberation and recovery modelling. The LA-ICP-MS technique is well-suited to gold and copper-sulfide analysis and line scans can be analysed significantly faster than the traditional MLA grain size assessment by surface mapping. The advantages of applying the LA-ICP-MS approach to grain size assessment include:

- Minimal analysis time, sample preparation, and sample damage,
- Simultaneous analysis of multiple elements over large range of elemental concentrations (up to six orders of magnitude),
- Micron to sub-micron grain identification.

Further evaluation of the pilot study results will be required to determine if this method provides a robust proxy for grain size based on a few line scans and whether this approach is practical for geometallurgical applications. The results of LA-ICP-MS grain size assessment will be compared to previously collected MLA grain size results for all samples in the pilot study sample set. Additionally, the statistics to determine how many analysis lines are required to adequately characterise a representative grain size for each 3 cm by 3 cm sample will need to be carefully evaluated using the pilot study results. Given that other grain size assessment techniques, such as MLA analysis, represent nearly 100% analysis coverage of the sample while the LA-ICP-MS data only represents 3.5% analysis coverage, the sampling statistics will be important to the application of this method.

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References

Application of mid-infrared reflectance spectroscopy for the identification of minerals present in oil and gas/mining exploration

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Abstract. This work aims to develop a new core logging technique based on reflectance spectroscopy in the mid-infrared domain (2.08 to 25 μm). This technique is suitable to analyse the mineralogy of rough surfaces and will be adapted on a rock strength testing machine that scratches the core surface. The Fourier transform infrared (FT-IR) spectrometer used in this work was tested on a list of minerals which are important in oil & gas and mining exploration. The list contains species of carbonates, halides, phosphates, sulphates, sulphides, tectosilicates and phyllosilicates. Then, a semi-automatic method was developed for mineral identification, mapping and quantification on the rough surfaces. It will be demonstrated that this process is powerful for the estimation of the mineral distribution at the exploration stage. Moreover, as it is non-destructive and quite fast, it will be helpful to extract additional data from the cores in a profitable way. This is critical to improve the resource efficiency, to reduce operational risks and to optimise the production in a sustainable way. These knowledges are the basis of the geometallurgical concept.

1 Introduction

Several techniques have already been developed for mineral identification by infrared spectroscopy. Different scales and wavelength domains are used.

First, hyperspectral imaging is widely used in the visible to near infrared and shortwave infrared (VNIR and SWIR, from 0.4 to 2.5 μm) for remote sensing applications (Taranik and Aslett 2009). Well known projects are AVIRIS (Airborne Visible/Infrared Imaging Spectrometer) and ASTER (Advanced Spaceborne Thermal Emission and Reflectance Radiometer) developed at the NASA Jet Propulsion Laboratory (van der Meer and de Jong 2001). Such techniques are also used for core logging, the Hyperspectral Core Imager (HCl-2) developed by Corescan is an example (Pasten et al. 2016). However, minerals such as tectosilicates, many oxides, sulphides and phosphates cannot be identified on these wavelength domains, and additional spectral ranges have to be studied. For example, the HyLogging system developed by the CSIRO covers a range between 6 and 14.5 μm (Schodlok et al. 2016), which is part of the mid-infrared domain (MIR, 3-30 μm).

Finally, the total MIR range is widely used for mineralogical purposes at the laboratory scale (Nakamoto 1963 and Chukanov 2014, among others). However, this technique uses transmittance spectra which usually require the dilution of the sample into a transparent medium and is thus not suitable for fast and non-destructive core logging.

In this work, the Fourier transform infrared (FT-IR) spectrometer covers the range from 2 to 25 μm usually used at the laboratory scale but will be used in diffuse reflectance mode. This technique will allow studying the mineralogy of fresh rough surfaces generated by the scratch test in a non-destructive way.

2 Theoretical aspects

In the mid-infrared domain, the spectral features of the minerals are due to the vibrational processes of their molecules caused by the energy of absorbed light. The absorptions occur solely at quantised energy levels corresponding to specific radiation frequencies. Therefore, the identification of minerals can be done by correlating the frequencies of absorption to the normal vibrations of isolated groups of atoms such as CO3^2-, SO4^2-, PO4^3- and SiO4^4- or neutral molecules such as H2O and NH3, which are considered independent in the structure. This method is thus adequate for carbonates, phosphates, silicates, etc., but much less for minerals composed of ionic liaisons like halides for which lattice vibrations have to be observed in the far-infrared (30 μm to 1 mm) (Chukanov 2014).

Infrared spectra of minerals are influenced by several factors. First, it is dependant of the symmetry of the real crystals that can be influenced by solid solutions, alterations and local defects. In addition, the particle size, the surface roughness (Fig. 1) and the crystallographic orientation of the samples have non-negligible effects on the spectra in the mid-infrared domain. This is why it is generally preferred to use transmittance or absorbance spectra obtained with an immersion medium (as KBr), which are independent of these effects and considered unique for a given mineral (Vincent and Hunt 1968; Chukanov 2014; Salisbury et al. 1987). For these reasons, it may be difficult to find relevant data in the literature for MIR reflectance spectra. Hopefully, three databases contain reflectance spectra of polished surfaces and powders of different particle sizes: the United States Geological Survey (USGS), the John Hopkins University (JHU) and the Jet Propulsion Laboratory (JPL) spectral libraries. They are all part of the ASTER spectral library (Baldridge et al. 2009).

The last factor to consider is the effect of mineral mixtures. According to Clark (1999), when two materials of known spectra are mixed, the resulting spectrum is not...
necessarily the linear combination of these two spectra. Indeed, there are two principal types of mixtures: linear mixtures and intimate mixtures. In the case of linear mixtures, the materials are optically separated and there is no multiple scattering between them while in intimate mixtures, the materials are in intimate contact (mineral grains of soil for instance) and multiple scattering occurs. In this case, the resulting signal is a highly non-linear combination of the initial spectra. Several authors demonstrated that there was a potential for deriving individual mineral abundance in a surface composed of grains by knowing the reflectance spectra of endmembers (Hapke 1981; Smith et al. 1985). However, in practice, many of the algorithms of spectral unmixing are based on the linear mixture hypothesis. They generally provide exploitable results, but can lead to approximations for intimate mixtures (Dobigeon et al. 2014).

3 Materials and method description

The FT-IR spectrometer is the ALPHA model from Bruker Optik with the A241/DL module to perform reflection measurements (Fig. 2). Each measurement corresponds to the spectrum of a zone of 7 mm of diameter on the sample surface. It can be used on any type of solid surface without sample preparation but also on powders. Its optimal spectral resolution is 4 cm⁻¹ for a time of measurement of about 1 minute per spectrum.

In addition, minerals which are important in oil and gas and mining exploration were selected (Table 1). Unfortunately, all the minerals of the list were not available as solid samples but every group is represented. The samples were analysed by X-ray diffraction (XRD) and appeared highly pure except samples 7 and 10 that appear as mixtures. First, spectra of minerals from the list were studied from the literature and the databases to assess the validity of mid-infrared reflectance spectroscopy for mineral identification. Then, the reflectance spectra of the high purity samples were measured on rough fresh surfaces with the ALPHA spectrometer and compared to the existing databases to verify their correspondence. Moreover, automatic identification algorithms were tested on these spectra.

![Figure 1](image1.png)

Figure 1. Reflectance spectra of highly pure and finely grained calcite surfaces measured with the ALPHA spectrometer. It can be seen that a modification of the particle size and/or of the roughness causes different modifications on reflectance spectra. First, it modifies the intensity of the spectral features, then, it can convert spectral features displayed as minima in maxima or inversely and finally, the frequency of the absorption feature is shifted. This explains why it is particularly difficult to perform analyses on reflectance spectra. Nevertheless, the information on the particle size and the surface roughness brought by the technique is valuable and may be used for other geometallurgical purposes.

![Figure 2](image2.png)

Figure 2. ALPHA spectrometer with the A241/DL configuration for reflection. The sample surface is placed against the metallic cone for measurements, the sampling spot is 7 mm in diameter (Bruker Optik GmbH 2014).

![Table 1](table1.png)

Table 1. List of minerals to analyse and their availability as solid samples. The symbol “/” means that the minerals were not available, as mentioned in the text.

Next, a drill core composed of a red conglomerate cut by two thinner black benches was used (Fig. 5). It is part of the rocks underlying the lower orebody of the Kamoto mine, Democratic Republic of the Congo and measures 16.8 cm long. It was scratched longitudinally to analyse the rock strength and a fresh rough surface was thus created along it. This groove surface is 1 cm wide. A reflectance spectrum was measured along the groove every 7 mm (size of the sampling spot), and 24 spectra were thus obtained. They were then analysed with the semi-automated method calibrated with the highly pure minerals spectra in order to identify the minerals, to map them and to quantify them on...
the fresh surface. In addition, the powder produced along the core by the scratch test was recovered and analysed by XRD to validate the results of the semi-automatic method. However, as this powder corresponds to a volume of destroyed rock, a perfect coincidence between the XRD results and the surface analysis is not expected. The powder contained about 35% dolomite, 27% quartz, 23% muscovite, 9% chlorite IIb (probably clinochlore) and 6% hematite. Trace of rutile was detected as well.

In a few words, this semi-automatic method uses three software: Opus (Bruker Optik) for spectra measurement and for mineral identification by using the three spectral libraries (USGS, JPL, JHU) ; Matlab (MathWorks) for building an hyperspectral image representing the drill core groove; Envi (Exelis Visual Information Solutions) to extract the most representative spectra of the image (the so called end-members, to avoid the treatment of each pixel one-by-one) and to perform mineral mapping and quantification by using spectral linear unmixing algorithms and the spectral libraries. The method is said to be semi-automatic because the mineral identification step is not trivial and requires the user’s validation and skills. The method nevertheless provided convincing results.

4 Results and discussion

The mid-infrared reflectance spectra of powders and polished surfaces were studied from the literature and the three databases for the minerals of interest (Table 1). It appeared they are reliable identification tools because each mineral has different spectra due to its specific structure and composition. Minerals from the same classes (ex. dolomite and calcite) have analogous spectra but their differentiation is possible when they are not part of complex mixtures. The exception concerns minerals which are really similar, such as orthoclase and sanidine, or Mg and Fe-clinochlore, for which the identification can lead to uncertainties, especially when they are mixed together. On the other hand, the MIR spectroscopy is not the most adequate method to study the occurrence of sulphides and halides; pyrite has only one feature while halite has a flat spectrum (no feature).

Then, the reflectance spectra of rough surfaces of high purity samples were compared to the existing databases. Despite small discrepancies, it has been shown that the behaviour of measured spectra was highly similar to the reference spectra. An example can be seen in figure 3 for albite and gypsum. It was also shown that the rough surfaces have intermediate spectra between polished section and powders due to the particle size and roughness effect. This can be seen in figure 4 for dolomite and quartz. USGS, JHU and JPL libraries can thus be used to analyse the spectra acquired with the ALPHA spectrometer on rough surfaces.

Finally, the Kamoto core was analysed with the semi-automated method in order to identify, map and quantify the minerals before knowing the XRD results, and without advanced geological information. The results are visible in figure 5. Clinochlore, dolomite, quartz, muscovite and hematite (even if it was not part of Table 1) were correctly identified by using the spectral libraries. However, the trace of rutile was not detected. In addition, the errors between the mean of the quantification results and the XRD are up to 14%, which is acceptable for the estimation of the mineral distribution. The errors are mainly due to two factors: the use of spectra from the databases (which are slightly different from the measured spectra due to mineralogical aspects, particle size and roughness effects) and the occurrence of intimate mixtures. Nevertheless, the most important aspect of these results is that two distinct zones of conglomerate and iron oxides can be observed. It proves that the technique can be efficient for mapping the different mineralogical zones of drill cores.
industry and for other geometallurgical purposes as it combines grain size and mineralogical information in a single measure. However, further research is needed to develop these particular topics.

Acknowledgements

This work mainly results form a master thesis conducted as part of the georesources engineering EMerald curriculum. Therefore, special thanks go to the EMerald staff for offering us the chance to participate in such a rewarding experience. Next, thanks go to Xavier Decamps for his involvement in this research, for his guidance, for the amount of data provided and especially for his time and his patience and to Pr. Frédéric Hatert for the XRD analyses. Mineralogical samples came from the Geological and the GeMMe departments of the University of Liège.

