MINERAL RESOURCES TO DISCOVER

Proceedings

Volume 1
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Mineral Resources to Discover
Proceedings
Volume 1
The 14th SGA Biennial Meeting is jointly organized by the Université Laval, Natural Ressources Canada (Geological Survey of Canada), the Ministère de l’Énergie et des Ressources naturelles du Québec, and the Institut national de la Recherche scientifique, Centre Eau Terre Environnement.

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**Set of 4 volumes**
Layout: Patrick Mercier-Langevin GSC
Claude Dion, André Tremblay MERN

Cover photograph: Visible gold at the Meadowbank gold mine, Nunavut, Canada (photo: B. Dubé, Geological Survey of Canada)
FOREWORD

It is with great pride that we welcome fellow mineral deposit geologists of the world to the 14th SGA Biennial Meeting, in Québec City, Canada, 20-23 August 2017. For the fourteenth edition of its biennial meetings, the SGA comes to North America for the first time, and more specifically to the oldest city on the continent, where French explorers established their first settlement in 1608. A World Heritage Site, Québec is a vibrant North American city that preserved a strong European heritage. In addition to being the capital of the Province of Québec, it is a very dynamic cultural, political, scientific and industrial center with a diversified economy, numerous research centers and two universities, and a constantly evolving high technology sector.

The Organizing Committee is particularly pleased to present you with an outstanding scientific program that comprises four symposia and 12 sessions, which are linked with short courses and field trips to famous mineral districts and regions from Northern Québec to Guiana. The scientific program includes cutting-edge research on major deposit types, from base to precious and high-technology metals, large scale geological processes to high precision laboratory techniques and experiments, and governmental geoscience programs roles and impacts in exploration to the acceptability of mineral resources development.

The SGA Québec 2017 meeting “Mineral Resources to Discover” is organized by dedicated volunteers from Université Laval, the Geological Survey of Canada, the Ministère de l’Énergie et des Ressources naturelles du Québec, the Institut national de la recherche scientifique– Centre Eau Terre Environnement (INRS-ETE), the DIVEX network, and Québec Business Destination. The SGA Québec 2017 wholeheartedly thanks its very generous partners for their support.

Welcome to Québec and enjoy a most interesting SGA Biennial Meeting!

Georges Beaudoin

Chair, SGA Québec 2017
The biennial meetings of the Society for Geology Applied to Mineral Deposits (SGA) are known for the high-level science that is being presented at each edition. For the 14th edition, the objective of the SGA Québec 2017 Scientific Program Committee was to be in that continuity. To achieve that, a program of global interest aligned with currently relevant topics for the scientific community as well as for industry was designed. The SGA meeting is held in North America for the first time and the program has a Canadian flavor with an emphasis on major precious and base metal deposits found in the broad spectrum of geologic settings present in Canada and that are present elsewhere. The program also includes a diversity of subjects that are related to mineral deposits, from exploration to production, through processing and social aspects. The 14th SGA Biennial Meeting is also the opportunity to recognize the work of some of our colleagues; two symposia are dedicated to scientists whose research is responsible for major advances in our understanding of ore-forming processes, and we have an amazing list of keynote presenters.

One of the key elements of the SGA biennial meeting are the Proceedings. The SGA Conference Papers represent lasting contributions that hold highly valuable and concise science. These Conference Papers necessitate a lot of work, first and foremost by the authors, but also by dedicated reviewers and editors. For the 14th edition, that represents over four hundred Conference Papers totalling over 1,500 pages.

The Scientific Program Committee most sincerely acknowledges all the authors and their co-authors for their contributions. We thank the symposia and sessions convenors who spent countless efforts to invite and convince colleagues and speakers to use SGA as an international platform to share their state-of-the-art research and knowledge. These convenors have taken great care reviewing Conference Papers and selecting over two hundred oral presentations, which includes over twenty keynotes, and about two hundred posters. We are grateful to the other members of Local Organizing Committee for the help and support in building the scientific program. Finally, we want to express our gratitude to Conférium, and its devoted staff for their work in preparing the 14th SGA Biennial Meeting scientific program.

Although it is becoming increasingly difficult to travel for conferences for many of us, events such as the SGA biennial meetings are prime opportunities to share knowledge, innovative ideas and data. This allows us to continuously improve geological and metallogenic models, and very importantly, to contribute at developing the next generation of geoscientists and explorationists. Scientific conferences remain essential in making our science move forward and in making it available to the scientific community and the industry. In light of this, we sincerely hope that the SGA Québec 2017 will represent, for all participants, a very rewarding experience.

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A symposium to recognize the work of A.E. Williams-Jones
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+ Marc Bardoux – Barrick Gold
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+ Christopher J.M. Lawley – Geological Survey of Canada

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Symposium SY01 - Gold through time and space

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Gold through time and space

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Abstract. The formation of gold deposits throughout Earth’s history has been highly episodic and focused on specific tectonic positions. It reflects fundamental changes in environmental conditions, biological evolution and styles of large-scale tectonism. Most of the known gold was first concentrated in the continental crust during a gold mega-event at 2.9 Ga in response to the emergence of photosynthesizing microbes under a reducing atmosphere. This provided the source of the richest, 2.9-2.7 Ga gold palaeoplacers and an overall Au-enrichment in marine sediments. Only after these gold-rich sediments had been subducted in places did the formation of larger orogenic, and eventually porphyry-type and epithermal gold as well as other gold deposits become possible. This explains the principal peak in orogenic gold deposits at 2.75 – 2.55 Ga. After the Archaean time sedimentary processes played a progressively diminishing role as the Mesoproterozoic placers became more and more eroded or buried, and hydrothermal and magmatic processes, driven by subduction and hydration of subcontinental lithospheric mantle, took over as major engines for the formation of larger gold deposits, predominantly along active plate boundaries.

1 Significance of gold deposit types

In today’s upper continental crustal rocks Au is present at uneconomic background levels of some 1.5 ppb but locally it is concentrated to ore grade with enrichment factors on the order of $10^3$ to $10^4$. The geological processes behind this extreme enrichment are manifold, giving rise to a great variety of different gold deposit types, which range in terms of genesis from magmatic to hydrothermal, metamorphic and sedimentary. The relative significance of the various gold-concentrating processes changed dramatically over Earth’s history and strongly varies between different (plate) tectonic settings.

In spite of the great variety in gold deposit types, there are essentially only three settings that account for close to 90 % of all known gold that is (or has been) concentrated in gold deposits (past production plus known resources): (i) syn-orogenic vein-type deposits that formed at deeper crustal levels of c. 5-15 km in collisional tectonic settings (c. 30 % of known gold), porphyry-related and epithermal gold deposits at shallower crustal levels in supra-subduction settings (c. 28 %), and (ii) conglomerate-hosted deposits of the Witwatersrand-type (c. 30 %). With most workers agreeing on a palaeoplacer origin of the latter (Frimmel et al. 2005), the question arises as to the primary source of this evidently mechanically reworked gold. If Carlin-type deposits, which account for some 4 % of total known gold, are considered as well, active plate margins become the by far most productive areas, having contributed probably >80 % of known gold in primary, hypogene gold deposits.

2 Secular variation in gold deposit formation

2.1 Orogenic gold

A strong correlation between the timing of mesozonal shear zone-hosted vein-type gold deposits, be it in siliciclastic rocks, banded iron formation or greenstones, and times of widespread orogeny has long been known (Goldfarb et al. 2001; 2005) – hence the term “orogenic gold”. Main peaks in the age of orogenic gold deposits are at 2.75-2.55 Ga, around 2.0 and 1.8 Ga, and between 0.6 and 0.05 Ga (Fig. 1). These relate to the formation of supercontinents, i.e. Kenorland, Columbia, Gondwana and Pangaea, respectively, as reflected by peaks in the number of corresponding U-Pb zircon ages. Only the formation of Rodinia is not reflected by an abundance of orogenic gold deposits.

It has been suggested that large orogenic gold deposits tend to form in crustal domains that are underlain by subducted lithosphere and a thin sub-continental lithospheric mantle, i.e., in areas with a short pre-mineralization crustal history (Bierlein et al. 2006). In this context a lack of correlation between age of orogenic gold deposits and juvenile crust formation as derived from Lu-Hf isotope data on zircon grains (Belousova et al. 2010) is noteworthy. Effectively no orogenic gold deposits are known from the times of highest rates of juvenile crust formation, i.e., from 4 to 3 Ga (with the exception of a very minor contribution at 3.04-3.08 Ga from the Barberton greenstone belt). This may be reflect not only the poor preservation of such old rocks but also a lack of subduction zones at that time when plate tectonics had not begun to operate on a large scale. Even if the source of Au and S to form orogenic gold deposits is assumed in pyrite-bound gold within pre-existing, mainly sedimentary, rocks, the dynamics and flow paths of regional metamorphic fluids released from rocks by vertical rather than horizontal (plate) tectonic processes would have been markedly different and not as amenable to form orogenic gold deposits.

2.2 Porphyry and epithermal gold

Porphyry and related epithermal gold deposits are largely restricted to the Phanerozoic Aeon with most of the known
deposits being not older than 100 Ma (Seedorf et al. 2005); only a few Proterozoic examples are known (Dubé et al. 1998). This is largely due to the low preservation potential of shallow crustal rocks in topographic highs, such as an Andean-type mountain belt. Places like Boddington in Western Australia might attest to porphyry-style mineralization having taken place as early as in Neoarchaeon times. The genetic link between subduction of oceanic crust and the formation of porphyry and epithermal deposits has been well-established. Release of volatiles and a series of metal compounds in the course of progressive metamorphism of the subducting slab typically leads to metasomatism of the overlying mantle wedge, partial melting of that mantle and associated metal flux from there into newly formed continental crust on top. Consequently, the maximum possible age for this type of mineralization is limited to the time after the change from predominantly vertical to horizontal tectonics, i.e., to the time after the onset of plate tectonics, which is believed to have been around 3.0 Ga (Shirey & Richardson 2011).

2.3 Witwatersrand-type gold

By far the largest amount of conglomerate-hosted gold has been mined from 2.90-2.71 Ga deposits in the Witwatersrand of South Africa, which alone accounts for almost one third of all known gold. Conglomerate-hosted gold mineralization is by no means restricted to the Witwatersrand Basin but is a style of mineralization observed on almost all cratons and is common to many siliciclastic successions that developed on Archaean to Palaeoproterozoic basement. The gold endowment is, however, highly variable. Although comparable conglomerates that are >2.9 Ga old exist, they contain orders of magnitude less gold. Globally, the time span 2.9-2.7 Ga seems to be exceptional in terms of gold concentration in fluvial to fluvio-deltaic conglomerates (Fig. 1). From 2.7 Ga the gold potential in this kind of deposit diminishes progressively. While economic deposits are known from the time interval 2.6-2.1 Ga, their total gold content pales in comparison to their older equivalents. Conglomerate-hosted gold deposits younger than 1.8 Ga are, in comparison, insignificant. A further apparent peak in placer gold formation in the Cenozoic (Fig. 1) is essentially a function of preservation potential and tells little about temporal changes in placer-forming processes.

3 Onset of the crustal gold cycle

From the above it becomes obvious that the by far largest concentration of gold into the continental crust took place between 2.9 and 2.7 Ga in the form of Witwatersrand-type deposits prior to the first peak in the formation of other gold deposit types (Fig. 1). This raises the question as to the source of all the gold that is concentrated in Witwatersrand and equivalent deposits elsewhere.

It may be argued that orogenic gold deposits had been widespread prior to 2.9 Ga but have since been eroded, with the Barberton greenstone-hosted gold representing a minor remnant. Such an orogenic gold source for the Witwatersrand deposits can be excluded, however, for several reasons (Frimmel 2014): (i) the spatial density of orogenic gold deposits in the source area of the Witwatersrand sediments had to be unrealistically high in order to explain the huge amount (estimated 90,000 t) of (detrital) gold in the Witwatersrand sediments; (ii) a remarkable lack of proper gold nuggets in the Witwatersrand ores and inclusions of primary gold within detrital quartz clasts that could be derived from an orogenic gold source; and (iii) a mismatch in the chemical composition between Witwatersrand gold and Barberton greenstone-hosted gold. Most notably, extremely high Os contents in Witwatersrand gold are at odds with a hydrothermal provenance and in stark contrast to the composition known from orogenic gold (including that from Barberton).

Figure 1. Temporal distribution of orogenic (grey) and Witwatersrand-type (yellow) gold deposits (modified and updated after Goldfarb et al. 2005) in comparison with number of U-Pb zircon ages as proxy of continental crustal growth and proportion of juvenile crust (from Belousova et al. 2010).

Porphyry-type mineralization should not have occurred at any significant level prior to 2.9 Ga. Consequently,
neither of the major hypogene gold deposit types could play a critical role as potential source of the huge amounts of syn-sedimentary gold in 2.9-2.7 Ga deposits and some alternative source is called for. For mass balance reasons, erosion of discrete Palaeo- to Mesoarchaean gold deposits of whatever type is unlikely to explain the palaeoplacer gold accumulation. Instead, mobilisation of background gold concentrations by pervasive leaching of huge rock volumes appears as only reasonable process to explain the extraordinary amount of Witwatersrand-type gold, provided a suitable trapping mechanism can be invoked.

Leaching of underlying rock successions by metamorphic fluids with subsequent deposition of gold in the conglomerates due to local redox gradients has been suggested (Phillips & Powell 2011). This hypothesis, which follows essentially an orogenic model, does not explain, however, the plentiful evidence of syn-sedimentary gold mineralization (e.g. presence of micro-nuggets defining together with other heavy minerals delicate sedimentary structures), the geometry of the stratiform ore bodies (which display the exact opposite of what is typically observed in orogenic deposits), and the chemistry of the gold (high Os content in contrast to very low Os content typical of gold transported by aqueous hydrothermal fluids), to name but a few.

To account for the syn-sedimentary timing of Witwatersrand-type gold mineralization and the conspicuous spatial association between gold and biogenic kerogen mats on 2.90 Ga palaeoerosion surfaces, it has been suggested that the first major concentration of gold in crustal rocks was achieved by microbially mediated fixation of gold from Mesoarchaean river and possibly also seawater (Frimmel 2014; Frimmel & Hennigh 2015, Heinrich 2015). According to this genetic model, intense chemical weathering under an acidic, reducing Mesoarchaean atmosphere efficiently leached background concentrations of Au from the Archaean basement rocks. The modelled composition of contemporaneous meteoric water implies Au solubility that was four orders of magnitude higher than in modern meteoric water, from which a very high fluvial Au flux off the Mesoarchaean land surface can be deduced (Fig. 2). Local oxidation on the surface of first oxygenic photosynthesizers (cyanobacteria), which had emerged by 2.9 Ga, provided the chemical trap for the precipitation of gold from the Archaean surface waters. This process was likely to have taken place along the margins of all Mesoarchaean land masses, be it on temporarily flooded river banks in braided river systems, estuaries, lagoons or in adjacent shallow-marine settings (Fig. 2). The preservation potential of these first concentrations of gold on probably cyanobacterial mats was extremely low because any subsequent transgressive event would invariably have led to the erosion of the delicate mats and the re-deposition of the gold therein as very fine-grained detrital gold. This microbially mediated concentration of gold on sedimentary surfaces was only possible over a restricted time span in the Mesoarchaean, when the evolution of life and that of the atmosphere and the hydrosphere played together to provide suitable conditions for what must have been the by far greatest gold event in Earth’s history at around 2.9 Ga.

4 Reworking of gold after 2.9 Ga

Much of the microbially fixed 2.9 Ga gold soon became reworked by sedimentary processes into placer deposits that are marked by small grain size of the detrital gold particles – a common phenomenon in gold deposits of the Kaapvaal Craton younger than 2.9 Ga (e.g., c. 2.8 Ga reefs in the upper Central Rand Group, Witwatersrand Supergroup, 2.71 Ga Venterspol Contact Reef, Venterdorp Supergroup, 2.66 Ga Black Reef, base of Transvaal Supergroup). Elsewhere the gold-rich sediments eventually became reworked tectonically, facilitated by the onset of plate tectonics, and recycled into the subcontinental lithospheric mantle only to provide sources for later Au-rich melts and fluids to ascend into newly formed continental crust. Thus, with a delay of some 150-350 million years, first orogenic gold deposits could form, leading to the main peak in orogenic gold formation at 2.75-2.55 Ga. From then onwards, orogenic gold deposits were available as potential source of younger palaeoplacer gold deposits, such as 2.76 Ga deposits in the Fortescue Group of the Pilbara Craton, the 2.65 Ga Moeda Formation in the Sào Francisco Craton, 2.45 Ga deposits in the lower Huronian Supergroup of the Superior Province, the >2.4 Ga Jacobina deposit and 1.90 Ga occurrences in the Roraima Supergroup in the Amazon-São Luis Craton, or the 2.10 Ga Tarkwa deposit in the West African Craton.

By Palaeoproterozoic times, the 2.9 Ga gold-rich microbial mats had been either eroded or covered by younger deposits and thus were not available anymore as source for the accumulation of younger palaeoplacers, effectively heralding the end of large gold palaeoplacer
deposition. This provides one explanation for the huge difference in gold endowment between the 2.9-2.7 Ga Witwatersrand reefs and the various other, younger conglomerate-hosted gold deposits elsewhere.