References

Sn deportment within the diverse lithological units of the Hämmerlein skarn (Erzgebirge, Germany): implications for minerals processing

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Abstract. The Hämmerlein skarn in the Erzgebirge, Germany, is assessed according to its beneficiation potential. A modified approach for automated mineralogy is used to evaluate the economic potential of the compositionally complex Sn ore. The lithological units show significant differences in modal mineralogy and Sn deportment. Petrographic observations and data from automated mineralogy suggest a close spatial relationship between chlorite and cassiterite, possibly pointing towards a cogenetic relationship. The association of these two minerals may be advantageous for beneficiation. Chlorite can easily be detected by a near-infrared detector used in commercially available sorting equipment. Chlorite- and cassiterite-rich rock fragments may thus be identified and separated for further processing by conventional milling, gravity separation and flotation.

1 Introduction

The Hämmerlein skarn is part of the world class Tellerhäuser deposit in the Erzgebirge, Germany. Current resources amount to 21400 t contained Sn at a cut-off grade of 0.2 wt. %. Together with three similar orebodies that occur in the immediate vicinity of the Hämmerlein skarn, the total inferred Sn resource amounts to 101500 t, with 2149 t In and 200200 t Zn (Treliver Minerals 2015). In the late 1970s, 49100 t of ore from the Hämmerlein skarn were mined and beneficiated in a pilot plant, but grade and recovery remained below expectations. Cited reasons for poor recovery the complex mineralogy, fine grain-sizes of valuable minerals, and the variety of Sn-bearing minerals (Schuppan and Hiller 2012). The predicted rise in global Sn consumption, limited availability of high grade deposits (Deutsche Rohstoffagentur 2014), and rising world market prices for Sn within the last year render the Tellerhäuser deposit an interesting exploration target (Treliver Minerals 2015).

In an earlier phase of this project, a suite of six samples from the Hämmerlein skarn was studied to constrain the Sn deportment of the different skarn lithotypes (Kern et al. 2017). The complex mineralogy required modification of the conventional approach of automated mineralogy. The developed method has a significant effect on the correct identification of mineral grains < 5 µm and includes minerals with minor Sn-contents in the deportment calculation. Besides cassiterite (SnO₂) there are several other minerals that contribute significantly to the Sn content. Examples are stokesite with a median Sn content (MSn) of 34.16 wt. %, titanite (MSn = 3.93 wt. %), epidote (MSn = 1.32 wt. %), and iron oxide minerals (MSn = 0.76 wt. %). However, cassiterite is the only Sn-bearing mineral in the studied ore that meets commercial requirements (Pawlek 1983) and that is thus of commercial interest.

This study documents the Sn deportment for the different lithological units of the Hämmerlein skarn based on the results of field geological observations and automated mineralogy. Implications for mineral processing and suggestions for flow sheet development are provided.

2 Geology and lithological units of the Hämmerlein skarn

Skarn is a calc-silicate-dominated rock type that typically forms at the expense of carbonate rocks during regional or contact metamorphism including intense metasomatic alteration by magmatic hydrothermal fluids (Meinert et al. 2005). The abundance of Sn in the crystal lattice of typically Sn poor minerals, such as garnet and titanite, is a common attribute of Sn skarns. Cassiterite abounds in most but not all Sn skarn deposits (e.g. Alderton and Jackson 1978) and may form during late retrograde skarn alteration or a post-genetic greisen-style alteration.
Major reviews for the genesis of Sn skarn deposits include Einaudi et al. (1981), Kwak (1987), Newberry (1998), and Meinert et al. (2005).

The Hämmerlein deposit is an example of a stratabound, compositionally complex and polymetallic ore deposit that comprises of two parts: a shale-hosted part and a Sn-In-Zn skarn (Schuppan and Hiller 2012). This paper deals with the skarn portion of the Hämmerlein deposit only. The lithologies were classified according to suggestions from the British Geological Survey (1999) for naming metamorphic rocks and the petrography and mineralogy of the samples were studied in detail by Kästner (2016). Figure 1 shows a face map from the latter study – illustrating typical relations between skarn lithologies.

3 Methods

Twenty-three samples from five different lithological units of the + 590 m level of the Hämmerlein skarn as well as the footwall (gneiss) and the hanging wall (mica schist) were examined. Between two and five hand specimens (Ø 10 – 20 cm) were collected from randomly chosen spots of each lithology, with the goal to acquire representative mineralogical data from each lithological unit. Suitable parts of the hand specimens were chosen for the preparation of 25 thin sections with a thickness of 30 µm. The remainder of the samples were comminuted to approximately 80 % passing 180 µm and prepared as grain mounts.

Samples were characterized using scanning electron microscopy (SEM)-based image analysis (aka automated mineralogy) with the modified approach by Kern et al. (2017). Grain-based X-ray mapping (GXMAP) as offered by the Mineral Liberation Analyzer (MLA) is a suitable measurement mode for the analyzed ore (Fandrich et al. 2007). Data processing was done using the software package MLA Suite 3.1.4.

X-ray powder diffraction (XRD) and bulk chemical analysis were used to reconcile data regarding modal mineral content and bulk geochemistry calculated from automated mineralogy data. Similar approaches for the characterization of complex ores have previously been used by e.g. Smythe et al. (2013), Parian et al. (2015) and Osbahr et al. (2015).

4 Results

In the following, the modal mineralogy and Sn deportment are presented for each lithological unit of the deposit. Mineral associations and mineral grain size distributions are evaluated and interpreted regarding their effect on mineral processing.

4.1 Modal mineralogy and Sn deportment by lithological unit

The modal mineralogy (Fig. 2) shows the variability in mineral contents within the different lithological units. Minerals were grouped wherever deemed suitable for simplification without compromising the characteristic attributes of each unit.

The Sn-deportment is best described as the quantitative distribution of the Sn content in a given volume of rock onto different minerals (Fig. 3). Represented are all Sn-bearing minerals that have been identified by MLA.
Cassiterite is the most important host for Sn in the studied samples. However, it is obvious that cassiterite dominates only in the chlorite lithology. Within the amphibole and iron oxide lithologies, other minerals contribute significantly to the Sn deportment and cassiterite accounts for only approximately 0.1 wt. % Sn. The garnet unit, pyroxene-epidote unit, mica schist, and gneiss are of no economic interest.

4.2 Mineral associations of cassiterite by lithological unit

Cassiterite is typically associated with rock-forming minerals from its host unit (Fig. 4). However, the amount of cassiterite associated with chlorite and quartz in the amphibole unit and the iron oxide unit is distinctly elevated, revealing a preferential association.

![Figure 4](image)

**Figure 4.** Mineral associations of cassiterite by lithological unit; only units with more than 0.1 wt. % Sn in cassiterite are displayed; legend and acronyms as in figure 2.

4.3 Mineral liberation and grain size distribution of cassiterite

The samples analyzed have an average particle size of 80 % < 180 µm. In comparison, the grain size of cassiterite is significantly smaller (80 % < 90 µm; see figure 5). More than 90 % or all cassiterite grains are very poorly liberated (Fig. 6).

![Figure 5](image)

**Figure 5.** Mineral grain size distribution of cassiterite and particle size distribution of all particles.

![Figure 6](image)

**Figure 6.** Mineral liberation by free surface of cassiterite.
5 Implications for minerals processing

Understanding the relation between chlorite and cassiterite in the skarn ore is regarded the key for successful minerals processing. The association between cassiterite and minerals from the chlorite unit is interpreted to be the result of a late metasomatic overprint of the prograde skarn assemblage. Field evidence (Fig. 1) illustrates that this late overprint crosscuts prograde skarn lithologies forming chlorite and cassiterite (± quartz ± fluorite ± arsenopyrite ± chlorapatite ± calcite).

The genetic link between cassiterite and chlorite is boon and bane: On the one hand, it offers the opportunity to use chlorite as a proxy for the identification of cassiterite-rich phases. A mechanical sorter equipped with a near-infrared (NIR) detector will be able to identify cassiterite-rich rock fragments that exceed a threshold value of approximately 5 – 15 wt. % (Fig. 7) and separate these from chlorite- and – by extension – cassiterite-poor rock fragments. If successfully applied, it is estimated that the mass flow could be reduced by as much as 68 wt. % whilst maintaining a cassiterite recovery of 97 wt. %. On the other hand, chlorite is known to respond readily to reagents that are used in cassiterite flotation. This may, of course, complicate the separation of the two minerals (Bulatovic 2010).

Another important drawback of the chlorite-cassiterite skarn ores is, of course, the fine grain size of cassiterite. To avoid unnecessary overgrinding, gravity separation techniques may be implemented before flotation at grain sizes between 0.5 cm and 0.5 mm. Later-on in the process, very fine-grained cassiterite (< 20 µm) could be concentrated using innovative techniques like two-liquid flotation or microbubble flotation.

Figure 7. Cassiterite vs. chlorite; data from 25 thin sections; All samples that are rich in cassiterite contain chlorite > 10 wt. %; acronyms as in figure 2.

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The importance of high quality drill cores for geometallurgy

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Abstract. Geometallurgy is crucial for efficient exploration, resource and reserve estimates, mining and metallurgical parameter definition. Subsurface deposits (up to about 50 m depths), such as laterites in tropical regions or bauxite deposits, placer Au deposits in permafrost regions and ores in breccia type deposits (diamonds) are heterogeneous at ore body scale, related to mixtures of loose and solid, soft and hard materials of variable grain sizes and contrasting physical properties. Sonic drilling (Eijkelkamp SonicSampDrill) with specially developed core shoes and rigs for these environments reach core recoveries of about 95% and smooth surfaces for high quality RGB imaging. In a Siberian subsurface placer Au mine, sonic drilling contributed to a significant increase of the reserves. Recently performed drill tests on fine grained heterogeneous Mn-tailings reach core recoveries of 95-100%. Furthermore, sonic drilling under dry conditions (no water consumption is time saving (about 50 m/day) speeding up the exploration period.

1 Introduction

Geometallurgical studies start on drill core material implying most complete logging in order to perform systematic sampling for statistical mineralogical and chemical studies. These results are used for modelling the resources and reserves, sampling for metallurgical and geotechnical testing. Conventional diamond drilling campaigns are time, cost and water intensive. Furthermore in particular ores occurring in soils or brecciated environments present challenges for conventional drilling with variable and insufficient recovery rates in the different horizons and partial destruction of the drill cores. For Ni-laterites, e.g. 88-94 % of core recovery can be obtained. Sonic drilling is more and more used as it reduces significantly the OPEX, reaches higher recovery rates and is environmental friendly. It is fast without any water use. Eijkelkamp SonicSampDrill specialized in sonic drilling develops core shoes and rigs adapted to various metal rich soils including mine tailings.

2 Sonic drilling

Sonic drilling is used for more than 40 years, but is more and more developed for soil environments with special developments on rigs and toolings. Sonic drilling on soils strongly reduces friction on the drill string and drill bit due to liquefaction, inertia effects and a temporary reduction of porosity of the soil. During core barrel advancement no fluids, air or muds are used for its advancement. This combination makes penetrating a large range of soils easy.

3 Placer gold in permafrost regions

The Far East of Siberia, a permafrost region, is rich in placer gold, which is mined at surface and underground. The sediments are composed of sands, gravels and loosely coherently or uncoherently levels of gold. The gravel beds are in part formed by glaciers. Gold occurs tabular, flaky, lumpy or as lode like grains.

Permafrost soils are subject to thawing in summer from the surface to a variable depth, comprising 30 cm to several hundreds of meters. The surface layer down to several meters, which experiences repeated freezing and thawing is called "active layer". The active layer slowly expels its water during the thawing periods of several months. This causes a morass, or a rough surface consisting mainly of rock fragments. Drilling in these materials causes problems. High quality sonic drilled cores helped to more efficiently model the gold reserve increasing the total reserves of about 6 %.

4 Nickel laterites-bauxites

Nickel laterites (0.5 to 3 % Ni) and bauxites (Al rich 35-65 % Al) are tropical (paleo- or modern) soils. Ni-laterites form on serpentinized peridotites belonging to ophiolites, while bauxites present paleo soils developed, or are transported on(to) granitic or carbonate–clay bearing rocks. These soils formed through alternating rainy and dry seasons, leading to leaching and accumulation of metals as concretions or veins, but metals also occur dispersed in the
matrix. These ores present heterogeneous materials both in grain size (μm to cm) and mechanical properties (hard and soft).

Ni-laterites were essentially mined for garnierite ore occurring in saprolites and/or tectonic breccia at the bottom of the laterite profile, the interface to the protolith (serpentinized peridotite). At present, many Ni laterite ores are of lower grades (1-2 %, cut-off grade about 0.8 wt.%) and higher mineralogical complexity, as Ni-mineral are dispersed in the rock matrix. Moreover, laterites can host up to 40-50 % of water. Intensive geometallurgical studies are required to define comminution parameters and to design beneficiation. Sonic Drilling tests were performed on the Weda Bay Ni deposit (ERAMET Group; www.erametgroup.com) in Indonesia. These laterites are highly heterogeneous and host saprolites of variable compositions including a high amount of swelling clay minerals (smectite). Although these sonic drill tests reach significantly improved recovery rate, significant development is still needed and ongoing at present in the H2020 SOLSA project.

5 Tailings

Metal recovery from tailing is interesting not only for the recoveries of the rest major metal (e.g. Mn, Fe, Ni) contents, but also for not-yet exploited metals, which are now of increasing value, for new technologies, such as Scandium from Al concentrates (residues from bauxite processing), used for alloys in the aeronautic industries, or Vanadium used for the new battery types.

A sonic drilling campaign about 1400 m in total (30 m bore holes) was recently performed by Eijkelkamp SonicSampDrill on different Mn-tailings in Czech Republic using CB4 single wall core barrel sampling. These tailings are composed of about 30 m fine grained very soft material < 1 mm), a flotation product, underlain by sand a gravel. The flotation material hosts 10-30 % of water randomly distributed at different levels. The objective of this campaign was to sample the tailings for chemical analyses, metallurgical and geotechnical tests. The drill core recovery reached 95-100 % with widely undisturbed core material (Fig. 4).
6 Conclusion

Sonic drilling rig and tools are under constant development to respond to the challenges of heterogeneous high water bearing metal bearing soils and tailings. Our equipment significantly enhances the drill core quality helping the mining and metallurgical industries to increase their resource and reserves. Geometallurgical studies (e.g. systematic mineralogical and chemical analyses) will improve the performance of the metallurgical parameters to anticipate dysfunction during processing.
HPGR vs ball mill: breakage analysis through mineral particles characterization: Preliminary results

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Abstract. This paper presents the preliminary results of an ongoing work which aims at exploring the breakage process and the fracture mode through the analysis of mineral grain and particle characteristics. In this work, the performance of a high pressure grinding rolls (HPGR) in comparison to a laboratory ball mill to liberate chalcopyrite and sphalerite in a sulphide massive ore was studied. Specifically, the type of fracture (random or transgranular vs non-random or intergranular) produced during grinding was assessed. A Mineral Liberation Analyzer was used to characterize sphalerite and chalcopyrite liberation, grain size distribution and phase specific surface area. Although preliminary, the results obtained showed some differences between the two types of mills in the production of liberated particles.

1 Introduction

In a very simplified way, mineral processing can be summarized into two stages: a first one to liberate valuable mineral/s from gangue; and a second one to separate valuable particles from gangue particles. This second stage will be inefficient if the target liberation was not achieved during the first step. The optimization of comminution processes is therefore important, not only because the size reduction circuit is responsible for minerals liberation, but also because it is the largest energy consumer in the mine (up to 70%, Daniel et al. 2010).

During comminution, minerals can be liberated by two different mechanisms: random and non-random size reduction (Fig. 1.b and 1.c respectively). During the former, random fractures divide particles into smaller ones, eventually producing liberated particles (Leißner et al. 2016). On the other hand, non-random breakage is considered to produce selective liberation, such as, but not only, liberation by detachment along grain boundaries (King, 2000). If such a breakage mode occurs, the ore may require less grinding to achieve the target liberation (Johnson 2012). Both type of breakage modes are supposed to occur simultaneously during the size reduction process. In addition, the ore characteristics (composition and texture) also play an important role on the liberation process (King 1982).

This work was carried out as part of a project which aims at evaluating the impact of HPGR as compared to ball mill on mineral concentration performances (namely, flotation and leaching). In this work, the sample used for the assessment of the HPGR impact on flotation performance was analysed. The sample came from the Matagami Cu-Zn mine. As part of the mineralogical characterization work, chalcopyrite and sphalerite liberation was characterized using Mineral Liberation Analyzer. The results obtained showed that the HPGR achieved a higher chalcopyrite and sphalerite liberation than the ball mill. This paper aims at exploring this difference in liberation through the information carried by mineral particles.

Figure 1. Illustration of random and non-random fracture modes leading to different liberation possibilities (from Pérez-Barnuevo 2014, after Jones 1987).

2 Samples and methodology

2.1 Samples

The sample analysed in this work came from Matagami mine, a volcanogenic massive sulphide deposit located in the northern Abitibi region (Québec), producing Cu and Zn concentrates.

The initial sample was split to produce two subsamples. One of them (≈ 200 kg) was crushed in consecutive stages in a HPGR to 100% passing 980 µm until a P_{80} = 524 µm was achieved. At each step, the material passing 980 µm
was removed, recirculating only the non-passing material. Fresh mineral was added at each step in order to compensate the removed material. The process was repeated until a constant recirculated charge was achieved. The second subsample was first crushed in a jaw crushe to 100% passing 1.7 mm. After the jaw crushe, the sample was ground in consecutive stages in a laboratory ball mill (12”x12”). The objective was to produce a sample with the same distribution than the sample obtained with the HPGR.

2.2 Characterization by mineral liberation analyzer (MLA)

In order to identify potential differences between the HPGR and Ball Mill performance in the liberation process of chalcopyrite and sphalerite, the two samples obtained after grinding with each mill were analysed using Mineral Liberation Analyzer. The material obtained after grinding was screened by ro-tap in twelve size fractions (+850, -850 +600, -600 +425, -425 +300, -300 +212, -212 +150, -150+106, -106 +75, -75 +53, -53 +38, -38 +20 and -20 µm). Each size fraction was split for polished section preparation and chemical assays by XRF. Even though graphite was added during polished section making, the -20 µm size fraction was not analysed by MLA due to high particles agglomeration, which could debase liberation analysis. Therefore, it should be noted that all graphs shown in this paper do not include the -20 µm size fraction.

In this paper, the results obtained for chalcopyrite and sphalerite liberation, grain size distribution and phase specific surface area (PSSA) are shown.

3 Results and discussion

3.1 Chemical assays

Table 1 shows size-by-size copper and zinc grade for the products obtained after grinding. Although both mills were fed with an identical sample, Cu and especially Zn grade were higher in the finest size fractions (< 75 µm) after the HPGR than the ball mill, which already points out a potential difference in the liberation of sphalerite and chalcopyrite.

<table>
<thead>
<tr>
<th>Size fraction</th>
<th>Cu grade (%)</th>
<th>Zn grade (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+850 µm</td>
<td>HPG: 4.6</td>
<td>Ball Mill: 6.4</td>
</tr>
<tr>
<td>-850 +600 µm</td>
<td>5.3</td>
<td>5.9</td>
</tr>
<tr>
<td>-600 +425 µm</td>
<td>4.7</td>
<td>6.1</td>
</tr>
<tr>
<td>-425 +300 µm</td>
<td>4.9</td>
<td>6.1</td>
</tr>
<tr>
<td>-300 +212 µm</td>
<td>4.9</td>
<td>6.2</td>
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<td>-212 +150 µm</td>
<td>5.2</td>
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<td>-150 +106 µm</td>
<td>5.6</td>
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<td>5.9</td>
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<td>7.0</td>
<td>6.5</td>
</tr>
<tr>
<td>-53 +38 µm</td>
<td>8.2</td>
<td>6.9</td>
</tr>
</tbody>
</table>

3.1 Liberation curves

The proportion of chalcopyrite in liberated particles (particles with mineral of interest with a grade higher than 95%) was 27% for the HPGR and 21% for the ball mill; the proportion of liberated sphalerite was 41% for the HPGR and 33% for the ball mill. Figure 2 shows chalcopyrite and sphalerite liberation by particle free surface for both HPGR and ball mill. As observed, the HPGR achieved higher liberation for both minerals than the ball mill. In order to understand this difference, grain size distribution and phase specific surface area (PSSA) were analysed.

3.2 Size distribution

Figure 3 shows the combined size distribution curves for feed, sphalerite (Sp) and chalcopyrite (Cp) grains. As observed, for the same particle distribution, the HPGR produced chalcopyrite and sphalerite grain size distribution finer than the ball mill.

3.3 Phase specific surface area

Phase specific surface area (PSSA) allows for the estimation of the area per unit volume of a given surface in a 2D image (Underwood 1970). This parameter is
proportional to the ratio between phase boundary length and phase area (Underwood 1970, Russ and Dehoff, 1999).

When characterizing mineral particles, there are two types of surface which are worth considering: the free surface of the mineral of interest (i.e. surface exposed to reactants) and the locked surface (i.e. surface of the mineral of interest bonded to other minerals in the particle). As the particle fineness increases, new free surface is generated by both random fracture and non-random fracture. In addition, if non-random fracture produces liberation by detachment, mineral intergrowth (or locked) surface is reduced.

Total phase specific surface area (PSSA) is obtained by summing up the free phase specific surface area (FPSSA) and the locked phase specific surface area (LPSSA) (Eq. 1; Leißner et al. 2016).

\[
PSSA = FPSSA + LPSSA \quad \text{(Eq.1)}
\]

In figure 4, size-by-size total PSSA for both chalcopyrite and sphalerite is shown. As observed, this parameter is almost constant (or show little variation) for the coarsest particles. This indicates that no (or few) new phase surface is being generated with fineness until the particle reaches a given size (around 106 µm for sphalerite and 75 µm for chalcopyrite). In addition, this graph shows that the total PSSA of coarser particles is higher for the HPGR than for the ball mill. However, there is an inversion of this trend for finer particles.

Figure 5 shows chalcopyrite and sphalerite size-by-size free PSSA. As observed, the generation of free surface increases when particle size decreases (Leißner et al. 2016). Both mills seem to generate free surface at the same rate with particle fineness.

Figure 6 shows size-by-size chalcopyrite and sphalerite locked PSSA. As observed, the intergrowth surface decreases for both minerals with particle fineness and for both mills. However, it seems that for the finest particles (< 106 µm) the HPGR reduces the locked surface to a greater extent than the ball mill (especially for chalcopyrite). This may lead to the production of less mixed particles in the finest size fractions by the HPGR than by the ball mill.

Since the grain size distribution (Fig. 3) shows that the HPGR produced grains of finer size than the ball mill, a higher free surface generation could be expected for the HPGR. However, as shown in figure 5, both mills presented very similar size-by-size free PSSA curves. According to the trends shown by figure 6, the HPGR seems to be more efficient to reduce the amount of locked surfaces (i.e. grain detachment), which may lead to liberated grains of finer size.

4 Conclusions

The mechanisms ruling the liberation of minerals are quite complex. There are many factors involved; some of them depend on the crushing and grinding systems used, while others are related to the ore characteristics (such as composition and texture). Therefore, a unique formula applicable to all cases is not viable. However, since the aim of all comminution circuits is to optimize the production of liberated mineral particles, the characterization of particle properties variations within these circuits may assist in the comprehension of this complex process.

In this work, a Mineral Liberation Analyzer was successfully used to evaluate differences in the chalcopyrite and sphalerite liberation achieved by a HPGR and a ball mill. The trends obtained in the characterization of grain size and phase specific surface area indicated that the HPGR is more efficient in the reduction of locked
surfaces for the particular ore analysed.

Although preliminary, the results obtained in this work show how process mineralogy can provide information to better understand mineral liberation processes. Further work should be done in order to explore how geometallurgy can make use of this approach for the optimization of comminution circuits.