With plate tectonics having become the principal driving force shaping the Earth’s crust since Neoarchaean times, the concentration of gold into ore grade was achieved less and less by mechanical, sedimentary reworking on the surface but more and more by redistribution through hydrothermal fluids and melts from mantle domains above subduction zones. This repeated recycling of gold in the subduction factory is well reflected by the gold chemistry, specifically its Os contents. Any recycling of gold by an aqueous hydrothermal fluid should lead to a loss in Os because of the extremely low solubility of that metal in most geological fluids. The oldest (Witwatersrand) gold is highly enriched in Os (on the order of 1-100 ppb, higher values reported by Kirk et al., 2002, are most likely due to contamination with osmiridium grains), whereas younger, hydrothermal gold (be it from its primary position or as reworked placer gold) typically contains orders of magnitude less Os (0.01-0.1 ppb). The comparatively juvenile hydrothermal golds are slightly enriched in Os (0.01-0.1 ppb). The comparatively juvenile hydrothermal golds are slightly enriched in Os (0.01-0.1 ppb). The comparatively juvenile hydrothermal golds are slightly enriched in Os (0.01-0.1 ppb).

The lack of larger Eoarchaean and Palaeoarchaean gold deposits is not just a function of the poor preservation of such ancient rocks but also due to paucity in gold-concentrating processes at that time. The latter may be due to a lack of a suitable gold source in the mantle from which the first continental crust fractionated. Any gold that might have been present in the mantle after maybe incomplete core-mantle fractionation or that might have been added by meteorites during the heavy bombardment phase ("late veneer hypothesis") would have been available for extraction from the mantle into continental crust only after some delay determined by the rate of mantle convection. Effective leaching of possibly elevated background Au concentrations in a deeply weathered Archaean continental crust enabled a high Au flux off the Archaean land surface by meteoric waters. Coseval emergence of first larger photosynthesizing microbial colonies at around 2.9 Ga made it possible to bind much of this gold. Thus, the greatest portion of crustal gold became concentrated in the sedimentary environment, where repeated mechanical reworking led to the formation of rich palaeoplacer deposits, mainly at 2.9-2.7 Ga. Gold flux back into the upper mantle – the source region of subsequent orogenic and porphyry-related gold, became possible only when Mesoarchaean gold-rich marine sediments began to be subducted in places. This led to the first and major peak in orogenic gold formation at 2.75-2.55 Ga. Subsequently, the sedimentary gold disappeared rapidly as potential source for crustal-scale gold recycling, and hydrothermal and magmatic processes became the dominant drivers to concentrate the precious metal into deposits at upper crustal levels.

5 Conclusions


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References


Gold deposits in metamorphic rocks—what we do know and what still confuses us in 2017

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Abstract. The descriptive deposit model for gold deposits in metamorphic rocks, or orogenic gold, has been well established for the past two to three decades. Nevertheless, particularly with development of many giant sub-gram, high-tonnage orebodies, as well as with the collection of new microanalytical data on minerals and fluids, the genetic deposit model seems to have grown more controversial, with numerous theories on fluid and metal sources and ore deposition. Despite this, a crustal metamorphic model for fluids and metals is most consistent with all geological, geochemical, and geochronological data. The tectonic trigger for the required thermal anomaly can be quite varied between different orogens, and ore-related materials may be sourced from the middle and upper crust, or even deeply subducted crust.

1 Introduction—How we got here

One century ago, gold ores were universally related to magmatic events and the ores were classified as epithermal, mesothermal, or hypothermal, based upon their mineralogy and thus P-T formational conditions (Lindgren 1933). This led to most gold deposits in metamorphic terranes being classified as mesothermal (200-300°C, 1.2-3.6 km) and hypothermal deposit (300-600°C, 3.6-15 km) types. Thus, what we now recognize as gold-rich VMS and orogenic gold deposits were lumped together as deposit types and orogenic gold deposits with different mineralization styles were split into two different deposit types (mesothermal and hypothermal). New classifications of gold deposits developed in the 1960s and 1970s were based on mineralization style or host rock type (Boyle 1979). Thus, types of deposits included examples that defined Witwatersrand and Alaska-Juneau as disseminated replacement deposits, Hollinger-McIntyre and Cripple Creek as fissure vein cavity fillings, and Yilgarn and Nevada deposits as lodes in volcanic environments.

The 1980s began with volumes and conferences on gold deposit types such as Greenstone Gold, BIF Gold, and Turbidite-hosted Gold, continuing with the ideas that different metamorphosed lithologies hosted different gold deposit types. At the same time, the significance of metamorphic fluids in gold ore formation was beginning to be recognized (Fyfe et al. 1978) and widely applied to Precambrian (Kerrich and Fyfe 1981) and Phanerozoic (Henley et al. 1976) provinces. This type of gold ore formation from metamorphic fluids was universally related to continental margin deformational events, an idea first applied to both Precambrian and Phanerozoic environments by Sawkins (1972) during the infancy of our understanding of plate tectonics. A unifying term of orogenic gold for these gold deposits in all types of metamorphic rocks was coined by Bohlke (1981), who pointed out the mesothermal and hypothermal settings, the syn- to post-orogenic timing, the variable mineralization styles, the Au-Sb-Hg association first addressed by Lindgren (1933), and the lack of such ores throughout much of the Proterozoic.

Exclusive of the unique Witwatersrand deposits, probably more than one half of the recognized global gold endowment (past production+reserves+resources) is associated with orogenic gold, particularly when we also consider the related placers. Among the world’s top gold producers, including countries such as China, Australia, Russia, Canada, and those of West Africa and Central Asia, orogenic gold deposits are the critical exploration targets. Descriptive comprehensive ore deposit models for these deposits are now well established (e.g., Groves et al. 1998) but, particularly as we develop more low-grade and high-tonnage resources, we are getting more diversity in genetic models and even more confused as to what is an orogenic gold deposit and what is not.

2 Changing definition of orogenic gold?

During the past 25 years, what is mined as “orogenic gold” has changed. Historically, orogenic gold deposits were structurally controlled quartz-carbonate veins associated with large-scale compressional to transpressional faults and characterized by carbonate alteration footprints and relatively high grades, commonly ≥5 g/t Au, which were mined by underground operations. The largest deposits, mainly of Archean age, had yielded a few hundred tonnes of gold up through the 1970s and prior to the onset of large-scale open pit mining. In recent years, however, many new developments have started up as lower grade, bulk minable deposits with resources >500-1000 t Au. The largest single gold deposit in Brazil, Paracatu, contains 450 t Au at an average grade of just 0.4 g/t gold. What we now consider ore would have been nothing more than a distal geochemical anomaly just a few decades ago. Furthermore, we now commonly mine orogenic gold at grades and tonnages that are common for gold-rich porphyry deposits, but historically did not characterize orogenic gold (Goldfarb and Groves 2015).

There are multiple reasons for this change in target definition, a change that has led to much of the confusion in recent literature. The higher price of gold has allowed development of lower-grade ores. Some are greenfield
developments, but many are in areas where high-grade ore has already been mined and large volumes of low-grade altered rocks could represent interesting present-day targets. But issues of sustainability, particularly regarding the environment, society, and perception, now play a much larger role. The cost of meeting all requirements for sustainable development is now great and may preclude development of small-scale operations. Even new world-class discoveries of significant tonnage, such as in remote parts to Alaska, may not move forward, whereas in areas such as Sonora, Mexico, with favorable infrastructure and an arid climate, large-tonnage sub-grab open pit operations developing orogenic gold are more economic.

Many of these low-grade deposits are dominated by highly disseminated ores that don’t look like classic orogenic gold deposit lodes. These disseminated ores may be part of the alteration footprint to historically mined high-grade orebodies, or present within disseminated sulfide grains surrounding high-grade veins or replacements yet to be discovered. More than 150 t Au, for example, were historically mined at Canadian Malartic from high-grade stockworks, breccias, and veins in graywacke, diorite, and porphyritic intrusions along a 2nd-order structure to the Larder Lake-Cadillac fault zone (De Souza et al. 2015). But presently more than 300 t Au of ore averaging 0.97 g/t is being recovered from the Canadian Malartic Mine open pit, with the majority being the lower grade footprint to the historically mined ores. Up to 30% of the new resource is porphyry-style mineralization associated with the ca. 2678 Ma porphries, whereas the bulk of the gold mineralization is associated with faults, shears, and high-strain zones. Although sometimes classified as an “intrusion-related gold deposit”, the main characteristics of the Canadian Malartic deposit are best explained by ca. 2670–2660 Ma orogenic gold superimposed onto a pre-existing gold-bearing magmatic/hydrothermal intrusion-related system (De Souza et al. 2015).

3 What new are we learning about the ore-forming fluids?

Much of what we learned about the ore-forming fluids for orogenic gold came from an explosion of fluid inclusion and stable isotope data collected from workers in numerous global gold provinces in the 1980s and 1990s. It seems we now know there is a common geochemical signature to expect for most deposits in all ages of metamorphic rocks, but interpretations of the meaning of such data commonly remains controversial and not definitive of a particular genesis (Goldfarb and Groves 2015). In fact, as we have developed new micro-analytical techniques during the past decades and applied new isotope systems to our studies of orogenic gold deposits, we simply have become more confused as to what these new data are really telling us.

There is little question that most orogenic gold deposits form from an aqueous-carbonic, relatively reduced, low to moderate salinity ore fluid with gold-hydrosulfide complexing. In a few orogenic gold districts, particularly some in West Africa, ore fluids are characterized by CO$_2$>>H$_2$O (e.g., Schmidt Mumm et al. 1997), in contrast to most provinces where ore fluids never exceed about XCO$_2$=0.2-0.3. This could reflect a high degree of fluid unmixing during gold deposition, but why just in West Africa and a few other locations? Alternatively, this could reflect the exceptional amount of devolatilized carbonaceous material within the sedimentary basinal rocks of the Man-Leo Shield (Goldfarb et al. 2017). In cases where CO$_2$ tends to be lacking in reported fluid inclusion studies of orogenic gold, it is possible the small size of inclusions prevented microscopic observation of clathrate during freezing experiments. Significant carbonate alteration surrounding orebodies indicates a C-bearing fluid even when CO$_2$ is not observed. Alternatively, the dominance of secondary fluid inclusions commonly leads to studies where workers may be examining fluids that have nothing to do with ore formation. Unlike other types of gold deposits formed at shallower depths, orogenic gold deposits form in zones of structural complexity at relatively great depths and such structures are reworked during tens of millions of years of unroofing. Identification of fluid inclusions of many different types trapped post ore deposition, some solely aqueous and others with very high salinities, has led to models that argue for the importance of fluid mixing or a variety of overprinting gold events but lack strong support when looking at the big picture.

It is also clear that orogenic gold deposits form from a fluid with consistently high $\delta^{18}$O values and $\delta^{34}$S and $\delta^{15}$N that vary with age of host terranes. Recently $\Delta^{33}$S has been suggested as a tracer for ore-related S, but Wyman et al. (2016) have shown interpretations of such data are problematic. Hydrogen isotope and noble gas data are typically obtained from bulk extraction of fluid inclusion waters from many generations of fluid inclusion waters, and thus may yield data that tells us little about fluid source areas. Furthermore, even when noble gas data are reliable, we tend to be looking at gold deposits that form along regional deep crustal fault systems. During their lifetime, these faults can tap, for example, both gases from the mantle and fluids and metals from elsewhere, and therefore the signature of noble gases may not relate to the ore-forming components. In the past decade, the economic geology literature has been filled with papers on trace element data related to gold concentrations in solid solution in ore-related pyrite from orogenic gold deposits. The value of these data is also questionable given that this refractory gold is typically not the ore and the gold that is going to the mill is not what is being studied.

Although the nature of the ore-depositing fluid is known, not only do sources remain debated, but the precipitation mechanism(s) for gold in these high- $\delta^{18}$O, aqueous-carbonic fluids are still debated. It is difficult to see temperature playing a significant role because of the obvious lack of mineral zoning over locally 2-3 km depth.
Huge pressure fluctuations are inherent to orogenic gold deposits and such changes may lead to extensive decreases in silica solubility and quartz deposition, although not significantly affecting gold solubility. However, associated changes in parameters such as fO₂ and pH would destabilize gold, as well as sulfidation of pre-existing material. Many workers try to relate gold deposition to a single cause, but most likely there are a number of interrelated causes that form the economic orebodies. Unlike many magmatic type deposits, orogenic gold ores form via multiple, perhaps hundreds, of pulses of fluid flow during millions of years of seismic events (e.g., Sibson et al. 1988) and thus even paragenesis is difficult to fully define. In many deposits, gold rich rims on sulfides, or gold-filled cracks in quartz or sulfides, suggests gold is relatively late. It is possible that early hydrothermal minerals provide sites of redox change that precipitate gold, sometimes prior to another pulse of quartz vein deposition in ribbon style veins.

4 Is there one genetic model?

A metamorphic source within the crust is now widely accepted for the ore-forming fluids for most orogenic gold systems with more detailed understanding of the fluid-forming process provided by workers such as Phillips and Powell (2010) and Tomkins (2010). Such work shows that prograde metamorphism of oceanic rocks will inherently form a fluid identical to that recognized within orogenic gold deposits. Syngenetic to diagenetic pyrite within such rocks, particularly where significant carbonaceous matter, provides the necessary sulfur to carry the Au, As, Sb, and (or) Hg that are associated with base metal-poor mineral occurrences derived from aqueous-carbonic fluids. Importantly, Tomkins (2010) showed how the concurrent breakdown of chlorite and pyrite as metamorphic temperatures reach upper greenschist to lower amphibolite temperatures was an essential part to the model.

Gold and other metals, present in high background concentrations in the diagenetic sulfides, complex with the sulfur and enter the ore-forming fluid, essentially a normal part of the Barrovian metamorphic process. Pitcairn et al. (2006) have documented in the Otago Schists how metasedimentary rocks are depleted in ore metals in deeper crustal levels that reached highest metamorphic grades. Recently Cave et al. (2016) working in the same rocks have shown how W, also common in orogenic gold lodes, is released during conversion of detrital rutile to titanite and thus also concentrated in many typical crustal metamorphic fluids. This supportive trace metal information for a crustal model of ore formation has been focused on Phanerozoic metasedimentary-dominant environments. The process is still uncertain for the metavolcanic-dominant Precambrian cratons. Some workers argue that limited carbonaceous metasedimentary sequences in the volcanic piles are a required fluid and metal source, whereas other studies favor devolatilization of seafloor-altered metavolcanic rocks.

Whereas it is difficult to argue against such undeniable data that show metamorphism of crustal rocks produces the fluid we observe to form orogenic gold, there is no single model that can be universally applied. Every orogenic belt and every regional metamorphic sequence have their own histories, and such histories vary based on many broad-scale tectonic controls. Thus, solely in the Alaskan part of the North American Cordillera, it has been shown that models may involve crustal heating and metamorphism due to crustal thickening, crustal thinning, or spreading ridge subduction (Goldfarb et al. 2005), with gold deposition on retrograde P-T paths. In the Precambrian, thermal events on the hotter Earth are less well understood and a number of important deposits have been overprinted by post-ore metamorphism, although the overall global significance of such seems limited (Kolb et al. 2015). But province or district models for older orogenic gold deposits are difficult to establish without still some doubt. In eastern China, Cretaceous orogenic gold is hosted by high-grade metamorphic Archean terranes, suggesting a model where the most likely fluid and metal source must be devolatilization of the subducting paleo-Pacific slab prior to reaching melt temperatures (Goldfarb and Santosh 2014).

It is also not clear whether any deposits defined as orogenic gold formed from a magmatic-hydrothermal fluid or a non-crustal fluid. Many deposits one might classify as orogenic have been classified as intrusion-related, but such a deposit type lacks definition. Intrusion-related gold deposits, as suggested by Sillitoe (1991), are not a deposit type, but rather a group of magmatic-hydrothermal deposit types, such as porphyries, skarns, replacement deposits, etc., that have a genetic association with typically oxidized intrusions. A deposit type, however, that has become popular is the reduced intrusion-related gold deposit (Hart et al. 2002), but these are rare, low-grade Au targets, and not commonly spatially associated with most deposits that resemble orogenic gold and have been called “intrusion-related”. Whether a group of magmatic-hydrothermal deposits may form at depth from aqueous-carbonic fluids, and show features similar to orrogenic gold and much different than deep porphyry ores, is far from certain and requires study to discriminate such gold systems. In addition, whether a relatively direct mantle contribution is required is also not clear. Hronsky et al. (2012) stressed the possible importance of fertilized subcontinental lithospheric mantle in formation of orogenic gold. But the fact that the orogenic gold deposits of the North American Cordillera lack any ancient North America material at depth, and solely subducted oceanic rocks, indicates such a non-crustal source for gold, if valid, is definitely not a necessity.

5 What makes the giants?

Explorationists are always seeking signs of what might define the location of a giant orogenic gold deposit or district, which could make or break a company during its
targeting program. As noted by Phillips et al. (1996), the key may be locating an area with a conjunction of a series of critical factors that relate to favorable source, plumbing system, and (or) trap. For orogenic gold, the greater the complexity and contrasts between units, the more favorable the environment for a giant deposit. There is no consistent spatial or compositional association of orogenic gold with magmatism and, as noted above, many different types of thermal events can trigger the metamorphism of crustal rocks. Groves et al. (2016) note that keys for exploring for orogenic giants will include (1) presence of lithoscale structures commonly major sutures; (2) geometrically complex systems of lower-order pre-existing fault systems; (3) uplift, likely triggered by changing stress on the main faults, causing fluid pressure to rise relative to overburden pressure; and (4) rheological contrasts leading to strain gradients and (or) chemical traps.