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Mineralogy of smelter- and mining-derived particles in semi-arid soils and their potential mobilization during wildfires

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Abstract: High levels of inorganic contaminants were found in semi-arid topsoils and soil biomass samples near the Tsumeb copper smelter in northern Namibia: up to 5800 ppm Cu, 1920 ppm As, 4880 ppm Pb, 3310 ppm Zn, 81 ppm Cd, 7.66 ppm Hg. Contamination occurs as particulates derived from mining activities (grains of ore minerals windblown from tailing disposal sites) or from smelting processes (metal-rich slags, dusts from flue-gas cleaning). Based on mineralogical investigation of these metalloid-bearing particulates, laboratory set-up was designed to simulate wildfire conditions. It was demonstrated that contaminants are partially released into the environment especially at temperatures above 700°C. In contrast to other contaminants, Hg derived from sulphide phases was released into the atmosphere at temperatures 350°C corresponding to low-severity wildfire conditions.

1 Introduction

We investigated contaminated semiarid area near an operating Cu smelter and old mine-tailing disposal sites in Tsumeb in the northern Namibia, where Cu, Pb, Zn and to lesser extent Ag and Ge were historically extracted. The Tsumeb deposit (age ~530 Ma) belongs to the Otavi Mountains region, which is a part of the Damara orogen (Kamona and Günzel 2007). Deposit is classified as a (Pb-Cu-Zn) Mississippi Valley type, where ore minerals are associated to limestones and dolomites.

About 27 Mt of ore has been historically extracted; this corresponds to 1.9 Mt Cu, 3 Mt Pb, 1 Mt Zn (Schneider 2016). The Tsumeb deposit was mined with several open pits and shafts. Nowadays, local mines are closed and the smelter equipped with Ausmelt and reveratory furnace is still operating; it processes As-rich Cu concentrate predominantly transported from the Chelopech mine in Bulgaria. The Tsumeb smelter is one of the few in the world processing As-rich ore concentrates with by-production of arsenolite (As₂O₃) (Ettler et al. 2016).

It has already been demonstrated that soils and plants from this area are highly polluted by dust particles originating from mining and mineral processing activities (Ettler et al. 2016; Kříbek et al. 2016; Mihaljevič et al. 2015). Produced and processed materials in local smelter are subsequently transported mainly by the action of wind (Kříbek et al. 2010).

In this paper, we focus on the mineralogy of mining- and smelter-derived particulates extracted from topsoils and soil biomass samples collected in the close vicinity the Tsumeb smelter (litter from marula and acacia trees, grass samples) and their behaviour during wildfires.

2 Material and methods

2.1 Sample collection

Topsoils and soil biomass samples were collected downwind the Tsumeb Cu smelter and adjacent dumps of slags and mine tailings. Biomass samples included litter collected under the main tree species in the area (marula tree, Sclerocarya birrea and acacia tree, Acacia spp.) supplemented with biomass samples from grassland. A representative portion of sample was milled in agate planetary ball mill (Fritsch Pulverisette) and used for bulk and combustion analyses.

2.2. Mineralogical determination

Heavy mineral fractions were separated from the bulk soil/litter samples in tetrabromethen. Phase compositions were determined using X-ray diffraction analysis (XRD) and specimens were prepared as polished section for additional analyses.

The TESCAN Integrated Mineral Analyzer (TIMA) (automatic SEM/EDS) was used for the analysis of modal compositions and for the automated search and identification of metalloid-bearing phases.

A JEOL JXA-8530F electron probe microanalyzer (EPMA) equipped with field emission gun (FEG) electron source was used for observation of the individual particles (scanning mode in back-scattered electrons, BSE) and semi-quantitative (energy dispersion spectrometry, EDS) and quantitative compositions (wavelength dispersion spectrometry, WDS). Particulates attached to biomass samples have been studied in situ using the same instrument.

2.3 Combustion experiments

Combustion experiments were performed in quartz-tube equipped oven with predefined temperature under the synthetic air-flow of 50 ml/s (PR Synthetic Air – X50S 200B) controlled with a flowmeter (CSI 6000, Ellutia, UK). The mass of 0.200 g of milled sample placed in
ceramic crucible was inserted into the central part of preheated oven and was exposed to elevated temperatures for 25 minutes (250-850°C, step 100°C). At the output of the oven flue gas containing volatilized contaminants was captured into the plastic vials filled with 5% HNO₃. After each step of experiment, contaminants (As, Cd, Cu, Pb, Zn) were analysed using ICP-MS (Thermo-Scientific Xseries®) not only in the acidic solution, but also a tube wash and the digested residual ash to assess the contaminant volatilization using the mass balance calculations.

3. Results and discussion

3.1 Contaminants in topsoils and soil biomass

The metal(loids) concentrations in topsoils and soil biomass samples from the Tsumeb area indicate high levels of contamination: up to 5800 ppm Cu, 1920 ppm As, 4880 ppm Pb, 3310 ppm Zn, 81 ppm Cd, 7.66 ppm Hg, which is in agreement with previous investigations (Ettler et al. 2016; Podolský et al. 2015; Mihaljević et al. 2015; Kříbek et al. 2016).

3.2 Mineralogy

Spherical particles originating from the smelting process, were commonly observed in all samples. They were mainly composed of Cu-Fe sulphides and glass-rich or spinel-rich slag-like particles (Fig. 1a,b). Angular shaped grains were probably wind-transported during the historical ore processing or from nearby mine-tailing disposal sites (Fig. 1c). These particles either contained gangue minerals (carbonates) or various sulphides, sulphosalts, arsenates or arsenites (Ettler et al. 2016).

Interestingly, arsenolite (As₂O₃) being a major compound emitted by the smelter (Ettler et al. 2016; Mihaljević et al. 2015) was seldom detected, probably due to its high solubility in the soil system. Only few minute grains of arsenolite have been detected directly at the surface of biomass samples (Fig. 1d).

3.2. Contaminant mobilization during wildfire

During the wildfire simulations, contaminants contained in the topsoils and soil biomass samples behaved differently as a function of temperature. Major release of As began at 450°C followed with a slight increase and local maximum at 650°C. In contrast, Zn exhibited local maximum at 350°C followed by a slowly decreasing tendency. Only low amount of Cd and Pb have been emitted at <750°C, whereas massive mobilization occurred at 850 °C (Fig. 2).

Wildfires are considered to be one of the main sources of atmospheric Hg pollution (Friedli et al. 2009). During the combustion process, Hg is mostly emitted as a Hg⁰ (Friedli et al. 2001). During our experimental work we firstly measured total content of Hg in all samples using Altec AMA 254 analyser. Measured values were surprisingly high, up to 7.66 ppm Hg. As already mentioned above, the local smelter currently processes ore concentrates from Bulgaria with up to 20.6 ppm Hg (Podolský et al. 2015); this value corresponds with our determination (20.0 ppm Hg). We hypothesize that Hg in the topsoils and biomass samples may be partly bound in wind-blown sulphides from concentrate dust deposited in the soils system.
All topsoil samples used for Hg thermal mobilization experiments behaved similarly (Fig. 3). Thermodesorption of Hg from Bulgarian concentrate occurs firstly at temperatures around 260 °C and culminates at 480 °C. In contrast, experiments with soil biomass samples indicate that emission of Hg has a sharp peak at 340 °C. This phenomenon can be related to local increase of temperature during biomass burning, which causes Hg release. This explanation can be supported by comparison of Hg released and weight loss of samples during the experiment performed (Fig. 4). Massive increase of weight loss at 350 °C indicates a more effective combustion and a potential temperature increase.

Our experiments confirmed previous findings (e.g., Friedli et al. 2001; Navrátil et al. 2009) that all the Hg content in tree litter can be released during temperatures corresponding to wildfires. That means that we can predict the amount of Hg, which can be potentially emitted from burned area during those events.

### 4. Conclusions

The Tsumeb area in the northern Namibia is highly polluted with smelter- and mining-derived particles, which are mainly located in soil biomass samples (litter) and topsoils. During wildfires these contaminants can be mobilized into the atmosphere. Our experimental observations indicate that wildfire severity (i.e., temperature) significantly affect contaminant transformation and remobilization.

### 5. Acknowledgements

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### 6. References


Towards a specific geometallurgical flowsheet for a marble operation using the IDEF0 methodology

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Abstract. Measurement while drilling (MWD) data represent additional information available at low cost while drilling boreholes in a mine or during tunnelling. An improved geometallurgical model at Brønnøy Kalk AS incorporating the results from MWD data analysis is under development. It is presented and visualised using the IDEF0 methodology.

The paper discusses and explains the link between the geometallurgical flowsheet and the value chain of working process executed in the Brønnøy Kalk AS open pit operation.

1 Introduction

Lamberg et al. (2013) and Lund and Lamberg (2014) defines a geometallurgical model as a combination of geological information and information related to mineral processing into a 3D predictive tool to be used in production planning and management of mining operations.

A geometallurgical model can basically be constructed using three different approaches (Lishchuk et al. 2015 and Lishchuk et al. 2016). Firstly, one can use the traditional approach using geochemistry and its link to recovery. Secondly, one can perform a large number of small-scale laboratory tests where all the inputs and outputs are controlled and measured. Following these tests, typically a multiple regression is applied to establish the links between geological information and processing performance. Proxies are used to a large extent. Thirdly, one can do mineralogical and textural characterization and the use of particle tracking techniques. Lamberg terms this the “mineralogical approach”. This approach focuses on the modal mineralogy and uses this information to establish the geometallurgical model.

In this part of the InRec-project, an attempt is done to exploit MWD-data and analysis of such data in a geometallurgical setting and use the IDEF0 methodology to visualise the development of the geometallurgical model involving MWD-data. In addition, a case specific geometallurgical flowsheet (Lang et al. in prep) is prepared.

2 Background

2.1 Mining operation

The mining company Brønnøy Kalk AS runs an open pit operation near the Brønnøysund town, Nordland County, Northern Norway. They produce annually approximately 2 million tonnes of marble that are delivered to the Omya ground calcium carbonate (GCC) plant in Elnesvågen. The GCC is used in paper production to increase its quality. The quality of the final product is primarily measured according to its whiteness. The process at Elnesvågen removes basically all the non-white minerals. See e.g. Bunkholt (2015).

During the mining operation, drill cuttings from all the holes inside geometrically defined blocks (smallest mining units (SMU)) in the blast are collected and the quality of the SMU is defined by the quality of these collective samples.

No direct link between in-situ geological characteristics and the processing performance (whiteness) has been found (Watne 2001), so a laboratory procedure has been developed to mimic the processing done at the processing plant in Elnesvågen. Watne developed in effect a geometallurgical model that during the InRec project will be updated and further developed with MWD-information.

2.2 IDEF0

Building a flowsheet follows the rules described in the IDEF0-methodology (IDEF 1994).

A process model according to the IDEF0-methodology consists of working processes tied together by inputs and outputs to form the value chain. Responsibility for the value chain progress starts and ends at these output / input intersections. The blue boxes (see Figure 1) are visually used to define where the responsibility for value chain progress changes from one person or organization to another.

Controlling and supporting elements can be considered to be outputs from supporting processes like maintenance or production planning. In the first case, the maintained drilling rig could be an output from the maintenance process and thereby a supporting element to the process “Production drilling”. In the latter example the drilling plans are the output from the planning process and thereby a controlling element of the “Production drilling” process.

Integrated Computer Aided Manufacturing Definition (IDEF) is a methodology initially developed by the US Air Force to describe manufacturing systems. The methodology consists of four methodologies, IDEF0, IDEF1 IDEF1x, IDEF3 for functional-, data-, dynamic analysis- and process modelling respectively.

The main components in IDEF0 modelling are functions (processes, activities or transformations), inputs, outputs and controlling- and supporting (mechanisms) elements (the so-called ICOMs).
Figure 1. The main components in IDEF0 modelling are functions (processes, activities or transformations), inputs, outputs and controlling- and supporting (mechanisms) elements (the so-called ICOMs).

Table 1 explains the ICOMs in more detail.

<table>
<thead>
<tr>
<th>ICOMs</th>
<th>Examples</th>
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<tbody>
<tr>
<td>Inputs</td>
<td>are requirements, information, problems, material or conditions. The input is used, consumed, or altered by the process.</td>
</tr>
<tr>
<td>Outputs</td>
<td>are results, information, products or conditions. The output is created or comes out of the process.</td>
</tr>
<tr>
<td>Controlling elements</td>
<td>are standards, regulations, legislation or plans. These elements are something that decides when and how the process might or must be executed.</td>
</tr>
<tr>
<td>Supporting elements</td>
<td>are human resources, tools, equipment, systems or facilities. This element is used but not consumed.</td>
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In Figure 1, the five elements are illustrated according to the IDEF0 standard with some modifications:

- The input enters the process from the left.
- The process transforms the input to an output, which exits to the right.
- The controlling elements enter the process from the top. These elements have influence on how or when the processes are performed.