Observations from some giant orogenic gold deposits and provinces may suggest specific examples of the type of parameters to look for. At Muruntau, the world’s largest orogenic gold deposit, a series of anomalies may help to explain the massive flow system. First, Muruntau and a series of adjacent deposits are localized along 2nd-order faults to an immense obvious jog on the continental scale South Tien Shan fault system. Second, local workers have long reported a very high gold background for the unmetamorphosed equivalents of the carbonaceous metasedimentary rocks that host Muruntau, thus providing a significant potential metal source at deeper crustal level. Third, a large block of allochthonous carbonate is located north of the pit, a lithology that is uncommon in growing continental margins. Such a unit could provide an important aquifer for fluid flow in the region, particularly if the ore-forming fluids had any acidity to help dissolved the accreted block. West Africa, hosts the world’s largest Precambrian orogenic gold deposit at Obuasi and dozens of other very large orogenic gold deposits, and has emerged as one of the world’s 3-4 major orogenic gold provinces. The Paleoproterozoic growth of West Africa, by Archaean craton break-up and then continental growth by “introversion”, and thus closure of internal basins, may explain the abnormal abundance of carbonaceous material in the terranes of the Man-Leo Shield from marine and near-shore terrestrial sources (Goldfarb et al. 2017). Such an extreme amount of organic matter would have provided very favorable metal and S sources (e.g., Tomkins 2010).

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Gold-rich porphyry deposits: types, settings, controls, and potential

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Abstract. Gold-rich porphyry deposits range from those in which Cu is the dominant metal through to Au-only end-members. The Cu-Au category is related to porphyry stocks of mainly quartz dioritic to granodioritic composition, with a majority of deposits linked to their alkaline equivalents. However, most porphyry Au deposits accompany diorite porphyries. Gold-rich porphyry deposits form in subduction-related, continental-margin and island arcs as well as in back-arc and syn- to post-collisional settings. Although highly oxidized asthenosphere and auriferous sulfide-enriched lithospheric mantle and lower crust may favor Au-rich porphyry deposit formation, it is their shallow emplacement (~2 km) that appears to be the dominant controlling factor. Shallow emplacement causes loss of H$_2$S to low-pressure vapor, suppressing Cu-Fe sulfides and promoting hydrothermal magnetite precipitation. Porphyry Au deposits, emplaced at even shallower (~1 km) depths, retain insufficient reduced S for even Cu-Fe sulfide formation. However, chemically reduced crustal profiles and intrusions also favor formation of Au-only deposits. Special deposit-scale features can enhance grade development. Porphyry Cu-Au deposits are more abundant and economically important than porphyry Au deposits.

1 Introduction

Porphyry systems, including high-sulfidation epithermal deposits in overlying lithocaps, have become an increasingly recognized and economically important source of Au over the past half century. Based on consideration of 39 representative examples from around the world, this paper highlights a spectrum of Au-rich porphyry deposits and briefly discusses their tectonic settings, genetic controls, and economic potential.

2 Types of Au-rich porphyry deposits

Most Au-rich porphyry deposits are Cu deposits with elevated Au contents (Fig. 1). The Au is either a co-product of Cu or, because of the large size of the resources, an important by-product. These Cu-Au deposits are transitional through Au-Cu examples (Cadia, Caspiche, Cerro Casale, Mt Milligan), in which Au clearly dominates economically, to Au-only end-members containing only a few hundred ppm Cu (Vila and Sillitoe 1991; Fig. 1). Although many of the Cu-Au deposits also contain Mo, the Kişladağ porphyry Au deposit is unusual because it is comparatively Mo rich (75-500 ppm; Baker et al. 2016).

Porphyry Cu-Au and Au-Cu deposits display good correlations between the two metals and, irrespective of Cu and Mo contents, average Au tenors of all Au-rich porphyry deposits fall in the <0.3–1.5 g/t range (Fig. 1).

Most Au-rich porphyry deposits are associated with multphase, calc-alkaline intrusions, which range from low- to high-K in composition. The Cu-Au deposits typically occur with quartz diorite, tonalite, or granodiorite porphyries whereas Au-only deposits are normally linked to dioritic phases. However, Bajo de la Alumbrera, Bingham Canyon, Cadia, Didipio, Galore Creek, Grasberg, Mount Polley, Northparkes, Red Chris, Rosia Poieni, and Skouries (Fig. 1) are centered on shoshonitic to alkaline porphyry intrusions, which are generally more felsic and, in some cases (e.g., Galore Creek), silica undersaturated. In common with porphyry Cu deposits in general, the intrusions accompanying nearly all Au-rich porphyry deposits belong to the magnetite-series (Ishihara 1977), the exception being the small Shotgun Au prospect (Fig. 1), which is centered on a reduced, ilmenite-series granite porphyry (Rombach and Newberry 2001).

Irrespective of the composition of the host intrusions, the bulk of the Au and any accompanying Cu in Au-rich porphyry deposits are almost invariably associated with potassic and/or overprinted chloride-sericite alteration containing multi-directional or sheeted arrays of quartz veinlets. The exception is the alkaline deposits of British Columbia (e.g., Galore Creek, Mount Polley), which can contain ore-related sodic and calcic-potassic as well as potassic alteration, commonly but not everywhere devoid of quartz veinlets (Lang et al. 1995).

3 Tectonic settings

Gold-rich porphyry deposits hosted by low- to high-K calc-alkaline rocks are typically integral parts of subduction-related magmatic arcs along either continental margins or island arcs (Fig. 1). In contrast, those with shoshonitic and alkaline affinities commonly occur in either back-arc (Bajo de la Alumbrera, Bingham Canyon, Didipio) or syn- to post-collisional (Cadia, Grasberg, Kişladağ, Mt Milligan, Northparkes, Ok Tedi, Pebble, Recsk, Rosia Poieni, Skouries, Tampakan) settings (Fig. 1). Active subduction zones probably did not directly underlie many of the shoshonitic and alkaline centers at the times of deposit formation (Richards 2009). However, most of the Late Triassic-Early Jurassic porphyry Cu-Au...
deposits (e.g., Galore Creek, Mount Polley) associated with alkaline rocks in British Columbia are currently thought to have formed during intra-arc extension (Barresi et al. 2015).

4 Genetic controls

Obviously, formation of Au-rich porphyry deposits is possible only where the parental magmas and derivative hydrothermal fluids are suitably endowed with Au. Endowment can be influenced by both magma source characteristics and the subsequent physico-chemical evolution of the fluids.

Where sulfide is abundant in the asthenospheric mantle source of subduction-related magmas, Cu partitions into the basaltic melt and Au is retained in the source; however, where residual sulfide abundance is extremely low, perhaps due to unusually high magma oxidation states, formation of Au-rich porphyry deposits is favored (Richards 2011). In the case of deposits in back-arc and syn- to post-collisional settings, the Au budget can be enhanced by partial melting of lithospheric mantle or lower crust that was enriched in Au during previous subduction episodes (Solomon 1990; Richards 2009, 2011). Such partial melting may be facilitated by lithospheric delamination and invasion by hotter asthenosphere (Cloos et al. 2005; Richards 2009). In the case of Bingham Canyon, however, even the mafic magma component appears to have lacked Au enrichment (Zhang and Audétat 2017).

Gold-rich porphyry deposits are generated more shallowly than porphyry Cu-Mo deposits (Cox and Singer 1992; Sillitoe 2000): at an average estimated paleodepth of 2.1 km, some 1.6 km shallower than their Mo-rich counterparts, based on a combination of geological features and fluid inclusion microthermometry (Murakami et al. 2010; Fig. 2). This fact is reflected by more common partial preservation of overlying volcanic edifices and associated lithocaps. Indeed, coeval volcanic rocks and/or lithocap remnants occur nearby more than half of the deposits plotted in figure 1. There is an empirical correlation between the exceptionally shallow formational depth of porphyry Au deposits and the dioritic composition of host intrusions, possibly reflecting extensional conditions that allowed mafic melts to invade to shallower levels, although the higher temperature of dioritic relative to more felsic magmas may also have been influential.

Murakami et al. (2010) explained the correlation between Au enrichment and shallow paleodepth and, hence, low pressure of porphyry deposit formation in terms of Au transport in a buoyant, S-rich, hydrous vapor coexisting with subordinate brine in two-phase magmatic systems. In shallow (<~3 km), low-pressure environments, the solubility of Au and Cu decreases with decreasing density of the ascending and rapidly expanding vapor plume, resulting in effective precipitation of both metals.

At extremely low pressures, as exemplified by the Au-only porphyry deposits formed within stratovolcanoes at paleodepths of <1 km in the Maricunga belt (Vila and Sillitoe, 1991; Muntean and Einaudi, 2000; Figs. 1 and 2), S fugacity was too low to generate appreciable amounts of
A major mineralogical difference between Au-rich porphyry deposits and their Mo-rich equivalents is the presence of hydrothermal magnetite, which can attain 3-10 volume % as both veinlets, with and without quartz, and disseminated grains (Sillitoe 1979; Cox and Singer 1992). Under the shallow, low-pressure conditions of Au-rich porphyry formation, progressive loss of H₂S to the vapor plume during ascent suppresses Cu-Fe sulfide formation and promotes magnetite deposition.

In marked contrast, the Au-only character of the unusual Shotgun porphyry prospect is attributed to the inability of the reduced magma and derivative ore-forming fluid to transport appreciable Cu (Rombach and Newberry 2001) rather than to ultra-shallow formation. La Colosa porphyry Au deposit, within a carbonaceous schist terrane, contains as much pyrrhotite as pyrite (Lodder et al. 2010), suggesting that a reduced fluid may also have played a key role there, bearing in mind that the quartz veinlets are typical of those in porphyry Cu deposits rather than banded as in classical, ultra-shallow porphyry Au deposits. Although the Mo content of porphyry deposits appears to be largely independent of paleodepth (Murakami et al. 2010), the reason for its notable concentration in the Kişladağ porphyry Au deposit is uncertain; however, a Au-Mo association characterizes some other Au deposit types related to shoshonitic and alkaline rocks (e.g., Cripple Creek; Jensen and Barton 2007).

Unusually high metal tenors in porphyry deposits are typically attributable to special geological conditions that are not exclusive to the Au-rich category (e.g., Sillitoe 2010). These include: low-permeability host rocks, such as massive limestone at Grasberg and Cerro Corona and phyllite at Golpu, which acted as aquitards that confined ore-forming fluids to the porphyry stocks in which exceptionally high Cu and Au grades developed (Fig. 1); Fe³⁺-rich wall rocks, exemplified by tholeiitic basalt in the Hugo Dummett deposit at Oyu Tolgoi, that facilitated Cu (but not Au) precipitation from the oxidized ore fluids and the consequent development of high Cu values (Fig. 1); proximal skarns, as at Ok Tedi and Recsk, with especially high Cu and Au grades; magmatic-hydrothermal breccias, as at Mt Milligan and Panguna, containing elevated Cu and Au values; pegmatites, including a brecciated massive quartz body, at Didipio, which contain exceptionally high Au grades (Wolfe and Cooke 2011; Fig. 1); and bornite-rich zones characterized by enhanced Au as well as Cu values (e.g., Galore Creek, Northparker, Santo Tomas II).

5 Economic potential

The most abundant Au-rich porphyry deposits belong to the Cu-Au category (Fig. 1), which – based on the record of mining – are also the most attractive economically because both metals are well correlated and recovered together in flotation concentrates. From the standpoint of size and grade, there is little to choose between deposits formed at continental margins or in island arcs and those assigned to back-arc and syn- to post-collisional settings, although the pre-eminent deposit, Grasberg, is probably post-collisional (Cloos et al. 2005; Fig. 1). Interestingly, two of the lowest-grade porphyry Cu-Au mines, at Aitik and Chapada (Fig. 1), are the oldest; both are Proterozoic and were subjected to collision-induced, amphibolite-facies metamorphism and ductile deformation, which gave rise to moderately to shallowly plunging, stretched orebodies and, hence, lower stripping ratios (Wanhainen et al. 2003; Oliveira et al. 2015).

Porphyry Au deposits are far less abundant than those containing Cu and Au and, notwithstanding their typically higher Au contents (Fig. 1), have not been widely exploited because Au recoveries using cyanidation are relatively low; indeed, only Kişladağ and Maricunga (formerly Refugio) have been successfully mined. In telescoped systems, Au-rich porphyry-type mineralization can be extensively overprinted by high sulfidation-state sulfide assemblages containing enargite and other deleterious As-bearing sulfosalts, creating metallurgical issues (e.g., Tampakan and Caspiche; Middleton et al. 2004; Sillitoe et al. 2013; Fig. 1).

Supergene sulfide oxidation commonly affects the economic potential of porphyry Cu-Au deposits hosted by pyrite-poor potassic alteration because Au present with oxidized Cu species is not recoverable; a fact learnt the hard way during early mining at Ok Tedi (Rush and Seegers 1990) and a severe impediment at Boyongan, which is unusually deeply oxidized (Braxton et al. 2009). In contrast, sulfide oxidation would result in increased Au recoveries from porphyry Au deposits treatable by heap-leach cyanidation.
6 Conclusions

This analysis supports shallow formational depth as the fundamental control on formation of Au-rich porphyry deposits, with porphyry Au deposits at the shallowest depths where Cu deposition is largely inhibited (Fig. 2). This conclusion implies that exploratory drilling beneath lithocaps should encounter porphyry Cu-Au and, especially, Au-only deposits at shallower depths than their Mo-rich equivalents. By the same token, preserved remnants of coeval volcanic edifices and contained lithocaps may be taken as a good indication that associated porphyry deposits are likely to be Au rich.

The ilmenite-series intrusions and/or reduced crustal profiles responsible for a few Au-only porphyry deposits as well as the specific deposit-scale geological features that can cause extraordinarily high Au and/or Cu tenors are readily identifiable and can be factored into exploration programs. However, sub- and deep-crustal parameters promoting Au availability – miniscule magmatic sulfide contents in the mantle during subduction and Au-rich sulfide concentrations in the upper mantle and/or lower crust at the time of syn- to post-subduction magmatism – are less tangible and, hence, difficult to apply during exploration. Nonetheless, they may be influential in the development of long-lived Au provinces (Sillitoe 2008).

Finally, it should be emphasized that Au-rich porphyry deposits are valid exploration targets throughout a broad spectrum of convergent margin settings worldwide, including island arcs, rifted arcs, continental margin (Andean-type) arcs, back-arc, and syn- and post-collisional belts. Notwithstanding the dominance of certain metallogenic belts by Au-rich porphyry deposits (e.g., Luzon Central Cordillera, Maricunga), any convergent margin setting can contain isolated Au-rich deposits even in relatively close proximity to Mo-rich examples.

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Proterozoic West African gold: why ‘When’ leads to ‘Where’

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Abstract. The location of mineral deposits is ultimately what concerns mining companies. Nevertheless, this “Where” is constrained spatially within one or a series of units and/or structures having deposited or formed at a specific time, the “When”. We would like to draw attention to this “When” dimension for gold exploration, taking as an example the remarkable gold endowment of the Proterozoic West African Craton (WAC), where combined structural and geochronological constraints allow several gold events to be distinguished in time: (1) Early orogenic gold deposits formed during the Eoeburnean orogeny, between 2190 and 2120 Ma; (2) Placer deposits hosted by the Tarkwa Group with maximum and minimum depositional ages respectively at ~2130 Ma and ~2100 Ma; and (3) Late orogenic gold deposits, hosted by brittle to brittle-ductile structures, formed during late Eburnean deformation between 2100 and 2000 Ma. The substantial geochronological data-set that now exists throughout the WAC discriminates the multiple lode gold events, and placers, formed during a single orogenic cycle, here the Eburnean orogeny. Further geochronological constraints on gold occurrences at the WAC scale is critical (1) for the determination of the appropriate time scale for orogenic gold systems that appear to be not exclusively associated with the late-stage(s) of an orogenic cycle, (2) for the identification of potential diachronism at the WAC scale, recently shown for late-magmatic events, and (3) for improving our ability to define the “Where”.

1 West African gold deposits

West Africa, with presently an endowment of approximately 10,000 t gold, is one of the world’s great gold provinces and the largest Paleoproterozoic gold producing region (Markwitz et al. 2016; Goldfarb et al. 2017). The gold resources are mainly concentrated within the Man-Leo shield which constitutes the southern part of the WAC, with the majority of gold resources concentrated within the Paleoproterozoic Baoulé-Mossi domain (Fig. 1). The ca. 2250-2000 Ma greenstone belts hosting the most important gold deposits are best recognized in southwest Ghana, northeast and westernmost Burkina Faso, southern Mali, northeast Guinea, and along the Kedougou-Kénebia inlier (Fig. 1). The majority of gold mines and deposits are proximal to major first-order structures with protracted tectonic histories (Fig. 1). Over the past ~20 years, several regional or local tectonic scenarios have been proposed for the
The deformational history of the WAC. The regional deformation event (D1 Eburnean orogeny) occurred between 2187 and 2158 Ma (Perrouty et al. 2012), and corresponds to a NE-SW to N-S shortening event resulting in kilometer-scale folding of Birimian terranes. This deformation evolved into NW-SE compression (D2 - Eburnean), with basin inversion and regional folding and thrusting, and was coeval with the deposition and folding of the Tarkwaian sediments. During the following deformational phases, defined as Eburnean (D3 to D6 depending on the study), the regional tectonic constraints led to transpressive movements with orientations ranging from NW-SE to SW-NE, occurring between ca. 2120 Ma and 1980 Ma on the basis of relative chronological and geochronological arguments described in Feybesse et al. (2006).