Supporting elements, or mechanisms, enter the process from below. Supporting elements are tools necessary to perform the process. They are used, but not consumed.

The different elements are connected via arrows. Arrows are either horizontal or vertical. If an arrow connecting two elements is bent it must be curved only using a 90° arc (see Figure 2).

A geometallurgical flowsheet (Lang et al. in prep) is a visualisation of the geometallurgical program executed to develop the geometallurgical model. This model is used to predict some key performance indicators based on data collected during the mining operation. The flowsheet is linked to the mining value chain since the output from a process that uses the model as a controlling element can be regarded as controlling elements of one or many of the primary processes in the value chain. This would vary from case to case.

2.3 Measurement while drilling (WMD)

Measurement while drilling (MWD) data is set of data which is collected while drilling boreholes in a mine or during tunnelling. The data included in this MWD case are: log time (YYYY-MM-DDThh:mm:ss), Depth (m), Penetration Rate (m/min), Percussion Pressure (bar), Dampening Pressure (bar), Feeder Pressure (bar), Flush Air Pressure (bar) and Rotation Pressure (bar) in 2cm intervals in every boreholes.

Rock materials encountered in mining are highly...
variable in strength, structure and grade. The mining processes such as blasting, grinding, crushing and liberation can have a relation with the MWD parameters (Rai et al. 2015). MWD analysis could be a useful tool for quantifying parameters other than ore grade, like rock strength and the structural characterization.

2.4 Sampling and quality parameters

At Brønnøy Kalk AS, a blast contains approximately 100,000 tons of marble. These blasts are then divided based on geometry into SMUs of approximately 5000 tonnes. Each of these SMUs will have 10-15 boreholes. The sample of drill cuttings are taken collectively from each SMU and are then tested in the lab for its quality parameters. The combined mixture of this sample will represent an average blended quality of each SMU. The main quality control parameters used at Brønnøy Kalk are whiteness, flotation loss, reagent consumption, and acid insoluble residue (Aasly & Ellefmo 2014). These quality parameters are used while blending and loading of the raw material.

3 Geometallurgical model incorporating MWD data and the value chain

The actual geometallurgical model establishing the relation between MWD data and other quality parameters using higher order nonlinear regression analysis is under development. The main processes in developing the geometallurgical model are to convert the high resolution MWD data to a block average data and establish a relation between MWD parameters and quality parameters. The workflow or the geometallurgical program necessary to establish the intended geometallurgical model is visualized below in figure 3 using IDEF0 method. The shaded blue boxes indicate that it is linked and detailed with another diagram. For example, in figure 3 the blue box representing MWD data is further visualised in figure 4 and broken down into the different variables.

During the mining process, improved blast specific KPIs is expected to be calculated using the MWD data as input and the previously established geometallurgical model as a controlling element. (see figure 5).

The blast KPIs are the quality parameters visualised in figure 6.

Figure 4. MWD data consist of “Penetration rate”, “Percussion pressure” etc.

During the mining process, improved blast specific KPIs is expected to be calculated using the MWD data as input and the previously established geometallurgical model as a controlling element. (see figure 5).

Figure 5. Geometallurgical model is the controlling element of the “estimation of blast specific KPIs” process.

The blast KPIs are the quality parameters visualised in figure 6.

Figure 6. Blast KPIs consist of “Whiteness”, “Acid insoluble residue”, “Reagent consumption” and “Flotation loss”.

Figure 3. Specific geometallurgical flowsheet visualising the development of the geometallurgical model using MWD data and quality parameters.
The blast KPIs are used as a controlling element while blending and loading the raw material. The current value chain of main working process of Brønnøy Kalk AS is visualised using IDEF0 methodology in figure 7.

Figure 7. The value chain of main working process. The established geometallurgical model is used in the highlighted part of value chain to calculate the blast KPIs.

4 Conclusions

In conclusion, the development of a geometallurgical model establishing a relation between MWD data and the marble quality parameters is visualised using the IDEF0-methodology. The actual model is under development and will be used in the blending activities at the mine. MWD-data analysis and the model could potentially also be used to determine a new sampling procedures and to calculate improved blast KPIs at Brønnøy Kalk AS. The geometallurgical model and its relationship with the mining value chain is also visualized using IDEF0 method. The IDEF0 methodology offers opportunities to visualise different aspects of both the mining value chain and the geometallurgical program. Using visualisation rules, different characteristics of the links between the ICOMs can be highlighted.

Acknowledgements

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Lang A et al (in Prep) Geometallurgical flowsheet development for industrial mineral operations
Relating different textural settings of gold to mineral processing – preliminary assessment of two massive sulphide deposits

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Abstract. Mining companies regularly look into potential improvements of gold recovery in producing mines, to increase revenue. In trying to do this, it is essential to have a good understanding of the textural settings of gold in the ore, and the gold mineralogy. Here, the textural relationships of gold in two deposits in northern Sweden are studied. The Renström and Maurliden deposits are of similar type, volcanic massive sulphide deposits, and are base metal producing mines. However, gold is an essential by-product, and it occurs texturally rather different between the two deposits. In Renström, gold occurs in the silicate matrix and closely associated with antimony minerals, and in Maurliden, gold occurs chiefly as fine-grained fracture fillings in arsenopyrite. These different settings of gold necessitate different approaches when trying to improve gold recovery. The findings of this study emphasize the importance of a detailed ore characterization, since even though the two deposits are of similar type, and formed from similar geological processes, the settings of gold vary. Detailed information on gold textures and mineralogy is vital for an optimized mineral processing, and of importance in the mineral exploration stage.

1 Introduction

Gold has historically been a commodity of great interest to society. Thus, mining companies are continuously looking to improve the recovery of gold in productive mines, thereby increasing revenue. In addition, brownfields exploration for gold is searching to increase the known resources. In trying to expand resources and improve recovery, it is crucial to have a good understanding for the different textural settings of gold in the ore, and the gold mineralogy.

The enrichment techniques for gold are controlled by the ore mineralogy, thus textural and mineralogical studies can assist and improve the mineral processing of these ores (Zhou and Cabri 2004). Wet gravity methods are useful for all types of ore, except when the gold occurs as inclusions, or is too fine-grained. The gold that occurs as inclusions in, or in grain boundaries to, different sulphide minerals may not be won directly. If the gold-containing sulphides are in fact themselves winnable, like copper or lead minerals, they are won in the flotation process and the gold is then extracted after smelting of the host mineral’s concentrate. To recover gold that occurs locked in pyrite or arsenopyrite, the first step would be to float a sulphide concentrate and then oxidise it through roasting, autoclave leaching or bacterial leaching, with subsequent cyanide leaching of the oxidation residue (Spry et al. 2004). If the gold occurs only in the grain boundaries of pyrite or arsenopyrite, then gold may be leached directly, rendering the mineral oxidation step unnecessary. If the gold is present as fine gold, tellurides or selenides, it is commonly won by direct flotation with frothers only. In many gold ore districts, gold occurs in all these described settings within the same deposit. Typically, traditional mineral processing unit operations are present in the beneficiation chain, often combined with a hydrometallurgical enrichment step.

To better understand the controls on mineral processing, and thereby enable an improved recovery of gold, the textural relationships of gold in two gold-bearing massive sulphide deposits in northern Sweden have been studied. The deposits, which are producing mines, are situated ca. 25 km apart and were formed through similar geological processes. Here we present preliminary gold textural data from the two deposits: Maurliden and Renström (Fig. 1).

2 District and deposit geology

Northern Sweden hosts three important ore districts; Northern Norrbotten, the Skellefte District, and the Gold Line (Fig. 1). Numerous metal deposits in these mining districts were generated during subduction of oceanic crust beneath the Archaean craton around 1.9 Ga, during the Svecokarelian orogeny (Weihed 2003). The Northern Norrbotten ore province is important for production of iron, copper and gold in Europe. The Gold Line is a relatively new ore district in Sweden that since 2005 is exploited. Several gold occurrences have been discovered in this area, of which the Svartliden gold deposit has been recently mined out and the company is now planning to mine also the nearby Fäboliden gold deposit.
2.1 Maurliden Zn-Cu-Au-Ag deposit

In the central part of the Skellefte District the Maurliden deposit, which constitutes several massive sulphide ore lenses extracted from an open pit mine, has been in production since 2000. The Maurliden Ostra ore body was mined 2009–2014 and the area now awaits reclamation. Reserves for the Maurliden ore body are estimated at 1.7 Mt of ore with 4.3% Zn, 0.3% Cu, 0.4% Pb, 1.6 ppm Au and 62 ppm Ag (New Boliden 2016). The deposit is hosted within a quartz-feldspar porphyritic pumice breccia-sandstone unit (Montelius 2005).

2.2 Renström Zn-Cu-Pb-Au-Ag deposit

The Renström main ore body, located in the eastern part of the Skellefte District, was discovered in 1928 and brought into production in 1952 (Allen and Svenson 2004). It is an underground mine, and currently Sweden’s deepest, at approx. 1400m. Reserves for Renström are estimated at 3.9 Mt of ore with 4.5% Zn, 0.7% Cu, 0.9% Pb, 1.9 ppm Au and 105 ppm Ag (New Boliden 2016).

The stratigraphy of the Renström area is complex with the occurrence of basaltic to rhyolitic volcanic rocks intruded by granitoids of variable compositions (Schlatter 2007).

3 Sampling and methods

Twenty samples were taken from three different drill cores from the Maurliden and Renström deposits. Based on assay data, gold-anomalous sections in drill cores were logged in detail and samples representing the different alteration- and mineralization assemblages within those sections were collected. Polished thin sections were prepared and a detailed examination was made using conventional optical and scanning electron microscopy for phase identification and textural analysis. Mineral liberation-, electron microprobe-, and laser ablation ICP-MS analysis will be done on the same samples and on concentrate samples in the near future to obtain quantitative data on gold occurrence and reveal the amount of refractory gold locked in sulphides and oxides.

4 Gold textures

4.1 Maurliden Zn-Cu-Au-Ag deposit

The Maurliden massive sulphide deposit is hosted by a feldspar-porphyritic rhyolite, in the central part of the Skellefte District (Fig. 1). The samples were taken from a Zn-rich part of the ore lens. Pyrite and arsenopyrite dominates the mineralogy of the samples, with accessory sphalerite, galena and chalcopyrite. Gold grains are generally very fine (<10 μm) and occur as fracture fillings in arsenopyrite (Fig. 2 A, B). The arsenopyrite is in turn associated with sphalerite, which is one of the main commodities in the mine. Gold grades of the Maurliden samples are below 0.7 ppm, with a mean value of 0.3 ppm.

4.2 Renström Zn-Cu-Pb-Au-Ag deposit

The Renström samples represent quartz-rich rocks with common sulphides from the G lens of the ore. Chemical assays revealed 3.74 ppm Au in the sampled section. In these samples, gold grains are generally <20μm but 20–50μm inclusions have also been observed, as well as ca. 100 μm long fracture fillings (Fig. 2C, D). These gold grains are dominantly hosted by quartz in the groundmass of the rock (Fig. 2C). Also, a few small (<5μm) gold grains occur between quartz and galena, and associated with Sb-bearing mineral phases (Fig. 2D). Gold grades of the Renström samples range between 0.1 and 1.9 ppm, with a mean value of 0.6 ppm.
Discussion

In the early stages of the planning and adjustment of metal extraction processes, a detailed characterization of the ore is crucial in order to improve metal recoveries. In mineral processing, one critical factor for the recovery of gold is the grain size distribution, which can result in poorer recovery (Harris 1990).