Most of the major orebodies are best classified as orogenic gold deposit types, although there are paleoplacer and porphyry-skarn deposits within some of the greenstone belts (Markwitz et al. 2016; Goldfarb et al. 2017; Le Mignot et al. 2017b; Lebrun et al. 2017; Masurel et al. 2017). The dominant model for gold-only mineralization in the WAC has historically argued for late-stage orogenic gold mineralization at the end stage of the Eburnean Orogeny (e.g. Allibone et al. 2002a and b; Tunks et al. 2004; Feybesse et al. 2006).

Figure 1. Simplified geological map of the West African craton showing locations of the main gold deposits (modified after the BRGM SIG Afrique map, Milesi et al. 2004).

2 Timing distribution of the West African gold

To date, combined structural and geochronological constraints allow several gold events to be distinguished (Fig. 2B; Allibone et al. 2002a and b; White et al. 2014; Markwitz et al. 2016; Perrouty et al. 2016; Mignot et al. 2017a; Le Mignot et al. 2017b; Fontaine et al. 2017; Fougerouse et al. 2017), which are detailed below:

- **Early orogenic gold deposits** formed during the Eoeburnean orogeny, i.e., between 2190 and 2120, as represented by an early stage of mineralization at Kiaka and Wass (Perrouty et al. 2016; Fontaine et al. 2017). Re-Os dating of early sulphides at these localities yielded ages of 2157±32 Ma for Kiaka and 2164±14 Ma for Wass (Le Mignot et al. 2017b; Fontaine et al. 2017). These ages are significant and provide the first absolute temporal constraints on gold-only Eoeburnean mineralization in the Birimian of West Africa. Undated gold events also highlight this early orogenic gold phase at Wona-Kona (Milesi et al. 1992; Augustin et al. 2016).

- **Placer deposits** hosted by the Tarkwa Group, the latter having maximum and minimum depositional ages of respectively ~2130 Ma (U-Pb and Pb-Pb dating on zircons from the Banket Formation; Davis et al. 1994; Hirdes and Nunoo 1994; Pigois et al. 2003), and ~2100 Ma (U-Pb dating on zircons on metagabbros and granitoids, Adadey et al. 2009; Oberthür et al. 1998).

- **Late orogenic gold deposits**, hosted by brittle structures, with higher grades (up to 60g/t in Kiaka), formed during late Eburnean deformation (D3-D5 events) between 2100 and 2000 Ma, as represented by Re-Os dating on sulfides at Wassa 2, Obuasi and potentially Nassara with larger uncertainties (Le Mignot et al. 2017a; Ouiya et al. 2016), as well as Damang (Pigois 2003; White et al. 2014; Le Mignot et al. 2017a). Structurally “late”, but undated gold events, are also described for Kiaka 2 (Le Mignot et al. 2017; Fontaine et al. 2017), and Inata (McCuaig et al. 2016).

3 Gold events through the Eburnean cycle

The age distributions of mineral deposits are commonly used to decipher secular patterns of global tectonic cycles related to the periodic assembly and dispersal of continents within supercontinent cycles (Groves et al. 2005; Frimmel 2008; Goldfarb et al. 2010; Fig. 2A). Improvements in the robustness, accuracy and precision of geochronological methods, advances in microsampling techniques and/or mineral separation, new developments allowing in-situ analyses, and increased analytical capacity of laboratories, have generated more systematic geochronological data on mineral systems (Stein 2014; and references therein).

Increasingly the geochronological dataset allows us (1) to zoom inside an orogenic timing peak (the forest), and then (2) to discriminate several sub-timing peaks (the trees) inside a single orogenic cycle (Le Mignot et al. 2017).
Figure 2B illustrates the multiple gold events, and placers, formed during the Eburnean orogeny in the WAC.

The total gold content for each deposit is indicated in Fig. 2B. Even if impossible to discriminate between each gold event in each deposit, these values may help to discuss about (1) the more prolific period for gold concentration, and/or (2) recycling versus new gold input for each gold event.

Evidence for multistage lode gold events in a single orogenic cycle has been recently suggested and/or highlighted in Yilgarn and the Superior provinces (Couture et al. 1994; Robert et al. 2005; Lawley et al. 2015), and in Tanzania in the Ubandian Belt (Lawley et al. 2013; Kazimoto et al. 2015). Wyman et al. (2016) discussed the time scale of processes leading to the development of orogenic systems, considered to be generally less than a few million years. For these authors, the occurrence of multiple generations of gold in a given region or even a single deposit testified to the complexity of individual orogenic events.

Figure 2. From global secular cycles to orogenic time scale
a. Temporal distribution of orogenic gold deposits through time (modified from Groves et al. 2005), b. Temporal distribution of gold deposits through the Eburnean orogeny in the WAC (modified from Le Mignot et al. 2017a). Two orogenic gold events are highlighted respectively from 2190 to 2120 Ma (diamonds), and 2100 to 2000 Ma (circles). Placers deposits are associated with the Tarkwaian sediments, and formed between 2130 and 2100 Ma. Total resources for each gold deposits are indicated in brackets.

4 Why the “When” does matter for gold exploration: from the wood to the trees

In the mineral system approach (Hronskey et al. 2009; McCuaig and Hronskey 2014; Groves 2015), the “Where” perspective” consists in moving from the “trees” (the deposit/ district scales) to the “forest” (the mineral system at the lithospheric scale). For the same mineral system approach, the “When” perspective is moving from the “forest” (the orogenic cycle, Goldfarb et al. 2001; Groves et al. 2005) to the “trees”, i.e. specific timing within the orogenic cycle (Lawley et al. 2015; Le Mignot et al. 2017). Further geochronological data on gold occurrences at the WAC scale are essential (1) for the determination of the appropriate time scale for orogenic gold systems which appear to be not exclusively associated with the late-stage(s) of an orogenic cycle, (2) for the identification of potential diachronism at the WAC scale, recently identified by Parra-Avila et al. (accepted) for late-magmatic events, and (3) for improving our ability to define the “Where”.

5 Conclusion

The Proterozoic gold of the WAC represents a good example of a polyphase gold mineralizing system, with gold deposits heterogeneously distributed in time during the Eburnean orogenic cycle. Although the late stages of the Eburnean orogeny constitute a prolific period for the formation of high-grade lode-gold mineralization, identification of less well-studied early-stage gold deposits, which can also contain large quantities of gold, is critical for gold exploration in the WAC. One major unresolved question is to determine if these gold events illustrate (1) the recycling of a single gold stock in the crust, and/or (2) different gold input(s) into the crust.

Acknowledgements

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Diversity of gold deposits in the Cenozoic West Tethyan magmatic belt, SE Europe: implications for exploration

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Abstract. The Western Tethyan magmatic belt developed during two main periods of Cretaceous and Cenozoic magmatism, and is host to numerous major Cu and Au deposits. The Cretaceous deposits are Cu-Au porphyry, high sulfidation epithermal and volcanic massive sulfide deposits, whereas in the Cenozoic Cu is significant only in porphyry systems. However, the Cenozoic contains approximately five times greater total Au endowment (for Au-deposits > 0.5 Moz), and also has a greater deposit host styles. A compilation of exploration discovery methods highlights the importance of historic workings as an initial vector, with 41% of the discoveries having this as a significant factor followed by geochemistry (34%), whilst Au-deposits > 0.5 Moz), and also has a greater deposit hosted styles. A compilation of exploration discovery methods highlights the importance of historic workings as an initial vector, with 41% of the discoveries having this as a significant factor followed by geochemistry (34%), whilst geology was a major factor in 15% and geophysics played an important role in only 6%. In terms of geological models porphyry and proximal epithermal systems are well understood and provide excellent guides for explorers, however, more distal deposits such as Au-rich carbonate replacement deposits and deposits with poorly constrained models such as sediment-hosted and intermediate sulfidation deposits are more challenging for exploration, and would benefit from improved applied research.

1 Introduction

The Western Tethyan magmatic belt (WTMB), here considered the portion of the Tethyan belt located within Romania, Serbia, Kosovo, Macedonia, Greece, Bulgaria and Turkey, formed during the Cretaceous through to the Cenozoic (Fig 1). The tectonic setting and geodynamic evolution along the 3,500 km strike of the WTMB is complex, but it broadly evolved from Cretaceous subduction-related arc magmatism between 90 and 70 Ma, followed by a resurgence of magmatism and volcanism during the Early Eocene (< 55 Ma) related to convergence and collision that continued through the Late Eocene to Early Oligocene, and then developed into widespread post-collision extension-related magmatism during the Miocene (Richards 2015).

Mineral deposits of the WTMB are dominantly magmatic-hydrothermal in origin with volcanic massive sulfide (VMS) deposits restricted to the Cretaceous (Table 1). The Cretaceous age deposits have been the focus of much historic and current copper and gold mining, including the large Bor porphyry (6.8 Moz Au; 5.1 Mt Cu) and Chelopech high sulfidation (HS) epithermal (3.94 Moz; 0.4 Mt Cu) deposits. The Cretaceous belt continues to be the focus of exploration activity with recent significant discoveries such as the Cukaru Peki Au-Cu porphyry-HS epithermal deposit (2.5 Moz Au; 1.2 Mt Cu) and the Hot Maden Au-Cu VMS system (3.2 Moz Au; 0.2 Mt Cu). However, the Cenozoic magmatic belt contains five times the Au endowment based on known deposits with > 0.5 Moz Au (Table 1). Furthermore, the Cenozoic deposit types are diverse in style including both porphyry Au-Cu and Au-only deposits, a full range of epithermal deposits from HS to intermediate (IS) to low sulfidation (LS) that include vein, breccia and replacement styles, as well as Au-rich distal carbonate-replacement and sediment-hosted deposits.

The purpose of this paper is to review the range in styles of Cenozoic magmatic-hydrothermal deposits in the WTMB and evaluate how this diversity presents both a challenge and opportunity in exploration through an assessment of the exploration techniques leading to their discovery.

<table>
<thead>
<tr>
<th>Cretaceous</th>
<th>Cenozoic</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Total Au (Moz)</td>
</tr>
<tr>
<td>Porphyry</td>
<td>1</td>
</tr>
<tr>
<td>HS Epithermal</td>
<td>4</td>
</tr>
<tr>
<td>LS Epithermal</td>
<td>5</td>
</tr>
<tr>
<td>IS Epithermal</td>
<td></td>
</tr>
<tr>
<td>Sediment</td>
<td>2</td>
</tr>
<tr>
<td>CRD</td>
<td></td>
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<tr>
<td>VMS</td>
<td>8</td>
</tr>
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</table>

Table 1. Summary of WTMB deposits with >0.5 Moz Au (based on SNL database, S&P Global Market Intelligence).

2 Examples of major Cenozoic gold deposits

2.1 Porphyry Au and Au-Cu deposits

Porphyry deposits account for the majority of Cu (10 Mt of Cu out of a total of 10.1 Mt) and the largest Au endowment (50 Moz) in the Cenozoic (Table 1). The most significant discoveries formed during the Miocene such as Rovina Valley (7.5 Moz Au; 0.7 Mt Cu) and the Apuseni district, Romania and Skouries (7.1 Moz Au; 1.8 Mt Cu) in the Halkidiki region, Greece. Rovina Valley, which comprises three different porphyry centres, and Skouries, are pencil porphyries (all four deposit diameters < 500m) and are characterized by strong quartz-magnetite veining and alteration within chlorite-sericite-biotite alteration (Rovina Valley) and biotite-K-feldspar alteration.
Figure 1. Location of Au deposits (> 0.5 Moz Au) related to Cretaceous and Tertiary magmatism in the WTMB.

(Skouries). They lack HS epithermal mineralization that is commonly associated with the Cretaceous porphyry systems.

The largest Cenozoic porphyry deposit in the WTMB is Kisladag (16.8 Moz Au), which for the belt is a unique Au-only Miocene porphyry system (Baker et al. 2016). Overall the deposit has a Cu %/Au ppm ≈ 0.03. The deposit was likely emplaced at shallow levels (< 1 km) into a stratovolcano with a strongly telescoped and complexly overprinting magmatic-hydrothermal system that formed within 400 k years. The main gold mineralization formed with potassic alteration in a series of monzonite intrusions that is surrounded by an outer shell of tourmaline and white mica, overprinted by pervasive argillic alteration. HS advanced argillic alteration cuts the porphyry and forms a lithocap adjacent to the deposit but is barren with respect to Au and Cu.

2.2 HS epithermal deposits

HS epithermal deposits in the Cenozoic are dominantly Eocene to Oligocene in age with the exception of the Oksut (1.38 Moz Au) deposit that formed at the Miocene-Pliocene boundary in south central Turkey. Two major clusters of HS deposits occur, Agi Dagi (1.94 Moz), Kirzali (0.87 Moz), Camyurt (0.59 Moz) and TV Tower (0.52 Moz) in the Biga Peninsula, Turkey, and Perama Hill (1.94 Moz) and Sapes (0.82 Moz) in Thrace, Greece. For the most part the Cenozoic deposits are Cu-poor and Au-grades in the majority of deposits are low (0.5 to 1.1 g/t) compared to the Cretaceous examples (1 to 3.2 g/t). However, Perama Hill (2.84 g/t) and Sapes (7.4 g/t) in Thrace have notably higher grades. Compared to the Cretaceous HS epithermal systems and the Cenozoic Biga Peninsula examples, the direct link to porphyry Cu systems is less evident in the Thrace region although this may reflect the lack of exploration as porphyry Cu occurrences are known (e.g., Pagoni Rachi; Voudouris et al. 2013). Sapes comprises three HS ore zones; St Demetrios and Scarp are shallow, low grade (2.5 g/t) oxide resources, whereas the main Viper zone (~550 koz) is deep (~250m) with an exceptional Au grade of over 17 g/t. The Viper lode is located in the hanging wall of a moderate to shallow dipping listric basal fault which coincides with the transition between advanced argillic and phyllic alteration. The Au mineralization occurs in high grade commonly banded quartz-rich veins and breccias with pyrite-enargite, surrounded by a broad (10’s m) low grade envelope of silica-pyrite-alunite alteration.
2.3 IS epithermal deposits

After porphyry Au-Cu deposits, IS epithermal systems contain the largest endowment of Au for a single deposit class in the WTMB (33 Moz Au). This may in part reflect difficulties in classification between end-member epithermal styles (Hedenquist et al., 2000) as well as overlap with other deposit types within WTMB IS epithermal system examples (see below). Nonetheless detailed research contributions on Rosia Montana (18.6 Moz Au; Wallier et al. 2006) and Copler (7.9 Moz Au; Imer et al. 2013) and the author’s own work on Certej (4.4 Moz Au) and Efemcukuru (2.2 Moz Au) confirm that these deposits are best classified as IS epithermal deposits.

Rosia Montana and Certej formed during the Miocene in the Au-endowed Apuseni district and share many geological similarities including: (1) breccia-hosted mineralization; (2) adularia and phyllic dominant alteration; (3) mineralization comprising quartz, adularia, carbonates (commonly Mn-rich), pyrite, Fe-poor sphalerite, galena, chalcopyrite, and tetrahedrite; (4) formation contemporaneous with shallow level andesite-dacite intrusions that also host nearby porphyry deposits (Rosia Poieni and Bolcana respectively). Both Rosia Montana and Certej cut Cretaceous calcareous flysch basement, and at Certej this hosts a significant component of the ore and has a Carlin-like character including calcification with strong silica-adularia replacement with Au-bearing arsenian pyrite.

Efemcukuru in western Anatolia, Turkey, is also Miocene in age but is a vein style IS epithermal deposit. The veins dip moderately to steeply NE within a normal fault array that also localized pre-mineral rhyolite dykes and calc-silicate (chlorite-epidote-actinolite-quartz) alteration. The veins are characterized by banded vein textures and multi-stage breccias containing abundant wall rock and vein fragments. Vein mineralogy is variable but predominantly consists of quartz-rhodochrosite-rhodonite-pyrite-galena-sphalerite. The high base metal and Mn-rich nature of the veins supports an IS classification for the deposit.

The other significant IS epithermal system in Turkey is the Eocene Copler deposit which is intimately associated with a sub-economic porphyry Cu-Au deposit that is overprinted by quartz-Mn carbonate-base metal-Au-barite veins. Carbonate replacement manto-style mineralization is also well developed at the contact between the porphyry and marble country rock (Imer et al. 2013).

2.4 LS epithermal deposits

Low sulfidation epithermal deposits in the Cenozoic also vary in style from examples such as the Miocene age Ovacik mine (3.2 Moz Au) that is a classic vein hosted deposit in an andesite volcanic sequence, to the Eocene sediment hosted Krumovgrad deposit (0.8 Moz Au) that is associated with a detachment fault. LS epithermal deposits are the least endowed epithermal deposit type in the WTMB (7.2 Moz Au) and although they have the highest average grade of epithermal deposit types (3.1 g/t Au), their range in grade (0.7 to 6 g/t Au) is not particularly high compared to world class bonanza style LS epithermal deposits that globally can commonly be > 10 g/t Au (Hedenquist et al. 2000).

2.5 Carbonate replacement deposits

Polymetallic carbonate replacement deposits (CRD) in the WTMB are dominantly recognised for their base metal and silver production such as Trepcsa in Kosovo and Madan in Bulgaria. However, in the Halkidiki region, Greece, deposits of this style contain significant amounts of Au with Olympics (5.4 Moz) being the largest example. The Oligocene age Olympics deposit is hosted by marble in a sequence of interlayered quartzo-feldspathic biotite gneiss and amphibolite (Siron et al., 2016). The ore displays a complex sulfide mineral assemblage varying from galena-sphalerite dominant to pyrite-rich massive sulfide with calcite-dolomite-rhodochrosite gangue. The highest Au-grades (> 10 g/t and commonly >30 g/t Au) occur in arsenopyrite-bearing massive sulfide with silica replacement of carbonate, and locally grades into arsenopyrite- and boulangerite-bearing siliceous breccias. Sulfide bodies exhibit coarse- and fine-grained massive and banded textures that cut and replace marble, and are largely discordant to foliation.

Three other polymetallic deposits occur to the south of Olympics along the Stratoni fault (Siron et al. 2016). The historic Madem Lakos mine (no reported Au resource) is skarn to CRD in style, whilst further west along the fault lies the operating polymetallic Mavres Petres mine (Au present but not recovered) and the advanced exploration project Piavitsa (1.9 Moz at 5.7 g/t Au). Both Piavitsa and Mavres Petres have a significant CRD component to them but are geologically complex due to their localization within the Stratoni fault. In terms of grade, the Au-bearing CRD’s are attractive, however, the Au is typically refractory with As-rich minerals.

2.6 Sediment-hosted deposits

There is significant ambiguity surrounding the classification of sediment-hosted Au deposits in the WTMB due to the overlap with other deposit styles and the poorly defined nature of sediment-hosted gold deposit models. For example, the Perama Hill and Krumovgrad deposits are both hosted by sandstone and conglomerate but are classified as HS and LS epithermal systems respectively based on their alteration characteristics and sulfide mineralogy (Marchev et al. 2004; Voudouris et al. 2011). Certej is an IS epithermal deposit but has a major ore type that is Carlin-like. The most significant classified sediment-hosted, Carlin-like Au deposit occurs in eastern Anatolia, Turkey, namely the Miocene age Mollakara deposit (4.5 Moz Au). Carlin-like features include calcification of calc-schists and sulfidic jasperoid zones (Çolakoğlu et al. 2011).
3 Exploration implications

In terms of commodity focus the Cretaceous is endowed in both Cu and Au in porphyry, HS epithermal and VMS deposits, whereas in the Cenozoic Cu is only of significance in the porphyry and IS epithermal deposits. Cenozoic HS epithermal deposits typically lack Cu and in general have low Au grades, with the notable exception of the very high grades at Sapes. LS epithermal systems are on average the highest grade epithermal targets in the belt but compared with global analogues lack true bonanza grades. Polymetallic gold-rich CRD’s are high grade but metallurgically difficult, and exploration models that enable prediction of which polymetallic CRD’s are Au-rich versus Au poor is currently lacking. Furthermore, exploration and deposit models for distal sediment-hosted systems are poorly constrained.

A compilation of exploration discovery methods for both the Cretaceous and Cenozoic deposits with > 0.5 Moz Au highlights the importance of historic workings as an initial vector (Fig 2); this was a significant factor in 41% of the discoveries. Geochemistry played the next most significant role in 34%, whilst geology was a major factor in 15% and geophysics played an important role in only 6% of the discoveries.

Figure 2. Key discovery methods WTMB deposits.

This review highlights a number of challenges for explorers and researchers. In terms of exploration, an important factor is historic workings but these are numerous throughout the belt so discriminating features that may indicate a significant deposit versus a sub-economic system is a major challenge. In terms of geological models porphyry and proximal epithermal systems are well understood and provide excellent guides for explorers, however, more distal deposits and deposits with poorly constrained models in the WTMB such as sediment-hosted and IS sulfidation deposits are more challenging for exploration, and would benefit from improved applied research.

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Fennoscandian orogenic gold in the context of regional orogenic evolution

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Abstract. Orogenic gold in Fennoscandia is dominated by Palaeoproterozoic occurrences. Smaller deposit numbers, so far, characterise the Archaean greenstone belts, and only a few have been discovered in the Neoproterozoic and Palaeozoic terrains. For the possible Mesoarchaean cases, all orogenic gold in Fennoscandia can be related to supercontinent assembly. Most of the deposits were formed at 2.72–2.64 Ga and 1.91–1.77 Ga, during the two main stages of crustal growth, i.e., the formation of the Kenorland and the Columbia. Palaeoproterozoic thermal overprint is common in the Archaean greenstones, but possibly hasn’t introduced any significant gold in the Archaean parts of the shield. Epigenetic occurrences where Cu, Co, Ni, or Sb are among the potential commodities in addition to gold characterise parts of Fennoscandian Palaeoproterozoic intracratonic basins subjected to 1.91–1.77 Ga orogenies. Most of these deposits may go into the subclass of ‘orogenic gold with anomalous metal associations’, but some, such as deposits enriched in Co or U, may go into other genetic categories. Yet, they all can be related to the orogenic evolution of the shield.

1 Introduction

Orogenic gold deposits are epigenetic gold occurrences with a distinct structural control, formed during an orogeny by orogenic fluids (Böhlke 1982; Groves et al. 1998). It is the dominant gold deposit type in nearly all metamorphosed terrains, and contains about one third of the global gold reserves (Goldfarb et al. 2005; Frimmel 2008). Also in the Fennoscandian shield, it dominates by the number of gold deposits, although the dominance is less obvious in the known gold endowment of all metallic mineral deposits (Eilu et al. 2016).

In Fennoscandia (the shield and the Caledonides), there are currently more than 90 deposits which are assumed to go into the orogenic gold class and have a defined resource (Eilu 2012; Eilu et al. 2016): 55 in Finland, 8 in Sweden, 14 in Norway, and 18 in the Russian part of the region (Fig. 1). Their indicated or suggested ages range from Mesoarchaean to Palaeozoic, with more than a half being Palaeoproterozoic.

For about 20 deposits, there is radiometric dating for mineralisation: sulphides, hydrothermal U-rich minerals, and silicates produced by alteration related to mineralisation have been dated (e.g., Ettner et al. 1994; Stein et al. 2000; Alm et al. 2003; Weihed et al. 2003; Saalmann et al. 2009; Wyche et al. 2015; Molnar et al. 2016a; Käpyaho et al. 2017). For most deposits, the timing is based on host rock ages and structural indications of relative timing (e.g., Eilu and Pankka 2010; Bark and Weihed 2012; Korsakova et al. 2012; Sandstad et al. 2012; Eilu 2015; Niiranen et al. 2015).

2 Orogenic gold related to tectonic evolution of Fennoscandia

2.1 Archaean

About 25 orogenic gold deposits have been discovered in the Archaean terrains of Fennoscandia, essentially in Finland and Russia (Fig. 1). All of the deposits where detailed investigations is available (all in Finland) were formed during the Neoarchaean, with mineralisation taking place close to the D3 or D4 stages of the Neoarchaean orogeny, i.e., between 2.72 and 2.64 Ga. For the Ilomantsi greenstone belt, the latest work suggests mineralisation at ca. 2.71 Ga (Molnar et al. 2016a; Käpyaho et al. 2017). These ages fit into the time of the global peak of Archaean orogenic gold mineralisation, of global Neoarchaean orogenic activity, and of peak crustal growth (Condie 2000; Groves et al. 2005). This was also the time when the supercontinent Kenorland, is suggested to have formed by collision of Fennoscandia and Laurentia (Groves et al. 2005; Mertanen and Pesonen 2012).

Parts of the Fennoscandian Archaean greenstone belts show an overprint by Palaeoproterozoic deformation. However, no Proterozoic gold mineralisation event has been recognised, despite the Proterozoic metamorphic recrystallisation and disturbances of isotopic systems (Kontinen et al. 1992; Hölttä et al. 2012; Molnar et al. 2016a; Käpyaho et al. 2017). Recent stable isotope and fluid inclusion research gives further support for Neoarchaean timing for mineralisation, with clear indications that the mineralising fluids were early and originating from prograde metamorphic devolatilisation (Molnar et al. 2016b; Fusswinkel et al. 2017).

The Fennoscandian deposits included into the orogenic gold category and suggested to be Mesoarchaean in age are all within the Russian part of the shield, hosted by Mesoarchaean parts of the greenstone belts (Korsakova et al. 2012). Very little of exploration for gold has taken place in that terrain, and all deposit age data appears circumstantial. The supposedly Mesoarchaean deposits may, in fact, be Neoarchaean or Palaeoproterozoic, as the terrain also includes both Neoarchaean and Palaeoproterozoic greenstone sequences. This scarcity of data also means that there may very well be many more orogenic gold deposits in the NW Russia than what is indicated in figure 1.
Disintegration of Kenorland created intracontinental basins between parts of Baltica (Archaean of part of Fennoscandia). The basins were filled by clastic sediments characterised by arenites, red beds and black shales, evaporates, and mafic-ultramafic intrusives and lavas. During ca. 2.1–1.95 Ga, with further extension, juvenile oceanic crust was formed in some of these basins (Lahtinen et al. 2008). No orogenic gold was formed at these stages, but the intracontinental basin evolution may have been important for preparing ground, development of saline orogenic fluids, and metal sources in the intracontinental sequences.
Assembly of the supercontinent Columbia started with arc and microcontinent accretion during 1.93–1.86 Ga, and was followed by continent-continent collision at 1.84–1.77 Ga and at 1.64–1.48 Ga producing a collage of orogenies across Fennoscandia (Lahtinen et al. 2008; Mertanen and Pesonen 2012). Some orogenic gold was possibly formed during the accretion stage, as suggested by the Re-Os age from auriferous arsenopyrite at the Suurikusuikko deposit, Central Lapland (1916 ± 19 Ma; Wyche et al. 2015). However, the most extensive orogenic gold stage seems to be related to the continent-continent collision in 1.84–1.77 Ga. Most of the few mineralisation ages that exist, form across Finland and in the northern parts of Norway and Sweden, point to this time period (Ettner et al. 1994; Weihed et al. 2003; Saalmann et al. 2009). Also, nearly all of the more controversial gold occurrences with enriched base metals or uranium are of similar ages (Billström et al. 2010; Eilu 2015; Molnar et al. 2016c).

There are several gold deposits in the northern and, possibly also, the easternmost Fennoscandia, which resemble typical orogenic gold deposits, but are anomalous as they contain Ag, Cu, Co, Ni, or Sb as potential commodities in addition to gold (Fig. 1). They also show higher ore fluid salinities than the typical orogenic gold systems (Ettner et al. 1994; Lindblom et al. 1996; Vanhanen 2001; Billström et al. 2010; Eilu 2015). It is possible that such deposits reflect mobilisation of basinal fluids under regional metamorphic conditions with the metals possibly (but not necessarily) enriched prior to an orogeny in the fluid source areas by, for example, diagenetic and other basinal processes (e.g., Goldfarb et al. 2001; Yardley and Graham 2002). A crustal evolution potentially favourable for such conditions characterises the Palaeoproterozoic intracratonic basins of Fennoscandia metamorphosed during the Columbia assembly (Kyläkoski et al. 2012; Melezhik et al. 2015). One must, however, keep in mind that some of the polymetallic gold deposits indicated in figure 1 (especially the Au-U occurrences), albeit clearly epigenetic, may have formed by processes different from what is described above, and should not be classified into the orogenic gold category (Molnar et al. 2016c; Ranta et al. 2017).

2.3 Neoproterozoic and Palaeozoic

A few small orogenic gold occurrences have been detected in areas postdating the Palaeoproterozoic within Fennoscandia. The Neoproterozoic deposits occur in a small belt across the Swedish-Norwegian border in the SW, in the domain of the Sveconorwegian orogen. Radiometric dating suggests mineralisation at ca. 973 Ma (Stein et al. 2000; Alm et al. 2003). If correct, this indicates mineralisation during the continent-continent collisional stages of the Rodinia assembly (Bingen et al. 2008).

Orogenic gold deposits have also been detected in the Palaeozoic terrains of the Fennoscandian Caledonides (Sandstad et al. 2012). No radiometric dating is available, but structural studies suggest mineralisation during the Caledonian collision at 430–390 Ma, that is, during the Laurasia (or Laurussia) collision, at the early stages of the Pangaea assembly (Grenne et al. 1999).

3 Summary

Fennoscandia records, at least, four stages of orogenic gold mineralisation: Neoproterozoic, Palaeoproterozoic, Neoproterozoic, and Palaeozoic. These stages can be related to accretional and collisional plate-tectonic stages, and to supercontinent assembly. The ages of orogenic gold in Fennoscandia also are, except for the early Neoproterozoic ages, similar to major global stages of orogenic gold mineralisation (Goldfarb et al. 2001). Probably most of the polymetallic epigenetic gold occurrences within the Fennoscandia go into the subcategory of ‘orogenic gold with anomalous metal associations’. However, some of the Au-Co and all of the Au-U occurrences reflect mineralisation processes difficult to put into any well-established genetic category.

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Early Cretaceous gold mineralization related to the North China Craton destruction

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Abstract. The North China Craton (NCC) hosts numerous gold deposits and is known as the most gold-productive region in China. These deposits are generally sited in the cratonic margin. Main gold districts include Jiaodong in the eastern margin, Xiaoqinling and Xiong’ershan in the southern margin, Jibeijidong, Chifeng-Chaoyang, Jinan, and Liaodong in the northern margin, and central Taihangshan in the central part of the craton. The gold deposits mostly formed within a few million years during the early Cretaceous (130–120 Ma), coeval with widespread occurrences of bimodal magmatism that marked the peak of lithospheric thinning or craton destruction of the NCC. Dehydration of the subducted and stagnant slab in the mantle transition zone has led to continuous hydration and considerable metasomatism of the mantle wedge beneath the NCC. The large-scale gold mineralization in the NCC in the early Cretaceous has a genetic relation to craton destruction. The westward subduction of the paleo-Pacific plate beneath the eastern China continental margin during the early Cretaceous provided an optimal setting for large-scale gold mineralization throughout the NCC.

1 Introduction

Stable cratons are the most important tectonic elements of the lithosphere. Old cratons are typified by a thick lithospheric root (>150 km), weak tectonism (lacking intense crustal deformation, large-scale magmatism and strong seismicity), low densities and water contents, existence of a refractory lithospheric mantle (harzburgite of Mg#>92, high 87Sr/86Sr, low 143Nd/144Nd), and strong mechanical and chemical coupling between the crust and mantle (Hieronymus et al. 2007; Wu et al. 2014). Except for weak deep-seated magmatism, both extensive magmatism and mineralization are basically absent within the cratons. The North China Craton (NCC) is one of the oldest cratons in the world with ~3.8 Ga crystallized crustal rocks, but showing obvious differences from other Archean cratons like the Kaapvaal Craton of southern Africa and the Canadian Shield of North America (Griffin et al. 2004; Wu et al. 2014). After the Archean-Paleoproterozoic cratonization (>1.8 Ga), the NCC remained relatively stable with a thick Archean lithospheric keel until the early Mesozoic. Recent studies on Palaeozoic kimberlite and mantle peridotite xenoliths in the Cenozoic basaltic shows that the eastern portion of the NCC has experienced lithospheric thinning and craton destruction during the Phanerozoic, which completely destroyed its original rigidity. Since the middle Mesozoic, large-scale structural deformation and magmatic activity has occurred in the eastern NCC, which was accompanied by a large-scale gold mineralization.

2 Nature of craton destruction in the North China Craton

An important tectonic inversion took place in the eastern NCC during Mesozoic, which caused a great lithospheric thinning, powerful interaction between mantle and crust, and a vast period of granitic intrusion and volcanism (Zhai et al., 2003). Based on studies on mantle xenoliths or mineral inclusions in diamonds trapped in the Ordovician kimberlites from the NCC, it has been estimated that the lithosphere of the NCC had a thickness of approx. 200 km when the kimberlites erupted at about 480 Ma. However, constraints from mantle xenoliths or mineral inclusions entrained in the Cenozoic basalts reveal that the Cenozoic lithosphere of the NCC has a thickness of less than 80 km (Zhu et al. 2015), which is also consistent with geophysical data. This suggests that the lithosphere of the NCC has thinned by more than 100 km since the early Paleozoic.

The mechanism for lithospheric thinning or craton destruction of the NCC is controversial. Two common theories are thermo-chemical/mechanical erosion (Xu, 2001) and delamination (Gao et al., 2009). Comprehensive research using geological, geophysical, and geochemical data has demonstrated that the NCC had been significantly modified or destroyed in the late Mesozoic. The destruction culminated at ca. 125 Ma (Zhu et al. 2012). It is proposed that subduction of the western paleo-Pacific (Izanagi) plate is the main dynamic factor that triggered the destruction of the NCC, which highlights the role of cratonic destruction in plate tectonics (Zhu and Zheng 2009). Craton destruction in the NCC was heterogeneous. The lithosphere beneath the eastern part (east of the Taihang Mountains) of the NCC has been significantly destroyed, leading to emplacement of intermediate-acidic igneous rocks throughout a large area (Menzies et al. 2007). The lithosphere beneath the central part (Taihang-Lvliang Mountains) was slightly modified, forming the north-south distributed Taihangshan magmatic rock belt, whereas lithosphere beneath the western part (Ordos block) remains unmodified.
3 Late Mesozoic gold mineralization in the North China Craton

Craton destruction in the eastern NCC not only can cause changes in lithospheric mantle properties, strong crustal extension, and lithospheric thinning, but can also lead to development of magmatic hydrothermal solutions, fluid channelling, and formation of ore-hosting space.