In Maurliden, the majority of the detected gold grains (n=17) occur as fracture fillings in arsenopyrite (Fig. 2A, B). Most of these gold grains are very fine-grained (<10 μm), which makes gravimetric extraction less effective (Harris 1990). The grains that are larger than 10 μm will likely be liberated during crushing and milling and will then be won in a wet-gravimetric process. To plan for a potentially improved metal recovery, it is important to determine the proportion of these fine-grained gold grains that are hosted by arsenopyrite in the ore body. Preliminary results from this study suggest that a significant part of the gold is difficult to win, and may be lost to the tailings. A way of improving the recovery would be to concentrate the gold-hosting arsenopyrite, and process that through finer grinding and cyanide leaching (Harris 1990). Then, the fine-grained gold may also be won.

The samples from the Renström deposit show two main modes of occurrence for gold. Gold grains (n=14) occur as inclusions and fracture fillings in quartz. These grains are between 1 and 100 μm (Fig. 2C), although the dominant grain size is <20 μm. Gold also occurs as very fine-grained inclusions in gold-bearing antimony minerals, possibly aurostibite, as can be seen in Figure 2D (inset). Also, in this case, the grain size distribution is an obvious factor in controlling the gold recovery. Gold grains smaller than 10 μm are likely lost to the tailings, so it is important to investigate the grain size distribution in better detail to determine the proportion lost. Gold grains >10 μm will likely be won through a wet-gravimetric circuit to take out the coarser gold mineral particles, followed by flotation to win the finer gold.

What is also obvious here, is that gold occurs not only as amalgam (Au-Ag-Hg alloy) but as possible aurostibite. Should a leaching step be part of the mineral process here, the dissolution rates of different gold minerals, preferably aurostibite that has a much slower dissolution rate...
The investigated deposits are of similar type, massive sulphide ores, and have been formed from similar geological processes; however, the modes of gold occurrences are rather different between the two deposits. In the nearby Kristineberg massive sulphide deposit, gold occurs mainly in a third mode, hosted by pyrite, sphalerite and galena (Bark et al. 2013). The ore from Kristineberg is treated differently depending on the gold grade of the ore. If the ore is low in gold, it is processed through a wet-gravimetric process, coupled with flotation. If the grade is higher, a leaching step is added. The gold grains that are hosted by sphalerite and galena are won by flotation, whereas the gold hosted by pyrite is likely lost to the tailings if the leaching process is not introduced (Bark et al. 2013).

The findings of this study emphasize the importance of a detailed ore characterization with respect to the mode of occurrence for gold. In three spatially and genetically related deposits, gold seems to occur in at least three different textural settings and mineral associations, warranting different approaches to the mineral processing of these ores.

As evident from this preliminary assessment of two massive sulphide deposits, basic textural investigations by both optical- and scanning electron microscopy of representative drill core samples from the ore, preferably already at an early exploration stage, are keys for the planning and optimization of the mineral processing of ores. These early stage assessments should be followed by textural quantification and detailed gold mineralogy, through for instance Mineral Liberation Analysis, electron microprobe and Laser Ablation ICP-MS. With this approach, also potential added by-products in the ore may be detected and quantified.

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Combined mineralogy and chemistry on drill cores: challenging for on-line-real-time analyses

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Abstract. In order to evaluate the instrumental parameters for the combined on-line-on-mine-real-time expert system SOLSA (http://www.solsa-mining.eu), portable and laboratory analyses were carried out on coarse granite, sandstone, serpentinized harzburgite and siliceous breccia. Each sample was studied at 5 different surface roughnesses (sonic or diamond drilled, cut, polished at 6 µm and 0.25 µm, sample powders). X-ray diffraction (XRD), portable Infra-Red (pIR) and X-ray-fluorescence (pXRF), and laboratory micro-Raman spectroscopy gave complementary and corroborating results. No major effect on the analyses was noted for the selected surface states. pXRF gave variable results except for the homogeneously serpentinized harzburgite, related to coarse or contrasting grain sizes or pores, small spot size (3 mm) and needs close-to-surface analyses. Portable IR (spot size 1.76 cm²) is carried out close to surfaces while Raman spectroscopy (1-2 µm) is performed at distance. Sampling strategies have to be defined for each lithology. Major challenges for a combined on-line analysis are to adapt the specificities of the techniques to (1) analyse similar surface areas (from ~2 cm² (pIR) to < µm (Raman)), (2) smartly combine all the techniques into a single instrument, and (3) develop appropriate databases to reach a reliable “real-time” outcome results, which can be used for more precise geomodeling, and to rapidly define exploration and beneficiation parameters.

1 Introduction

Combined mineralogical and chemical analyses on drill cores are highly demanded by mining and metallurgical companies to speed up exploration, mining and define geometallurgical parameters for beneficiation. At present, analyses are done by exploiting only a single technique, such as hyperspectral imaging, XRF or LIBS (Cudahy et al. 2009; Roache et al. 2011; Haest et al. 2012). The coupling of different analytical instruments is still a technological challenge. The SOLSA project, sponsored by the EU-H2020 Raw Material program, targets to construct an expert system coupling sonic drilling with XRF, XRD, hyperspectral imaging and Raman spectroscopy. In order to define optimal instrumental parameters for combined on-line-real-time-on-mine analyses, we probed sonic and diamond drill core materials from sedimentary, magmatic and hydrothermally altered rock as well as sample powders (Fig. 1 a-e) by a cross-method approach.

2 Sample material and analytical methods

Sonic and diamond drilled core parts were cut from the core material (20 mm² x 6 mm). Four types of surface conditions were studied: (a) convex surface as drilled, (b) diamond saw-cut, (c) polished at 6 µm, (d) polished at 0.25 µm and (e) powdered at < 80 µm (Fig 2). Multiple measurements (pIR, pXRF, Raman spectroscopy) were carried out on each surface of the 4 surface states on coarse sandstone, coarse granite, porous breccia and serpentinized harzburgite, in order to evaluate the effects of the surface roughness on the different techniques.
Figure 1. Sonic drilled cores (Royal Eijkelkamp, NL) of sandstone (a), and granite (b); diamond drilled cores (SLN, NC) of serpentinized harzburgite (c) and breccia (d); e: powdered samples (< 80 μm) of the abovementioned sample materials.

Handheld X-ray fluorescence (pXRF) analyses were performed by Thermo Fisher NITON XL3t 980 (BRGM & ERAMET-COMILOG, 120 s acquisition time, 4 filters, mining mode, diameter of the analytical window: 0.3 cm). Five measurements were acquired on different zones of each sample type. Handheld infra-red spectroscopy (pIR) was carried with an ASD FieldSpec 3 (BRGM, band width: 350 to 2500 nm, 3-10 nm spectral resolution, area of the analytical window 1.76 cm²). For each sample, 10 spectra (=20 measurements: 1/10 s) were compared in order to ensure the absence of aberration, and summed to obtain the final reflectance spectrum. Micro-Raman spectroscopy was performed with Jobin-Yvon LabRam HR800 (University of Verona; 633 nm He-Ne laser, powers at the sample surface: 1.5, 3 and 6 mW; spot size 1-2 μm, integration time 20 s and 100 s), and with ThermoScientific DXR (CRISMAT-ENSICAEN, 532 nm laser, power at the sample surface: 1 mW, spot size 0.6 μm, and integration time of 120 s). XRD was carried out on powdered samples with a Siemens D5000 diffractometer (BRGM; Co-tube, 2θ range from 4° to 84°, with 0.03° step and 13.5 s/point). DIFFRAC Plus EVA software was used for the interpretation of the X-ray diffraction patterns. Quantitative mineralogy was estimated using Rietveld refinement and MAUD software.

3 Results

Peridotite. XRD powder analysis shows 57 wt.% serpentine, 29 wt.% forsterite, 11 wt.% enstatite, 3 wt.% talc and traces of amphibole (Fig. 3). pXRF analyses on the powder surface indicate 21.9 ± 0.2 wt.% Si, 20.6 ± 0.9 wt.% Mg, 5.9 ± 0.1 wt.% Fe, 88 ± 7 ppm V, 39 ± 1 ppm Ti, 2194 ± 43 ppm Ni, 1417 ± 119 ppm Cr, 40 ± 5 ppm Zn and 896 ± 45 ppm Mn. Analyses on the drilled, cut and polished surfaces show higher values for Si (22.8-24.2 wt.%), Mg (23.1-26.1 wt.%) and Ti (41-63 ppm), similar contents of Fe, Ni, Zn, Mn, and variable contents of V and Cr compared to those on the powdered sample.

Granite. XRD powder analysis shows a composition of 27 wt.% quartz, 20 wt.% microcline, 28 wt.% albite, 24 wt.% mica and/or illite and 1 wt.% chlorite. pIR shows the presence of bound water and illite, in agreement with XRD analyses. Micro-Raman spectroscopy confirms the presence of quartz, albite, and muscovite and additionally detains gypsum, magnesium sulphate, rutile, anatase, calcite and hematite (Fig. 5). pXRF on powder surface indicates 39.3 ± 0.4 wt.% Si, 9.2 ± 0.2 wt.% Al, 0.6 ± 0.1 wt.% Ca, 4.2 ± 0.1 wt.% K, 95 ± 13 ppm Zr, 59 ± 1 ppm Sr, 301 ± 39 ppm Ba, 43 ± 7 ppm Zn, 38 ± 4 ppm Pb, 0.9 ± 0.1 wt.% Fe, 136 ± 10 ppm V, 961 ± 64 ppm Ti and Ni below the detection limits. Analyses on drilled, cut and polished surfaces show higher
Si contents (42-46 wt.%), and variable contents of the other elements. Cr was detected on polished surfaces (235–324 ppm). These heterogeneous results are due to the coarse grain size of the granite.

Figure 4. Portable hyperspectral spectra on the 5 different surfaces (as drilled, as cut, polished 6 μm and 0.25 μm, and powder surface).

Sandstone. XRD powder analysis shows a composition of 100 wt.% quartz (Fig. 3). pIR analyses on the powdered samples give generally higher reflectance than the analyses on the drilled, cut or polished surfaces. Polishing slightly decreases the reflectance and slightly increases the peak intensity. pIR indicates the presence of bound water and illite or montmorillonite (Fig. 4). Micro-Raman spectroscopy confirms the presence of quartz and detects anatase, pyrite, maghemite, goethite and zircon. pXRF on the powder shows 55.2 ± 0.5 wt.% Si, 132 ± 16 ppm Zr, 0.02 ± 0.01 wt.% Fe, 55 ± 6 ppm V, 358 ± 59 ppm Ti, 0.05 ± 0.01 wt.% K, and 0.01 ± 0.01 wt.% Ca. Analyses on the drilled, cut and polished surfaces are lower in particular for the trace elements Zr (50-100 ppm) and Ti (99-256 ppm). Fe is heterogeneously distributed (260-600 ppm). From the chemical analyses, it can be concluded that minor amounts of zircons, iron oxihydroxides and Ti-oxides are present. This is confirmed by Raman spectroscopy. The traces of illite are indicated by traces of K, the traces of Ca may be related to carbonates.

Figure 5. Raman spectra of the minerals formed on (a) Sandstone (b) Breccia (c) Peridotite and (d) Granite. All spectra are compared to those presented in RRUFF Raman database http://rruff.info.

Breccia. According to XRD powder analyses, the sample contains 100 wt.% of quartz with traces of hematite.
and goethite (Fig. 3). pIR spectra do not allow to identify quartz, as the latter is detected around 9000 nm (TIR region). Water molecules are identified at 1420 and 1920 nm. The 500 nm band may correspond to goethite (Fig. 4). Micro-Raman spectroscopy confirms quartz as the major phase, and the presence of hematite and goethite. Furthermore, hedenbergite, forsterite, calcite, magnetite and maghemite were detected (Fig. 5). pXRF on the breccia powder indicates 53.5 ± 0.2 wt.% Si, 1.7 ± 0.1 wt.% Fe, 3722 ± 59 ppm Ni and 786 ± 57 ppm Cr. Sawn surfaces generally result into lower and highly variable concentrations (241-1520 ppm Ni; 12 ppm – 86-480 ppm Cr). Ni and Fe are positively correlated, indicating a common phase. Cr traces may reflect chromite, as Cr is not correlated to Ni or Fe. Raman analyses give important arguments (1) that the breccia is an alteration product of harzburgites; (2) the redox-conditions of breccia formation.

4 Discussion and conclusions

Table 1. Summary of major results of the combined sensor analyses on the 4 lithologies and 5 surface states.

This study shows how, in heterogeneous coarse grained and porous materials, a multi-technique approach is needed to obtain reliable chemical and mineralogical characterization. Table 1 summarises the results of combined portable sensors and laboratory instruments. Moreover, the presented data show that different surface treatments on the same sample have only minor effects on XRD, micro-Raman, pIR and pXRF measurements.

At present, a multi-technique approach is time consuming and requires different laboratory apparatuses. In order to integrate XRD, XRF, micro-Raman, and IR on a single probe operating at on-line-on-mine conditions there are some major technical challenges including (1) the adaption of powerful laboratory XRD and Raman spectrometers to a compact on-line-on-mine instrument; (2) the adaption and robotisation of the combined sensor system to overcome the problem of the different spot sizes from cm (IR) to mm (XRF) down to micrometric scales (Raman spectroscopy).

Finally, a reliable analysis cannot leave out of consideration the development of a mineral library adequate to the specific characteristics of the ore and waste to be analysed. This database should be comprehensive for Raman, XRD and hyperspectral data.

Acknowledgements

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References


ARTMin: Mineral classification based on fully deconvoluted EDS spectrums acquired by automated SEM

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Abstract. Automated mineral classification assisted by scanning electron microscope is a well-prime tool for geometallurgy. It allows a reliable quantitative characterization of the processed material. Usual mineral classification techniques are based on EDS X-ray spectrum fingerprinting and were developed about 40 years ago. Since the computer capabilities have tremendously increased in the past decade, real time deconvolution of every EDS spectrum is now achievable, although not of common use. Mineral classification based on semi-quantitative analyses is capable of discriminating similar mineral species, especially amongst silicate minerals meanwhile decreasing the misclassification. The ARTMin routine, developed for post-processing of analysis obtained with Oxford Instruments EDS-SDD detector, allows the acquisition and processing of fully deconvoluted EDS spectrums at a fast rate (6000 particles/hour for a single EDS detector), phase recognition and segmentation, automated mineral classification, mineral proportions, relative perimeter and degree of liberation.

1 Introduction

One of the foundations of geometallurgy is to refer to mineral proportions, rather than bulk chemical analyses, in order to predict or explain the behaviour of ore in mills. Mineral proportions on cohesive or particulate material can be measured with a conventional point counting under a microscope, image analysis, or more conveniently with specially adapted automated scanning electron microscope (SEM). Usually referred as MLA and QEMSCAN, (trademarks of FEI Co.), automated SEM can detect and outline the various particles or phases on a thin section, a drilling core or a polished mount. It can measure the particles morphological characteristics (length, width, axis ratio, area, perimeter, etc.), acquire an X-ray spectrum with an energy dispersive spectrometer (EDS), and even depict the relation between various phases (attachment, liberation, encapsulation, etc.). Each particle or phase is then imaged and indexed just as for a data entry, enabling cataloguing and statistics to be calculated.

However, these applications were developed initially in the 1970s, for SEM equipped with liquid nitrogen EDS and computers with limited capacities (Miller et al. 1982, Reid et al. 1984). To circumvent these initial limitations, short-cut procedures were used for phase classification. MLA classify mineral phases based on EDS spectrum matching (fingerprinting), where a 2000 counts spectrum is acquired on a particle and compared to a spectrum library (Sylvestre 2012). Classification result is based on best least square fitting of the acquired spectrum compared to the library. QEMSCAN use a similar process, where the spectrum is acquired on a pixel-by-pixel basis on the course of scanning fast, and the mineral spectrum reconstructed through adding pixel counts. X-ray spectrums of 1000 counts per pixels are usually acquired which yield to a detection limits of 2-3 % (Grafe et al. 2011).

EDS spectrum matching has its practical limitations, either in regard to the number of spectrums in the library that can be efficiently compared with, as well as distinctiveness between such spectrums. Therefore, minerals with similar composition, hence similar spectrums, cannot be efficiently discriminated, and complex mineral assemblage containing many species cannot be efficiently classified.

Recent increases of computing capacities now enable the complete deconvolution of EDS spectrums into normalized semi-quantitative analyses at the same rate as spectrums are acquired, even by the fastest EDS-SDD multiple detectors. As an example, the software Aztec (Oxford Instruments) efficiently deconvolutes spectrums acquired on each detected particles and convert them to weight percentages, which are used for real time mineral classification. This procedure is far more accurate and reliable in mineral classification, even for look-alike phases and complex solid solutions. It also enables discriminating silicate minerals with similar composition. Furthermore, no spectrum library acquisition is required for each project, as a universal classification algorithm is used.

Most mineralogists are acquainted to classify minerals using elemental or oxide abundance as weight proportions, from which they built their classification tree or discrimination diagrams. As an example, ilmenite with more than 2% MgO will be classed as picroilmenite and chrome-pyropes will be classified as G9 or G10 based on their calcium and chromium content. This system works for minerals with distinctive characters and not too wide diversity, such as carbonates, phosphates, simple sulphides, and simple silicates such as quartz and feldspar. However, some mineral families, such as ferromagnesian or calcic silicates, are far too diverse in composition, including...
abundant and complex solid solution to be efficiently classified by decisional trees, which rapidly become too complex and entangled. The case of amphiboles, pyroxene and garnet is notorious, as well is most phyllosilicates. A similar situation exists for oxides (spinel, polycrase, Ti-Nb oxides, etc.) sulphosalts and platinum group minerals. Classification using decision trees are better conducted using atomic proportions, since they are dictated by their formula. Using atomic proportion provides a more robust and easily visualized classification.

From atomic proportion, stoichiometry of the mineral can be calculated. The difficulty with stoichiometry calculation relates to elements which may occupy more than one site and are involved in polyvalent diadochic substitution or have multiple valencies. Iron is the most notorious, being present either as ferrous Fe+2 or ferric Fe+3, and then occupying different sites. Ferrous iron has complete substitution with other divalent metals such as Mg+2, Mn+2 or even Ca+2, while ferric iron substitute with trivalent cations such as Al+3 and Cr+3. In polyvalent diadochic substitutions are more complex, involving groups of metals with diverse valencies, only the sum of which being constant. The jadeite substitution in pyroxene is a common example Mg+2Ca+2<>Al+3Na+1. Finally, last difficulties in building a universal algorithm to calculate stoichiometry reside in those different minerals structures are based on different sums of cations and the presence of undetectable elements such as hydroxyl radicals. Classical issue is differentiating calcic garnet and epidote. Such calculation capabilities are not embedded is Aztec (OI), nor it is in MLA or QEMSCAN software (FEI), and partly available in Mineralogic (Zeiss).

The difficulty in using complex calculation such as stoichiometry deconvolution or complicated decision trees resides in the fact that particle analyses are not precise. EDS spectrum acquisition is limited to small counts to maintain speed and efficiency. MLA uses 2000 counts for its classification, while Mineralogic uses 3000 counts. The number of counts used by Aztec is decided by the user, and remains a trade-off between precision and speed. Deconvoluting analyzes from such low count yields in imprecision propagation and results that deviate from ideal stoichiometric composition.

To overcome these limitations, ARTMin (Automated Reconnaissance Technique for Mineral) routine was developed based on fully deconvoluted EDS spectrums as acquired automatically by SEM and proprietary software in C++. Initially developed for the classification of heavy minerals for diamond exploration, the routine finds its application in geometallurgy.

2 Methods

2.1 Equipment

ARTMin routine has been developed for a 2013 Zeiss EVO MA15HD scanning electron microscope equipped with a LaB₆ source, SE and VPSE-CL detector, CZBSE multi-segment detector, and X-Max 150 EDS-SDD detector from Oxford Instruments.

Although not optimized for fast mineral classification such as a MLA or QEMSCAN instrument, this versatile instrument is almost entirely dedicated to mineral analysis. EDS spectrums are deconvoluted into normalized semi-quantitative analysis as well as fully quantitative analysis (EMPA quality, Newbury and Ritchie, (2015) with the use of Aztec software (OI). Routine particle discrimination and analysis is conducted with Aztec Feature and Large Area Mapper software.

2.2 Particles detection

Aztec Feature was not developed explicitly for mineral classification and geometallurgy applications. This versatile particles recognition software was initially developed for industrial and forensic applications. Particles or phases discrimination is conducted with the use of backscattered electrons (BSE) images, based on grey shades, just as for MLA and QEMSCAN. However, particle or phase classification uses a customizable algorithm which involves intricate BSE intensity, EDS spectrum similarities and peak counts, morphological parameters, and most importantly chemical analysis such as elemental abundance or ratios from the fully deconvoluted EDS spectrum.

The equipment, as currently configured, is capable of achieving acquisition, deconvolution and classification of about 6000 particles per hour. The use of multiple smaller detectors would improve performance accordingly.

2.3 ARTMin

Analyses obtained from particles in Aztec can easily be exported in weight percentages to excel for post-processing. From there, the analysis and the BSE mosaic image of the polished epoxy mount or thin section are uploaded in ARTMin.

Figure 1. Particle classification based on their chemical microanalysis, as performed by ARTMin. Most of these mineral classes are silicates with complex solid solutions such as almandine, grossular, hornblende, augite, hypersthene, epidote, etc.

Particle images are extracted and indexed in a
portfolio, in a very similar manner as for QEMSCAN and MLA, each of which with its chemical analysis and morphological parameters. Classification algorithms are applied to the analytical database, and particle images are colour coded just as for MLA and QEMSCAN (Fig.1).

To circumvent the issue of low precision, particles or mineral analysis are compared to a reference library of theoretical composition calculated from mineral formula. Mineral class is assigned according to the least geometrical distance in a N-dimensions space, dimensions being abundances of constituting elements.

Minerals with solid solutions are not represented by points in the N-space, but rather by mixing lines, plane, tetrahedrons or hyper-polyhedron depending on the number of elements involved in the substitution (e.g.: Fe Mg and Mn in pyroxene, Ca and Si being fixed). In minerals with more than one possible substitution (e.g.: garnet with the Ca-Fe\(^{3+}\)-Mg-Mn and the Al-Fe\(^{3+}\)-Cr substitution sets), fitting has to be done in regard of multiple polyhedra in the N-space. Finally, minerals with polyvalent diadochic substitution, such as the albite-anorthite series (Na,Al,Si <> Ca,2Al) a complex set of strings linking the cords.

Calculation of aforementioned analytical objects is tedious. To ease such, for each set of solid solutions, mixing lines were simulated by generating a set of intermediate compositions, and generating intermediate minerals in the library. Least distance fitting is then calculated from the unknown mineral to the nearest solid solution minerals.

### 3 Results

#### 3.1 ARTMin classification

The level of confidence on the classification is estimated from the calculated Euclidian distance between the analysis and the closest theoretical mineral composition, zero being a perfect classification and elevated values representing a misclassification. By experience, a misclassification occurs if the least fitting distance exceeds 10%. The misclassification can be caused by a missing library’s mineral, mixed signals or, more rarely, an important analytical error due to uncorrected interferences or discrepant matrix correction.

The classification efficiency has been tested by crushing a single crystal garnet and analyzing its multiple fragments with the ARTMin SEM based routine. The distribution of the deviation of the analyses from the closest reference analysis (dark bars on figure 2) closely matches the distribution of the deviation between the analyses and its Euclidian average (light grey bars on figure 2). Thus, the efficiency of the classification is little affected by the low precision of the analyses as long as the overall accuracy is correct. The residual difference between the two distributions is considered as caused by impurities in the mineral or analytical discrepancies related to spectrum deconvolution.

Once particles are properly classified, morphological attributes (shape, size, perimeter, etc.), associations and liberation are quantified such as for conventional QEMSCAN and MLA procedure.
identification results. Proper silicate classification enables identification of geometallurgical domains as well as detection of minor phases unseen by XRD analysis. Minor or accessory phases are of importance since they may cause contamination issues or reflect recovery problems. Sulphide abundance and speciation have been obtained despite their low abundance.

Figure 4. Mineral proportion pie charts, excluding minor mineral phases (<1%).