The NCC is the most economically important gold region in China, and also one of the most important gold districts in the world (Goldfarb et al., 2014). Gold deposits in the NCC are generally sited in the cratonic margin (Fig. 1). Main gold districts include Jiaodong in the eastern margin, Xiaoqinling and Xiong’ershan in the southern margin, Jibei-Jidong, Chifeng-Chaoyang, Ji’nan, and Liaodong in the northern margin, and central Taihangshan in the central part of the craton. The ore-hosting wallrocks of these districts are similar, and mainly comprise Archean-Proterozoic metamorphic rocks, Mesoproterozoic and Neoproterozoic volcanic rocks, and Phanerozoic granitoids.

![Figure 1. Map of the NCC and distribution of major gold deposits in several gold districts (after Zhu et al. 2015)](image)

Geochronology using $^{40}$Ar/$^{39}$Ar dating of hydrothermal K-bearing alteration minerals (sericite, K-feldspar, muscovite, biotite) and fluid inclusions extracted from ore-related quartz, Rb-Sr isochron dating of gold-bearing pyrite, and SHRIMP U-Pb dating of hydrothermal zircons all demonstrated that gold deposits in the NCC formed in the early Cretaceous, mainly between 130 to 120 Ma (Fig. 2). This fully indicates that the gold mineralization is closely related to the destruction of the NCC.

In the eastern margin of NCC, ore-forming fluids of the two main styles of gold deposits share similar physical and chemical properties. In the early mineralizing stage, ore-forming fluids belong to the H$_2$O-CO$_2$-NaCl system, which is characterized by high to medium temperatures (250-410 °C), elevated CO$_2$, and low salinities (< 9 wt% NaCl eq.). The fluids evolved into a H$_2$O-CO$_2$-NaCl system at medium to low temperatures (200-330 °C), with decreased amounts of CO$_2$ and more variable salinities (0.5-15 wt% NaCl eq.) during the middle mineralizing stage. Finally, in the late mineralizing stage, the ore-forming fluids evolved into a H$_2$O-NaCl system at low temperatures (< 100-230 °C), low salinities (< 5 wt% NaCl eq.), and with no measurable CO$_2$. The properties of the ore-forming fluids in the Xiaoqinling and Xiong’ershan districts in the southern margin of the NCC and Central Taihangshan in the central NCC are similar to those in the eastern margin of NCC. However, several gold deposits are unique, such as the Qiyugou gold deposit in the Xiong’ershan district, and the Yixingzhi gold deposit in the central Taihangshan district, which are controlled by cryptoexplosive breccia pipes. The salinities of ore-forming fluids in these deposits vary from 6 wt% NaCl eq. to 22 wt% NaCl eq., with the highest salinity of as much as 35 wt% NaCl eq., and the peak salinities of less than or close to 10 wt% NaCl eq. These features are thought to be related to concealed magmatic bodies. Although there are similarities in fluid properties and evolution between altered rock type and quartz vein type gold deposits, the ore-forming mechanisms appear to be different. The mineralization in the altered rock type gold deposits resulted from intense water-rock interaction between the ore-forming fluids and wallrocks, whereas precipitation of gold is possibly a consequence of phase separation or boiling of the ore-forming fluids in response to pressure and temperature fluctuations within the quartz vein type gold deposits.

![Figure 2. Age framework of gold deposits, Mesozoic granitoids and mafic dikes in the different districts, NCC. (a) the eastern NCC; (b) the southern NCC; (c) the northern NCC; (d) the central NCC](image)
Hydrogen and oxygen stable isotope analyses showed that the early Cretaceous gold deposits from different regions in the NCC have similar isotopic compositions. Most of the hydrogen and oxygen isotope data lie between the magmatic water field and the global meteoric water line, demonstrating that the initial ore-forming fluids could have a magmatic source, and meteoric water should be involved in the ore-forming process during hydrothermal system circulation and evolution. Carbon stable isotope values ($\delta^{13}C = -7$ to $-3\%o$) for the early Cretaceous gold deposits in the NCC indicate that the ore-forming fluids might have originated from degassing or devolatilization of mantle-derived magmas. In contrast, sulfur isotope data for the gold deposits are highly variable. For example, $\delta^{34}S$ values of the Jiaodong gold deposits range from $-5.6\%o$ to $+14.1\%o$, which are distinct from those of chondrite or mantle-derived rocks, and indicate the presence of enriched sources from $^{34}S$-rich magmas or degassing of mantle wedges that were metasomatized by slab fluids (Fan et al. 2007). Helium-argon isotope analyses indicated that mantle-derived fluids played a key role in the formation of the early Cretaceous gold deposits in the NCC.

4 Craton destruction and large scale gold mineralization

The NCC was welded to be eastern part of Eurasian continent by Dabie-Sulu collisional orogeny in the south and Xingmeng collisional orogeny in the north during the late Paleozoic and early Mesozoic, and then it was highly influenced by the NNE-trending Pacific margin tectonic domain (Zhai et al. 2003). Evolution of continental crust in the region entered a new period of intracontinental orogeny. This intense tectonic inversion marked the end of pre-Mesozoic basin-and-range systematics, and established a basic tectonic pattern that has dominated the NCC since late Mesozoic. From Jurassic to Cretaceous, the eastern part of the NCC and the whole of eastern China witnessed a major tectonic transformation from N-S compression to NNE-SSW shearing. Accompanying the early transformation and the onset of extension, adakitic lower crust-derived granitic batholiths were emplaced, which uplifted the Precambrian basement rocks. In the Jiaodong peninsula of the eastern NCC, for example, the Linglong and Kunyushan granitic batholiths were emplaced at ca. 160 Ma within metamorphic basement represented by the Archean Jiaodong Group and Proterozoic Jingshan Group (Yang et al. 2012).

During the Cretaceous, the Chinese continent experienced westward subduction of the paleo-Pacific plate and the subducted slab stagnated at the mantle transition boundary. This led to the partial melting, non-stationary flow of the upper mantle, intense metasomatism of the lithospheric mantle, or so-called craton destruction. The craton destruction was marked by large-scale magmatism, strong extensional ductile deformation, and rift-basin formation, all of which indicate that the cratonic lithosphere has been destabilized (Zhu et al. 2012). Typical products are a series of intermediate and basic dikes and intermediate-felsic plutons with mixed lower crust–mantle features that formed during the early Cretaceous and were accompanied by the widespread formation of numerous ore deposits. The Jiaodong gold deposits and the coeval Guojialing and Sanfoshan granodioritic plutons and numerous intermediate to mafic and lamprophyre dikes (ca. 120 Ma; Fan et al. 2007) in the eastern margin of the NCC, Xiaoqinzling gold deposits and the coeval Wenyu and Liangliangshan granitoids in the southern NCC (ca. 130 Ma: Li et al. 2012), and the Shihu and Yixingzhai gold deposits and the Mapeng and Sunzhuang plutons in the Taihang Mountains in the central NCC (ca. 130 Ma: Li et al. 2013) are among the products of the early Cretaceous magmatic-hydrothermal events. Most of the gold ores were formed in a transitional compression to extensional tectonic regime. The NE–SW ore-controlling fractures in the Jiaodong district show complex sinistral and dextral shearing during the ore-forming events, with dominant sinistral movement in the early stages and dextral in the later stages. Large-scale inhomogeneous lithospheric thinning beneath the NCC has been regarded as a direct geodynamic consequence of the extensive ore-forming events. Because the magmatism and mineralization are mostly concentrated in the early Cretaceous, rapid and large-scale heterogeneous delamination would also be a feasible model for the thinning or craton destruction of the NCC.

The distribution of the major ore deposits in the NCC shows that the margins of the craton are the most favourable domains for mineralization, as these regions are more prone to be involved in tectonic regimes of subduction and collision and to channelling of ore fluids. Accompanied by craton destruction, both basic and medium-acidic magmas in the lower-middle crust experienced strong fluid exsolution due to rapid pressure reduction, which generated auriferous fluids. When intruding to shallower levels at rapid rates, magma will soon become saturated, also leading to the formation of auriferous fluids. The resulted cryptoexplosive emplacement will bring about the formation of cryptoexplosive breccia type gold deposits, such as the Qiuyugou gold deposit in the Xiong’ershan gold district, southern NCC, and the Yixingzhai gold deposit in the central part of the NCC. Abundant lamprophyre dikes occur in both Jiaodong and Xiaoqinzling gold districts, which indicate that the lithospheric mantle of the eastern NCC contained abundant water in the early Cretaceous. Strong extension would have caused water-rich lithospheric mantle to partially melt and degas, and the resultant mantle fluids would have migrated upwards to form the metallogenic systems along lithospheric-scale faults such as the Tan-Lu and Luanchuan faults. This model explains why early Cretaceous gold deposits occur in the eastern and southern margins of the NCC, such as in the Jiaodong and Xiaoqinzling gold districts, and the cyclic mineralization of craton destruction-related gold deposits.
Lithospheric extension could also cause development of secondary fractures in the middle-upper crust, thereby governing the spatial distribution of gold ore-bearing dikes, deposits, and districts. For example, gold deposits in the Jiaodong district are clearly controlled by secondary faults related to the Tan-Lu fault. In addition, subduction of the paleo-Pacific plate could have led to reactivation of early major and secondary faults, which either served as channels for auriferous fluids or preferentially formed gold deposits. Atmospheric water could infiltrate downward or migrate laterally along extensional fault systems formed during the craton destruction processes and eventually could mix with mineralizing fluids derived mainly from mantle melts. Fluid mixing should, therefore, be another important mechanism for the deposition of gold.

Zhu et al. (2015) have demonstrated well the possible relations between genesis of gold deposits and craton destruction in the NCC, and summarized the main controls of asthenospheric/lithospheric mantle-derived magma on gold mineralization as follows: (1) Mantle magma partially provides the gold and volatiles. (2) Mantle magma could underplate or intrude the lower crust and cause extensive partial melting of the lower crust. Subsequently, the magmas would ascend and may form transitory magma chambers at various crustal depths where sulfur may have fractionated to form Au-rich sulfide accumulations in the magma chambers (Muntean et al., 2011). New fluxes of more mafic magmas entering the magma chamber would have melted the sulfide accumulations to form more Au-proflic magmas (Botcharnikov et al., 2011). (3) Metal sulfides that accumulate locally in the magma chamber can be dissolved by the exsolved fluids from the magmas, or can be injected into mafic melts evolved within the magma chamber, which form gold-rich magmas. Auriferous fluid phases would be separated during the ascent into the upper crust and rapid decompression of the mafic magmas. These magmatic fluids commonly migrate along faults for a long distance, precipitate ore materials in a short time interval, and are characterized by low gradients in temperature and salinity (Muntean et al., 2011). (4) Mafic magmas can provide heat sources for metallogenesis and circulation of crustal fluids as well. Some gold in the metamorphosed mafic volcanic rocks of the NCC was leached by the hydrothermal fluid circulation (Sun et al., 2013).

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References


Geology and insights on the genesis of the Éléonore gold mine, Eeyou Istchee James Bay, Superior Province, Québec, Canada

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Abstract. The Éléonore gold deposit is predominantly hosted in metamorphosed and polydeformed Archean (<2675 Ma) turbiditic rocks of the La Grande subprovince, very near the tectonometamorphic boundary with the Opinaca subprovince. Gold mineralization consists of NNW-trending subparallel zones with a vertical extent of at least 1.4 km. Gold zones are associated with Ca-bearing, K- and B-rich alteration assemblages. Key geological features are as follows: 1) proximity to the Opinaca-La Grande boundary; 2) polyphase deformation with D1 and early D2 structures acting as structural conduits for the auriferous fluid(s) and/or controlling ore distribution and geometry; 3) CaO, MnO, K2O and B enrichments coupled with Na2O depletions; 4) löllingite-arsenopyrite-pyrrhotite ore assemblage and Au-As±Sb-Bi-W-Sn-Se-Te metallic signature; 5) locally auriferous, ca. 2612 Ma reduced tonalite/granodiorite, and ca. 2620-2603 Ma pegmatites; and 6) δ18O and δ34S signatures in agreement with metamorphic and magmatic sources for the mineralizing fluids. Gold mineralization at Éléonore is metamorphosed. It has recorded a complex multistage structural, metamorphic and magmatic history as illustrated by the well preserved characteristics of the ore system at subsurface that evolves into highly deformed and metamorphosed ore at depth where high-grade ore is, in part, hosted by paragneiss.

1 Introduction
The Éléonore gold mine entered into production in April 2015 and currently contains reserves of 4.57 Moz at 6.07 g/t Au, measured and indicated resources of 0.93 Moz at 5.66 g/t Au, and inferred resources of 2.35 Moz at 7.52 g/t Au (Goldcorp Inc., June 2016). In 2016, the mine produced 274 000 ounces of gold (Goldcorp, February 2017). Here, we describe the atypical nature of the deposit and its regional setting, with an emphasis on the timing and controls of deformation, metamorphism and coeval magmatism on the nature and distribution of gold mineralization.

2 Regional setting
The Eeyou Istchee James Bay region is located in the northeastern part of the Superior Province (Fig. 1). In this area, large granulite domains are part of the Nemiscou, Opinaca (OP) and Ashuanipi subprovinces. Local volcano-sedimentary sequences (Fig. 1) with syn- to late-tectonic intrusions and relics of reworked Mesoproterozoic basement belong to the La Grande (LG) subprovince (Goutier et Dion 2004). The OP-LG contact is the first-order metatect for gold (Ravenelle et al. 2010). The Low Formation (LF), part of the LG subprovince, hosts most of the ore at Éléonore and was deposited between <2714 and <2675 Ma (Ravenelle 2013). The LF includes wacke, aluminosilicate-bearing pelite, arenitic lenses and heterolithic conglomerate (Bandyayera et Fliszár 2007; Bandyayera et al. 2010; Fontaine et al. 2010). These sedimentary units are intruded by <2674-2668 Ma feldspar-phryic diorite porphyries (V. McNicoll, unpublished), 2612 Ma syn- to late-tectonic Cheechoo tonalite/granodiorite (Fontaine et al., 2015) and abundant ca. 2620-2603 Ma pegmatites (Ravenelle et al. 2010; Dubé et al. 2011; Ravenelle 2013; Fontaine et al. 2015).
Figure 1. Location of the Éléonore mine in the Superior Province and geological map of the mine area. References: 1: (Dubé et al. 2011); 2: (Ravenelle et al. 2010); 3: (Fontaine et al. 2015); 4: (Goutier et al. 2000); 5: (David et al. 2010); 6: (Morfin et al. 2013); 7: (V. McNicoll, unpublished); 8: (Bandyayera et al. Fliszár 2007); 9: (J. David 2005, unpublished).

The Cheechoo intrusion, which hosts newly recognized gold mineralization (Sirios 2016; Azimut Exploration 2017), is a foliated and recrystallized tonalite/granodiorite with a reduced oxidation state (ilmenite series), emplaced within the LF (Fig. 1). In the OP, regional granulite facies metamorphism and anatexis occurred over >30 m.y. (Morfin et al. 2013). Syn-D2 metamorphism, deformation and contemporaneous leucogranite veins/dykes injection occurred earlier in the granulite facies migmatites of the OP from the metamorphic peak at ca. 2671 Ma to the granite solidus at 2637 Ma (Morfin et al. 2013, 2014). Whereas within the lower-grade LG supracrustal rocks, it lasted to ca. 2620-2603 Ma (Dubé et al., 2011), suggesting diachronism in the timing of tectono-metamorphic events from the high-grade OP to the lower grade LG in a “deep-earlier” process (Stüwe 1998).

3 Geology of the Éléonore mine

In the mine area, an older sedimentary assemblage consisting of <2714 Ma massive wacke and <2697 Ma aluminosilicate-bearing pelite (Ravenelle 2013) lies structurally above a younger sedimentary assemblage. The latter is characterized by thinly bedded wacke dated at <2675 Ma (Ravenelle et al. 2010) interbedded with massive wacke and host the bulk of the gold mineralization. Various generations of leucogranitic veins and abundant barren and locally gold-bearing pegmatites (ca. 2620-2603 Ma) intruded the sedimentary rocks (Dubé et al. 2011). Although some pegmatites are mineralized, most are barren and younger than the mineralization and cross-cut the bulk of the ore (Fig. 2E). The intensity of the metamorphism recorded by the sedimentary rocks and the strain recorded by the leucogranitic veins, pegmatites and sediments, increases towards the contact with the OP subprovince, where paragneiss, migmatites and pegmatites gradually become more abundant. The metamorphic peak is estimated at 650-820°C and <6-7 kbars (Morfin et al. 2013; Fontaine et al. 2015). Polyphase deformation (D1-D3) affects the turbiditic sequence. The mineralized zones are located within a steeply plunging folded structure resulting from the interference pattern between F2 and F3 folds (Ravenelle, 2013). The NNW-trending auriferous zones (Fig. 2A and B) are surrounded by distal hydrothermal alteration, developed in both the footwall and the hangingwall of an interpreted D1 reverse fault (Fig. 2A and C). The hydrothermal system is laterally zoned with «distal» calcium-bearing replacement (>250 m), intermediate Ca-bearing (actinolite, diopside, hedenbergite) alteration (75 to 100 m), proximal Ca-bearing, K (biotite, phlogopite, muscovite, microcline) and B-rich (schorl and dravite) ore assemblages (Ravenelle et al. 2010; Ravenelle 2013; Fontaine et al. 2015). Alteration zones are commonly characterized by granoblastic recrystallization textures including poeciloblasts of hydrothermal minerals. The varied mineralization styles and complex paragenesis include stockworks with replacement zones composed of quartz, dravite, microcline, biotite, phlogopite with 1-5% of fine arsenopyrite, löllingite, pyrrhotite (Fig. 2F), quartz-
actinolite-diopside-tourmaline-arsenopyrite veins (Fig. 2D), auriferous quartz-actinolite-diopside veins, auriferous D₂ high-strain zones, and local high-grade quartz and leucocratic quartz-feldspar veins with local visible gold (Ravenelle et al. 2010; Fontaine et al. 2015). With depth, mineralization styles evolve from stockwork and replacement zones (Fig. 2F) to a highly deformed, transposed and metamorphosed ore hosted in paragneiss with löllingite, arsenopyrite, pyrrhotite assemblages (Fig. 2G). Retrospection to lower greenschist and locally prehnite-pumpellyite is common (Ravenelle et al. 2010).

4 Structural controls on gold mineralization

The mineralized zones are preferentially hosted within a thinly bedded wacke (~2675Ma) in the footwall of aluminosilicate-bearing pelite, and massive wacke (Ravenelle et al. 2010). The thinly bedded wacke is a discontinuous unit which acted as physical trap for gold mineralization due, at least in part, to the competency contrasts with the homogenous surrounding massive wacke or pelite. An interpreted D₁ reverse fault juxtaposes two distinct sedimentary assemblages (Fig. 2A and C). D₁ and early-D₂ structures are interpreted as key structural features for the fault/fracture controlled infiltration and/or trapping of the auriferous hydrothermal fluids. Progressive D₂ deformation, increasing shortening, formation of high-strain zones, transposition of F₂ fold hinges and local short limbs located in asymmetric parasitic F₂ folds are typical structural attributes (Ravenelle et al. 2010; Fontaine et al. 2015). They create structurally controlled, sub-vertical ore shoots that are collinear with F₂ fold axes and L₂ mineral lineations (Fig. 2A). D₃ is characterized by NE-trending open folding and associated crenulation cleavage.

Figure 2. A: Geology of the 410 level; B: 3D isometric view of the main mineralized zones illustrating ore shoot collinear with the main fold axis; C: Section 5839535 with K₂O/Na₂O ratio showing the proximal potassic alteration. D: Quartz-diopside-actinolite-tourmaline-arsenopyrite-pyrrhotite-gold vein from the 6000 zone; E: Pegmatite containing foliated ore fragments; F: Quartz stockwork of the 5050 zone with microcline alteration in vein selvages and dravite veinlets at high angle to the bedding; G: Metamorphosed equivalent of the 5050 zone. These samples contain gold-enriched assemblages with textures of metamorphosed sulfides.
5 Geochemical and isotopic signatures

The hydrothermal footprint includes: 1) CaO, MnO and local MgO enrichment in the Ca-bearing alteration, 2) K$_2$O and B enrichment in proximal alteration and ore coupled with depletion in Na$_2$O, and 3) Au-As-Sb-Bi-W-Sn-Se-Te signature with low base metals. Whole-rock $\delta^{18}$O analyses of altered rocks and in-situ $\delta^{34}$S analyses of gold-bearing arsenopyrite are similar to those of other orogenic gold deposits.

6 Discussion and conclusion

The formation, evolution and preservation of gold mineralization at Éléonore are related to the OP-LG first-order structure and associated second- and third-order structures, metamorphic front and magmatism. Ca-K-Si-B hydrothermal activity is associated with Au-As-Sb-Bi-W-Sn-Se-Te signature, polyphase deformation and intrusion of a 2612 Ma tonalite/granodiorite and 2620–2603 Ma signature with low base metals. Whole-rock aureole deposits and some controversial orogenic deposits, as well as pluton-related thermal area, the metallic signature, ore and alteration assemblages, the main deformation and metamorphism in the deposit metamorphosed equivalent to quartz-carbonate veins and silicate-bearing veins and replacement could represent multistage history, illustrated by the locally original 2005; Robert et al. 2007).

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References


Episodic formation of the world-class Waihi epithermal Au-Ag vein system, Hauraki Goldfield, New Zealand

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Abstract. The world-class Waihi vein system in New Zealand has produced more than 248,400 kg Au and 1.43 million kg Ag. New high-precision 40Ar/39Ar dates of adularia from different veins show that some veins formed at different times (6.15 Ma Martha vs. 5.83 and 5.85 Ma Empire and Welcome, respectively), even though they have similar mineralogy. The Martha vein formed over a period of approximately 150,000 years. The Moonlight vein, which has a different ore mineral assemblage, appears to have formed over a longer time interval that spanned formation of the Martha, Welcome, and Empire veins. These dates suggest that some veins in the Waihi vein system formed relatively quickly during only part of the lifetime of the hydrothermal system, whereas other veins may have formed over longer periods of time. However, the Au endowment of the Martha vein exceeds the Au endowment of the Moonlight vein, indicating that the total lifetime of the vein-forming hydrothermal system does not determine metal endowment.

1 Introduction

One of the major questions in mineral deposit research is whether orebodies form continuously over long periods of time, or instead form episodically during shorter, time-focussed bursts of activity. Continuing improvement in the accuracy and precision of geochronology techniques, and the application of these techniques to a larger suite of minerals is providing new insights into ore-forming processes (e.g., Cheng et al. 2013; Chiaradia et al. 2013; Lawley et al. 2013; Hickey et al. 2014). Here, we describe new high-precision 40Ar/39Ar dates of adularia from the world-class Waihi vein system in New Zealand, where previous research has demonstrated that different veins have different ore mineral assemblages (Mauk et al. 2016). Adularia dates show that some veins formed at different times, but the differences in timing do not correlate with differences in vein mineralogy.

2 Regional and local geology

The Hauraki Goldfield in New Zealand contains more than 50 adularia-sericite epithermal deposits that formed episodically during reorganization of the Miocene Northland and Colville volcanic arcs in the New Zealand region of the southwest Pacific (Christie et al. 2007; Mauk et al. 2011). Deposit ages in the goldfield range from 16.3 Ma in the north to 2 Ma in the south, and comprise two distinct groups: (1) from ~16.3 to ~10.8 Ma, epithermal veins and porphyry-style mineralization formed in the northern province in an arc that was dominated by andesitic volcanism, and (2) from 6.9 to 6.0 Ma epithermal veins in the eastern and southern provinces formed in extensional settings in an arc that was erupting andesite and rhyolite (Mauk et al. 2011). Even though Hauraki Goldfield mineralization discontinuously lasted more than 11 Ma, more than 80 percent of the known gold endowment was deposited between 6.9 and 6.0 Ma (Christie et al. 2007; Mauk et al. 2011).

The world class Waihi vein system—with past production of more than 248,400 kg (7.7 Moz) gold and 1.43 million kg (44 Moz) silver—is the largest deposit in the goldfield (Brathwaite and Faure 2002; Christie et al. 2007; Lorraine Torckler, written communication, 2016). The Waihi vein system includes the Martha, Favona, Correnso, Union, and Trio deposits (Fig. 1). Veins predominantly occur in porphyritic two-pyroxene andesite of the Waipupu Formation, which has undergone intense and pervasive hydrothermal alteration (Brathwaite and Christie 1996). Hydrothermal alteration in the Waihi district envelops all known deposits, and a 10 km² area of demagnetisation shows where hydrothermal alteration has destroyed igneous magnetite (Morrell et al. 2011).

The Martha deposit has a complex braided form that consists of several predominantly NE-striking lodes including Martha, Welcome, Empire, and Royal (Spörli and Cargill 2011). The Favona and Union Hill deposits lie to the east of Martha, and the Union, Amaranth, Correnso, and Trio deposits occur in the area between Martha and Favona (Fig. 1). The Moonlight vein is a hanging wall splay of Favona (Fig. 1). Herein, we refer to Martha, Favona, Moonlight, and Cowshed as the outermost veins of the district, and Amaranth, Trio, and Union as the central veins.

Electrum is the main ore-forming mineral within the Waihi district deposits; acanthite (Ag₂S), tetrahedrite (Cu₁₂Sb₄S₁₃), and aguilarite (Ag₄SeS) occur in variable abundances throughout the vein system, but the Sb-, As-,
and Se-bearing minerals are most abundant in the Favona and Moonlight veins. Base metal sulfide minerals—sphalerite, galena, and chalcopyrite—also commonly occur in veins; these are most abundant in the central veins, and they increase in abundance at depth in the outermost veins (Brathwaite and Faure 2002; Simpson and Mauk 2007; Mauk et al. 2016). Compared to the outermost veins, mineralogical and textural data are consistent with the central veins forming at a deeper structural level, or from hydrothermal fluids with different chemistry, or both (Mauk et al. 2016).

Previous 40Ar/39Ar dates of adularia from the Martha deposit provide a preferred age of 6.16 ± 0.06 Ma, and one 40Ar/39Ar date of adularia from the Moonlight deposit yielded 6.05 ± 0.04 Ma (Mauk et al. 2011). Because of the near-overlap of these dates, most workers had assumed that all deposits in the Waihi vein system had formed more-or-less synchronously.

3 Methods

We separated at least 4 mg of adularia from each vein that was analysed. All samples have Auckland University (AU) numbers and are lodged in the collection of the Geology Department at the University of Auckland. 40Ar/39Ar data were acquired at the U.S. Geological Survey in Denver, Colorado, USA, using the analytical methods described in the appendix of Aleinikoff et al. (2016), with the following exceptions: (1) the irradiation length was 5 megawatt hours, (2) two SAEST™ GP-50 getters were used, and (3) the only standard used was the Fish Canyon tuff (FCT) sanidine, with an age of 28.201 Ma (Kuiper et al. 2008).

4 Results

Table 1 summarizes the 40Ar/39Ar dates from this study, and shows previously published results from the Waihi vein system. All errors are reported at 2σ. Data for previous results are in Mauk et al. (2011), and raw data that underpin this study are included in Skinner (2014). In addition to the dates shown in Table 1, we used Isoplot™ (Ludwig 2003) and all available isochron dates to calculate weighted mean isochron ages for each vein—Moonlight: 5.73 ± 0.19 Ma, Martha: 6.15 ± 0.07 Ma, Welcome: 5.85 ± 0.03 Ma, and Empire: 5.83 ± 0.05 Ma.

<table>
<thead>
<tr>
<th>AU</th>
<th>Location</th>
<th>Plateau date (Ma)</th>
<th>Isochron date (Ma)</th>
<th>Source</th>
</tr>
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<tr>
<td>65769</td>
<td>Empire FW</td>
<td>5.88 ± 0.10</td>
<td>5.79 ± 0.13</td>
<td>This study</td>
</tr>
<tr>
<td>65771</td>
<td>Empire FW</td>
<td>5.91 ± 0.19</td>
<td>5.84 ± 0.06</td>
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</tr>
<tr>
<td>65749</td>
<td>Welcome - center of vein 1030 RL</td>
<td>6.00 ± 0.05</td>
<td>5.86 ± 0.05</td>
<td>This study</td>
</tr>
<tr>
<td>65741</td>
<td>Welcome - SE vein edge 1030 RL</td>
<td>5.86 ± 0.03</td>
<td>5.85 ± 0.03</td>
<td>This study</td>
</tr>
<tr>
<td>65781</td>
<td>Welcome vein</td>
<td>5.88 ± 0.10</td>
<td>5.79 ± 0.13</td>
<td>This study</td>
</tr>
<tr>
<td>55008</td>
<td>Martha</td>
<td>6.14 ± 0.04</td>
<td>6.10 ± 0.04</td>
<td>Mauk et al., 2011</td>
</tr>
<tr>
<td>55008</td>
<td>Martha</td>
<td>6.20 ± 0.07</td>
<td>6.18 ± 0.08</td>
<td>Mauk et al., 2011</td>
</tr>
<tr>
<td>65736</td>
<td>Martha - center of vein 1030 RL</td>
<td>6.03 ± 0.15</td>
<td>6.08 ± 0.05</td>
<td>This study</td>
</tr>
<tr>
<td>65789</td>
<td>Martha - NW vein edge 1030 RL</td>
<td>None</td>
<td>5.93 ± 0.06</td>
<td>This study</td>
</tr>
<tr>
<td>65780</td>
<td>Martha - SE vein edge 950 RL</td>
<td>6.10 ± 0.15</td>
<td>6.02 ± 0.05</td>
<td>This study</td>
</tr>
<tr>
<td>52123</td>
<td>Moonlight vein</td>
<td>5.79 ± 0.13</td>
<td>5.73 ± 0.19</td>
<td>This study</td>
</tr>
<tr>
<td>55007</td>
<td>Moonlight vein</td>
<td>6.01 ± 0.14</td>
<td></td>
<td>Mauk et al., 2011</td>
</tr>
<tr>
<td>55007</td>
<td>Moonlight vein</td>
<td>6.07 ± 0.10</td>
<td></td>
<td>Mauk et al., 2011</td>
</tr>
</tbody>
</table>

Table 1. 40Ar/39Ar dates of adularia from veins in the Waihi vein system. Raw data that underpin this study are reported in Skinner (2014), and previously published data are reported in Mauk et al. (2011). “AU” is the University of Auckland sample collection number.

5 Discussion

Dates of adularia from three samples from the Martha vein—AU 65736, AU 65739, and AU65780—combine to establish the duration of the hydrothermal events that formed that vein. The oldest date, 6.08 ± 0.05 Ma, is from the center of the Martha vein. A sample from the northwestern margin of this vein produced a date of 5.93 ± 0.06 Ma, and a sample from the southeastern margin of the vein yielded a date of 6.02 ± 0.05 Ma. In a simple vein that fills from edge to center, one would expect the dates at the vein margins to be the oldest. However, the veins in the Waihi vein system are very complex, showing many cross-cutting relationships. Unfortunately, the exposures where we collected these samples were too dirty and too weathered to allow mapping of cross-cutting relationships in the field (Fig. 2), but we presume that the youngest date at the vein margin reflects later fill by a separate stage. At the 2σ level, the date from the northwestern margin does not overlap with the date from the center of the vein, so these dates combine to indicate that the Martha vein formed in approximately 150,000 years. Although the
dates are analytically distinct, the time span between them is relatively short, and falls well within the 100,000 to 800,000 years of hydrothermal circulation that can be sustained by a single intrusive episode (Cathles et al. 1997). Detailed work on the Hosen-1 vein in the Hishikari deposit showed that it formed over a similar lifetime of approximately 250,000 years (Sanematsu et al. 2006).

The weighted mean ages for different veins also provide insight into the evolution of the Waihi vein system. The preferred age of the Welcome vein is 5.85 ± 0.03 Ma, which is nearly identical to the preferred age of 5.83 ± 0.05 Ma for the Empire vein. These ages are younger than, and do not overlap with the preferred age of 6.15 ± 0.07 Ma for the Martha vein. However, the youngest date from the Martha vein—the isochron date of 5.93 ± 0.06 Ma from AU65739—does overlap the dates from the Welcome and Empire veins at the 2σ level. Nonetheless, the difference in most dates, and the significant differences in the preferred ages indicate that the Martha vein formed before the Welcome and Empire veins, although Martha vein formation may have overlapped slightly with formation of the younger veins. We suggest that because the Welcome and Empire veins are hanging-wall splays of the Martha vein, later development of these splays may reflect previously unrecognized changes in the structural evolution of the Waihi vein system.

The two dates from the Welcome vein that have the greatest precision—AU65749 from the vein center and AU65741 from the SW margin of the vein—overlap within error, and available data indicate that this vein formed in 220,000 years or less.

The preferred age of the Moonlight deposit is 5.73 ± 0.19 Ma. This age is the weighted mean of dates from two samples that have relatively large errors, and do not overlap at the 1σ level. Available data are consistent with formation of the Moonlight vein synchronously with formation of the Martha, Welcome, and Empire veins. However, additional dates with greater precision are required to confirm this.

The differences in ore mineral assemblages that have been documented from different veins in the Waihi vein system cannot be accounted for by different pulses of hydrothermal fluids at different times. Dates from the Moonlight vein, which is relatively enriched in As-, Sb-, and Se-bearing minerals, overlap dates from the Martha, Welcome, and Empire veins, which contain acanthite as their predominant Ag mineral. There are no dates of the base metal rich Amaranth, Trio, and Union veins from the central portion of the Waihi vein system.