3.2 Sample size curve

To reduce the SEM acquisition time, the sample size shall be optimized. For each specific project, a sample size curve (SSC) is calculated. The SSC aims to relate the effect the particle population size has on its distribution, or otherwise stated, how many particles is needed to obtain a definite precision on the proportion measurement. A SSC is computed from a large population of grains in a single sample using a Monte-Carlo simulation. A large number of iterations using a randomly selected number of grains is using to compute the statistics of specific mineral abundance. A relative standard deviation (RSD) is then calculated for different sizes of subsamples, and reported as a SSC (Fig. 5). For small sub sample, RSD is expected to increase due to distribution heterogeneity for constituent phases, or nugget distribution of minor phases. Since different mineral phases have specific size distribution and irregular shapes, their SSC will differ within the same sample and will deviate from idealistic curves. Depend on the project limitations, an acceptable sampling error can be estimated and the acquisition process is optimized. More examples will be presented.

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References


Work index determination using grinding curves obtained through parametric comminution with a conventional shatterbox

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Abstract. Bond (1952) characterized the relationship between the energy required by the ball mill for size reduction, the process feed, and product sizing. His studies lead to increase efficiency of grinding circuits, which directly impact processing costs. Today, Bond’s test is widely used. However, it is lengthy and complex, hence costly, to realise and typically conducted upon a restricted set of sample per project. This study aims to develop a new method of determination of the Bond work index from the data that can be recovered from routine assaying sample preparation. The method enables to characterize the resistance to grinding of lithology for every core sample, which can be used in mine planning. The method is simple: it required to use rocks which Bond work indexes are known with the standard Bond’s test. Then, similar parameters are measured after the selected rocks were grinded with conventional laboratory ring mill. These parameters were deconvolved into equations that allow calculating work indexes. Preliminary findings are encouraging, although specific calibration are needed for each individual projects. Numerical analyses of the results are currently in progress.

1 Introduction

Accurate milling costs estimation is a priority to operate in low grade deposit, since they typically represent the highest operating cost. They are based on the resistance of the material to grinding, and on the efficiency of the circuit for the hardnes of this material. The grinding circuit and its energetic cost need to be studied carefully, since it will determine the overall throughput and efficiency of the entire mill. Operations are typically optimized for a certain work index and throughput, dictated by the power draw of the mill. Processing of harder material leads to a reduction of the throughput and a lower productivity of the beneficiation plan. Processing of softer material leads to increase of throughput, overflow and efficiency loss in the beneficiation plan.

Bond (1952) has established the general relationship between energy required for size reduction, the process feed, and product sizing. Today, Bond’s Test is widely used to design industrial grinding mill circuits.

However, measuring Bond’ work indexes is a long and complex experimental procedure, subject to operating issues. This test is costly, and typically conducted only on a few representative samples per deposit. The current study aim to develop a procedure to calculate the Bond’ work indexes based on measurement obtained from the preparation of core sample with a ring mill. Grain size distributions are measured before and after grinding by ring mill as routine procedure for QAQC in most laboratories. By controlling the operating parameters of the mill (time, mass, …), it shall be feasible to report the grain size reduction to work indexes. Numerical analysis enabled to deconvolve the results into an equation that enable to calculate work index, and to evaluate the effects of the various parameters such as milling time, wearing of the pucks, etc.

The procedure allows to easily calculating the work indexes for every core sample, which can be added to the assays database, resource calculation, block model and mining plan.

2 The Bond’s test

2.1 Definition

The Bond’s test is an experimental procedure which aims to determinate the Bond work index of a rock using a Bond ball mill. This test is a simulation of a dry and locked-cycle grinding circuit which have been entirely established by Bond (1952). The procedure is well recognized in the industry, and regularly used for the sizing of the equipment in grinding circuits.

The Bond mill is a miniature ball mill used in laboratory to estimated Bond’s index with a circulating load of 250%.

Bond’s index is a parameter which expresses the resistance of the material to grinding. It’s defined as the gross energy required in kilowatt-hours per tons of feed needed to reduce a very large feed to such a size that 80% of the undersize passes through 100 µm screen:

\[ W = \frac{W_i}{P} \]

Where :
- \( W \) : Work input in kilowatt-hours per short ton (kWh.t⁻¹)
- \( W_i \) : Bond work index (kWh.t⁻¹)
- \( P \) : Opening of the tested mesh size passing 80% of the last-cycle sieve undersize product (µm)
- \( F \) : Test-sieve mesh size passing 80% of the feed before grinding (µm)
To calculate the work index in laboratory, Bond first derived the equation:

\[
\frac{G}{P_c} = W_i \quad (2)
\]

Where:

- \( G \): Weight of the test-sieve fresh undersize per mill revolution (g.min\(^{-1}\))
- \( P_c \): Test-sieve mesh size (usually 106 µm) (µm)

Then, Bond deduced a revised formula that is currently in use:

\[
W_i = \frac{G}{P_c} \quad (3)
\]

### 2.2 Experimental protocol

The standard Bond’s test was realised according to the procedures describe by Bond (1961), Kaya et al. (2003) and Ahmahi and Shahsavari (2009).

The Bond’s test required first the material to be crushed with a jaw crusher because the test can only be achieved on particle smaller than 3.35 mm. The Bond ball mill used for this study was custom built according to the conventional size required (304.8 x 304.8 mm) defined by Bond himself. The revised formula for \( W_i \) calculation was calibrated for more accurate results. A sieve shaker was also used for determining the grinding distribution in Bond’s tests.

The achievement of the test constitutes several cycles, the end of the test is fixed when the last three cycles reach equilibrium. The test represents a locked-cycle, so the material is firstly crushed, and then sieved. At the end of every cycle, the undersize product is recovered and the oversize product is reinjected in the Bond mill with an amount of fresh feed equivalent to the recovered product (Fig. 1).

![Figure 1. Schematic illustrating Bond’s test as a locked grinding circuit](image)

### 3 Ring Mill test

Many tests have been conducted on a ring mill before defined the experimental procedure of this study. This was required to characterize the variability of this instrument and its capacity of grinding with respect to various input parameters such as time.

Ring mill’s bowls used for the test are RockLabs manganese steel with a nominal capacity between 200 and 250g of material. A laser particle sizer (Fritsch Analysette 22) was also used for determining grain size distribution before and after crushing instead of sieve shaker. This device provides faster results than sieve shaker and is more accurate for estimations on small grain sizes.

The experimental protocol aims to assess grinding capacity of material by ring mill with respect to time. Therefore, seven aliquots of 200g from a same rock were grinded with ring mill for different periods between 15s and ± 4 min. Grain size distribution was determined by laser particle sizer.

### 4 Results

Five different rocks have been tested with a Bond mill and a ring mill: quartz vein, magnetite, calcite marble, granite and limestone. These rocks have known \( W_i \) so they were used to validated the procedure.

### 4.1 Bond’s tests

Table 1 below shows Bond test results with formula (3) calibrated for IOS’s Bond mill. Results obtained agree with \( W_i \) values of similar rocks reported in literature.

**Table 1. Results of Bond tests on selected rocks**

<table>
<thead>
<tr>
<th>Rock</th>
<th>( W_i )</th>
<th>Expected ( W_i )</th>
<th>( P_c ) (µM)</th>
<th>( G ) (G.MIN(^{-1}))</th>
<th>( P ) (µM)</th>
<th>( F ) (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>15</td>
<td>14.4</td>
<td>106</td>
<td>1.14</td>
<td>195</td>
<td>1630</td>
</tr>
<tr>
<td>Magnetite</td>
<td>12</td>
<td>11</td>
<td>106</td>
<td>1.53</td>
<td>220</td>
<td>2325</td>
</tr>
<tr>
<td>Calcite</td>
<td>10</td>
<td>n.d.</td>
<td>106</td>
<td>2.23</td>
<td>215</td>
<td>1190</td>
</tr>
<tr>
<td>Granite</td>
<td>12</td>
<td>9.9</td>
<td>106</td>
<td>1.78</td>
<td>237</td>
<td>1740</td>
</tr>
<tr>
<td>Limestone</td>
<td>10</td>
<td>9.9</td>
<td>106</td>
<td>2.05</td>
<td>200</td>
<td>1220</td>
</tr>
</tbody>
</table>

\(^1\) Weiss (1985)

### 4.2 Ring mill tests

Ring mill grinding of the various samples shows a proportional increase of undersize 106 µm with grinding time. Linear regressions on results are satisfying for all the rocks tested. Figure 2 illustrates the example of Quartz.
Conclusions

Preliminary conclusion of this work suggests that Bond’s work index determination by ring mill test is possible and could be calculated from routine sample grinding for assaying purpose. Parameters from equation (3) in Bond’s test, such as $P_c$, $G$, $P$ and $F$, can be determined in the course of routine grinding, as long as the procedure is parametrized.

At the moment of writing, large amount of data remained to be processed. Preliminary conclusions can be draw and variables can be calculated. $P_c$, which is the test-sieve mesh size, is defined as $106\ \mu m$ for both tests. $F$ is reliant on grain size fresh feed, so it is identical for both tests because same materials were used. The weight of the test-sieve fresh undersize per mill revolution $G$ can effectively be related to results from the ring mill test. As mentioned earlier, grinding by ring mill reaches equilibrium in regards to undersize product generated with respect to time, beyond which no further grain size reduction is gained. Although a universal relation between grain size reductions of the two tests cannot yet be proposed, a case by case relation is achieved. An equation relating Bond’s work index and ring mill results, along with its limitations, is expected to be presented.

It is anticipated that the method would allows calculating a hardness proxy for every assayed sample in the course of resource definition. In project where hardness has been defined as a critical parameter, it would be then possible to integrate this value to the geometallurgical model to forecast the behavior of every single mining block in the milling circuit.

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References


Figure 2. Relation between volume % at -106 µm with grinding time for quartz samples.

$y = 14.943x + 59.303$
$R^2 = 0.9937$
Sample selection based on predefined multivariate geochemical domains

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Abstract. An important aspect that deserves attention in the development of any experimental work is the sampling strategy. Assuring statistical robustness for accurate representation during sample selection is an aspect sometimes neglected in mining operations. There has been considerable development on the theory behind sampling, although without the mining industry fully embracing it in practical terms. The present paper provides an alternative sample selection method developed for implementation into an industrial minerals mining operation based on previously defined geochemical domains.

1 Introduction

The Nabbaren is a nepheline syenite deposit, located on the Stjernøy island in the Seiland petrographic province, in western Finnmark County, northern Norway. The deposit has an area ca. 13 km², and it is exploited for its content of nepheline and K-feldspar, with 34 wt.% and 56 wt.%, respectively (Geis 1979; Heier 1961).

For planning and production purposes, the raw material is categorized into four material qualities. These are based on concentrate geochemical composition and recovery after magnetic separation through lab testing. This categorization has been taken into consideration when the deposit is divided into geochemical domains, which are further used in plant feed blending strategies. These domains are volumes distributed throughout the deposit where each quality can be found.

Although suitable for the present mining and beneficiation strategy of the company, the current categorization presents an issue due to overlapping geochemical intervals and a qualitative differentiation between the relevance level of certain characteristics over others (i.e. primary vs. secondary characteristics), making material definition subjective.

2 Objective

The aim of this poster is to present an alternative method to discretize material qualities based on the geochemistry of the concentrate produced in the laboratory. This method can be sub-divided into two parts: (a) the implementation of a scoring system for characteristic relevance, based on the same geochemical composition and magnetic separation recovery criteria currently used, and (b) sample selection based on statistical differentiation to avoid the selection of outliers.

The application of this alternative methodology will help reduce the current subjectivity that is present during sample definition. In addition, it offers fast-tracked and statistically robust sample selection.

3 Alternative selection method

The method uses a scoring system to quantify the primary and secondary criteria based on weight factors. The factors will define a point where material qualities do not show any further change in their basic statistics (e.g. constant number of samples, and constant mean, median, standard deviation, etc. over the criteria defined). That point is observed when different factors are applied during classification. Once the point is settled, then samples are ready for selection.

The selection requires basic statistic tools (e.g. Mcgill et al. 1978) applied to every criterion defined for each material quality. Each criterion is selected from a certain confidence range (i.e. between 25 and 75% quantiles), to avoid outliers. When a criterion is located within the respective range, it will be considered within specification, in the opposite case it will be outside specification.

Finally, when the number of criteria within specification are higher than the ones outside, then the data set will be considered as eligible for sample selection and further work, whilst the ones outside will not.

The method it based on tools available in Leapfrog Geo v4.0 and ioGAS v6.2.1 software.
The poster will present and discuss the results from the implementation of this methodology in the Stjernøy deposit.

References