Results herein combined with previously published results indicate that the Waihi vein system formed between approximately 6.2 and 5.7 Ma, with an approximate duration of 0.5 Ma. This overall timespan is similar to that recorded at several other deposits where detailed geochronology exists—Hishikari, Japan: ~0.6 Ma (Sanematsu et al. 2006); Midas, Nevada: <0.6 Ma (Leavitt et al. 2004); Buckskin Mountain ~0.5 Ma (Vikre 2007); Tuscarora, Nevada: at most 0.3 Ma (Castor et al. 2003); Porgera, Papua New Guinea: ≤0.1 Ma (Ronacher et al. 2002); Ladolam gold, Papua New Guinea: 0.5 to 0.6 Ma (Carman 2003); and Round Mountain, Nevada: as little as 50,000 years (Henry et al. 1997). These timespans clearly demonstrate that world-class epithermal deposits can form relatively quickly—in less than 0.5 Ma, and that protracted fluid flow of more than 1 Ma is not required to form large deposits. Nonetheless, other epithermal deposits formed over timespans that exceeded 1 Ma, including the Sleeper deposit, Nevada (2.5 Ma, Conrad et al. 1993), and the El Peñón district in Chile (1.26 Ma, Warren et al. 2008).

Figure 2. Field photograph showing the relationships among samples collected from the Martha vein along the 1030 RL in the open pit.

6 Conclusions

New 40Ar/39Ar dates of adularia from the Waihi vein system, combined with previously published dates, show that the Martha vein formed earlier than its hanging-wall splays: the Empire and Welcome veins. These results may reflect a change in the stress fields in the area of the Martha mine, though additional work would be required to test this hypothesis. Even though the Waihi vein system has distinct variations in ore mineral assemblages from different veins, these variations do not correlate with different ages of different veins. Epithermal mineralization in the Waihi vein system deposited more than 8 Moz Au in approximately 0.5 Ma. The Martha vein, which has been one of the largest Au producers in the Waihi vein system, formed in approximately 150,000 years. Future work may provide even greater insights into the evolution of this world-class epithermal vein system.

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Orogenic gold veins related to transpressional shear zones along the north-western contact of the La Grande and Opinaca subprovinces, Eeyou Istchee James Bay, Québec, Canada

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Abstract. Numerous occurrences of orogenic gold quartz veins are distributed along the north-western contact of the Archean La Grande and Opinaca subprovinces (Eeyou Istchee James Bay). These veins are generally associated with reverse to dextral oblique-slip, brittle-ductile shear zones that are oriented subparallel to parallel with the contact. The multiple generations of veins comprise early quartz-carbonate veins crosscut by later quartz-tourmaline-carbonate veins. Early sulfide assemblages are dominated by pyrrhotite, followed by later arsenopyrite-pyrite assemblages. Significant gold grades are largely associated with late-kinematic arsenopyrite in volcano-sedimentary and igneous mafic host rocks, and with pyrite-chalcopyrite in veins hosted in tonalite. Three structural types of vein are observed; major subvertical, foliation parallel shear veins, subhorizontal and subvertical extension/oblique extension veins. Veins formed from these processes are interpreted as cogenetic and coeval. The estimated finite strain ellipsoids of veins show a constant orientation of Z axes and permutation of the Y and X axes. Our interpretations suggest that a majority of the orogenic gold veins were formed, and partially deformed, during transpression with a N-S oriented compressional deformation component locally expressed in reverse-sense movement, and a partitioned dextral oblique-slip component. This event can be attributed to a late major D3-M3 regional tectono-metamorphic event.

1 Introduction

Orogenic gold deposits are temporally and spatially associated with crustal-scale structures commonly associated with transpressional tectonic environments (Groves et al. 1998; Goldfarb et al. 2005). In the Archean Superior Province, orogenic gold vein fields constitute a significant portion of gold deposits, and are commonly related to second and third order brittle-ductile structures produced through multiple deformation events (Robert 1994; Robert and Poulsen 2001; Dubé and Gosselin 2007). The Eeyou Istchee James Bay region, located in the eastern Superior Province represents a new, and highly prospective area, which became known by the discovery of the world-class Roberto gold deposit (Éléonore Mine) (Fontaine et al. 2015). Gold mineralization is characterized by various mineralization styles in the region, and appears to be predominantly distributed along the contact of the La Grande and Opinaca subprovinces (LGO contact). Significant prospects include Zone32, Orfée Zone and Marco Zone (Goutier et al. 2002; Ravenelle et al. 2010; Aucoin et al. 2012; Mercier-Langevin et al. 2012; Bogatu and Huot 2016). The focus of our study is the north-western LGO contact which hosts numerous gold-bearing quartz vein occurrences similar to mineralization styles observed in the well-known Abitibi greenstone belt. As mineralization endowments in the LGO comprise many small scale occurrences, it has received a little attention. However, understanding their metallogenic characteristics may provide not only constraints for better exploration criteria, but may also significantly improve our understanding of the nature and tectono-metamorphic history of the LGO contact. We present preliminary results of our work providing the first insights on their mineralogy, structural relationships and possible implications for the tectonic evolution of the area.

2 Geological setting

The Eeyou Istchee James Bay region constitutes variably reworked Mesoarchean to Neoarchean supracrustal volcano-sedimentary packages and plutonic rocks (Goutier et al. 2001; Goutier et al. 2002; Bandyayera et al. 2010). In the study area, the La Grande subprovince consists of an ancient plutonic basement (Langelier Complex, 3452-2788 Ma: Goutier et al. 2001) which is overlain by the younger submarine, supracrustal volcano-sedimentary sequence of the Yasinski Group (2750-2725 Ma: Goutier et al. 2001). The supracrustal rocks are intruded by large volumes of tonalitic to dioritic intrusions of the Duncan suite (2716-2709 Ma: Goutier et al. 2001). The younger Opinaca subprovince (Laguiche Complex) consists of sedimentary rocks varying from felspathic wackes to monotonous biotite paragneiss with numerous syntectonic intrusions and pegmatites (2710 Ma to 2618 Ma: Goutier et al. 2001; Augland et al. 2016). The LGO contact in the study area is mainly interpreted as continuous shear zones and faults
concordant to the stratigraphy and commonly obliterated by intrusions and rarely preserved as a depositional contact (Goutier et al. 2016).

The La Grande and Opinaca subprovinces underwent three major regional tectono-metamorphic events (Goutier et al. 2001). While evidence of D1 is only preserved in the rocks older plutonic basement, the D2 affected the supracrustal rocks of the La Grande domain (Goutier et al. 2001; Mercier-Langevin et al. 2012). The D3 event strongly deformed sedimentary rocks of the Laguiche Complex, supracrustal rocks of the Yasicski Group, and Duncan intrusions. This event is characterized by N-S to NNW-SSE compression resulting in the formation of the ENE-WSW trending folds, penetrative foliation, as well as steeply dipping shear zones (Côté-Roberge et al. 2016; Goutier et al. 2016). In the Opinaca subprovince, several tectono-metamorphic phases are defined with metamorphism increasing gradually from NNW to SSE, progressing from greenschist to granulite facies in asymmetric patterns (Côté-Roberge et al. 2016). In contrast, southern parts of the LGO contact exhibit rapid changes of the metamorphic grade (Gauthier et al. 2007; Bandyayera et al. 2010; Ravenelle et al. 2010; Fontaine et al. 2015).

3 Characteristics of shear zones

Many brittle-ductile shear zones in the region form networks subparallel to parallel to lithological contacts and the interpreted LGO contact. They are typically anastomosing array of individual, discontinuous high strain zones. They exhibit varying ductile and brittle deformation textures. They are characterized by a variably developed ENE-WSW trending (mean 253/83°. Fig. 1), steeply dipping proto- to mylonitic foliation ($S_{n+1}$) which texturally transitions to the regional penetrative foliation with similar orientation. An early foliation $S_a$, where preserved, is strongly crenulated ($F_{n+1}$) and transposed by $S_{n+1}$ (e.g. S1/S2 in Mercier-Langevin et al. 2012). A regional, steeply plunging, stretching lineation orientation is dominant along the shear zones with some variations from subvertical to subhorizontal (Fig. 1). Folds observed at outcrop scale include intrafolial folds, asymmetric, close to isoclinal ‘Z’ folds with few ‘S’ folds. The fold axes are distributed along the mean plane of mylonitic foliation, in similar orientations to stretching lineations (Fig. 1). The shear zones possess a range of kinematic indicators including C-C’ structures, bookshelf textures, intrafolial folds, asymmetric porphyroclasts, all indicating reverse to dextral oblique-slip movements. At the microscopic scale, the mylonitic foliation is defined by continuous to spaced foliation and alternating bands of phyllosilicates, quartz, and carbonates in fine-grained volcanic protoliths. Spaced, anastomosed foliations accompanied with flattened grains are common in competent igneous rocks. Quartz exhibits bulging and subgrain rotation recrystallization textures. Sericite altered porphyroclasts of feldspars exhibit partial rotation, and minor early bulging recrystallization.

4 Orogenic gold veins

4.1 Mineralogy and alteration

Seven principal occurrences, along 40 km of strike length of the north-western LGO contact, were studied in detail (Fig. 1). Gold-bearing veins, closely associated with shear zones, developed in various supracrustal rocks and intrusions of the La Grande subprovince. Based on mineralogy and relative crosscutting relationships, two vein generations are documented. Early quartz-carbonate (ankerite-calcite) veins and veinlets represent a minor population of gold bearing veins while the second, later vein generation, characterized by a quartz-tourmaline-carbonate (calcite) assemblage constitutes the majority of gold-bearing veins within the study area. Sulfides occur within both veins and alteration haloes. They comprise varying amounts (up to 10% in total) of arsenopyrite, pyrrhotite, pyrite, and chalcopyrite, with traces of tellurides, galena, and sphalerite. Pyrrhotit-dominated assemblages predate the arsenopyrite-pyrite assemblages and are commonly preserved in both distal alterations and early quartz-carbonate veins. In most of the occurrences, significant gold grades are associated with paragenetically late-kinematic euhedral arsenopyrite. However, predominantly the pyrite-
chalcopryrite assemblage lacking arsenopyrite is characteristic for veins hosted in tonalite (e.g. Veine and Wogogoosh occurrences). Visible gold commonly forms inclusions or fills fractures in sulfides, though free gold grains can be found interstitial to quartz, carbonates, and tourmaline.

Hydrothermal alteration is commonly well-developed around the veins (up to several meters) and alteration mineral assemblages vary among the occurrences. Generally, proximal alteration is characterized by biotite and/or sericite-chlorite assemblages as well as strong replacement of host rock by tourmaline. Narrow albite selvages occur around veins in tonalite. Distal alteration is usually defined by the presence of carbonates (calcite-ankerite). A late, regionally widespread, hematite-epidote-calcite alteration partially overprints the early alteration assemblages along pre-existing structures.

### 4.2 Vein types and structural characteristics

The early minor quartz-carbonate veins are concentrated in fold hinges of $F_{n+1}$ folds in the Wedding-As occurrence, and occur as strongly transposed stockwork along the main shear zone at the Wogogoosh occurrence (Fig 2A). The second, quartz-tourmaline-carbonate veins form three major types according to vein geometry and their relationships to shear zones (Fig. 3) (Robert and Poulsen 2001): (1) subvertical shear (fault-fill) veins (2) subhorizontal extension/oblique extension veins; and (3) subvertical extension/oblique extension veins. The subvertical shear veins (1) represent the most common type and are oriented parallel to subparallel to the ENE-WSW trending mylonitic foliation (Fig. 2A). They extend up to tens of meters and their thickness may vary up to 1-2 meters. Generally, they possess laminated textures comprising bands of quartz, tourmaline and foliated wall rock aligned at a low angle to vein walls. Local boudinage, folding, and the various orientations of bands within veins, imply emplacement during progressive deformation. The subvertical orientation of slickensides on the wall-rock slivers and tourmaline bands clearly indicate the development of veins during reverse movement. At the microscopic scale, quartz grains are locally strongly flattened and exhibit ductile intracrystalline deformation textures such as undulatory extinction, bulging and subgrain rotation recrystallization. Subvertical extension/oblique extension veins (2) are spatially related to local shear zones and commonly developed adjacent to shear veins (Fig. 2B). Their N-S orientations at the high-angle to the stretching lineations strongly indicate contemporaneous emplacement with shear veins. Their thickness varies from a few millimeters to tens of centimeters. Subsequent folding and transposition modified their original orientation within high strain zones. However, they are well preserved in competent host rocks where they may exhibit gentle folding. They exhibit open-space filling textures, some indicating multiple openings. Such textures include fibrous tourmaline perpendicular or oblique to the fractures, and formation of internal layering (crack-seal textures). Subvertical extension/oblique extension veins (3) oriented N-S show similar features and textures to vein type (2). They are developed in narrow dikes along the shear zones or form en echelon gash vein arrays.

### 5 Interpretations and conclusions

Our observations indicate that two gold-bearing vein generations with distinct mineral assemblages, early quartz-carbonate and later, widespread quartz-tourmaline-carbonate may have developed from two distinct hydrothermal events. However, their respective absolute timing remains unconstrained. These events may be similar to the Val-d’Or area where two generations of veins, early quartz-carbonate and late quartz-tourmaline-carbonate veins were interpreted to form at different times based on the absolute dating of crosscutting syntectonic dikes (Couture et al. 1994). Ore minerals comprise early pyrrhotite assemblages followed by later arsenopyrite-pyrite assemblages. Gold grades are largely associated with late-kinematic arsenopyrite in volcano-sedimentary and igneous mafic host rocks, and with pyrite-chalcopryrite veins hosted in tonalite, suggesting fluid-rock interaction may have a strong influence on the composition of ore assemblages (Ridley and Diamond 2000). Early gold inclusions in sulfide is followed by later gold in fractures and interstices of sulfides indicates postfilling and remobilization during the late stage of progressive deformation. Hydrothermal alteration assemblages are typical of orogenic gold deposits (Groves et al. 1998). The mineral uniformity amongst all three structural types
suggests coeval and cogenetic emplacement along steeply dipping shear zones. Microstructures observed in quartz (bulging and subgrain rotation recrystallization, Stipp et al. 2002) and feldspars (bulging recrystallization, Passchier and Trouw 2005) from veins and deformed host rocks imply greenschist facies temperatures during progressive deformation. This is consistent with regional metamorphic facies interpretations (Goutier et al. 2001; Côté-Roberge et al. 2016). A summary diagram of estimated finite strain ellipsoids of veins (Fig. 3) shows a constant orientation of minimum Z axes along all occurrences while the intermediate Y and maximum X axes permutate. The formation and partial deformation of the late quartz-tourmaline-carbonate veins can be interpreted to occur during transpression with a N-S compressional deformation component accommodated by reverse motion, and local partitioning of the predominantly dextral oblique-slip component. In comparison to the regional geological history put forth by other researchers, the emplacement of the orogenic veins during the transpression can be attributed to the major D3 and M3 regional event which affected both La Grande and Opinaca subprovinces between 2.67-2.60 Ma (Goutier et al. 2001; Morfin et al. 2013).

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Divining gold in VMS systems: News from the seafloor

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Abstract. The controls on Au enrichment in VMS deposits have been a persistent theme in ore deposits research for more than 30 years. A major motivation is that Au production from massive sulfide deposits accounts for a significant portion of their metal value, and some VMS deposits are world-class gold mines containing more than 100 t Au. Early research on the behavior of Au in VMS systems focused on aqueous complexing in seawater-dominated hydrothermal fluids and leaching of Au-enriched source rocks; subsequent studies have focused on possible direct magmatic contributions of Au and the important role of boiling. Continuing efforts to document different types of seafloor hydrothermal systems in the present-day oceans, including a remarkable diversity of geodynamic settings, host rocks, fluid compositions and styles of mineralization, are providing new clues to the different causes of Au enrichment with important implications for exploration.

1 Introduction

The main geological characteristics of gold-rich VMS deposits have been extensively reviewed (e.g., Hannington et al. 1986; Large et al. 1989; Hannington and Scott 1989a,b; Large 1992; Poulsen and Hannington 1996; Sillitoe et al. 1996; Hannington et al. 1999a; Huston 2000; Dubé et al. 2007). From these studies, it is clear that highly variable amounts of gold may be found in different VMS systems, both in terms of grade and total gold content. Mercier-Langevin et al. (2011) identified a number of specific geological attributes of Au-rich VMS. Some resemble hybrid VMS-epithermal systems (e.g., Eskay Creek), whereas others are characterized by alteration or sulfide mineral assemblages that indicate a direct magmatic contribution to the hydrothermal fluids. Typically when gold is present, a plausible (if not always correct) explanation for the enrichment can be advanced. However, the majority of VMS deposits have relatively low gold grades (<1 g/t), with a “long tail” of Au-poor systems. Many contain virtually no Au at all, the absence of which is often difficult to explain when similar deposits nearby may be anomalously Au-rich.

2 Grade distribution and Au-rich giants

Gold in VMS deposits occurs in two principal geochemical associations: Cu-Au and Zn-Au (e.g., Figure 1). This distinctly bimodal grade distribution can occur in separate Cu-Au and Zn-Au deposits or within different zones of an individual deposit. Generally, there is no correlation between the gold grade or total gold content of a deposit and the particular Cu-Au or Zn-Au association (Mercier-Langevin et al. 2011). The most Au-rich ores commonly include complex mineral assemblages, for example, with abundant arsenopyrite, bornite, tennantite, or other sulfosalts and tellurides that are rare or absent in Au-poor deposits. Anomalous trace element geochemistry is also typical, including co-enrichments of the epithermal suite (Ag, As, Sb, Hg) in Zn-Au deposits and other elements interpreted to reflect a direct magmatic input (e.g., Bi, Se, Te) in Cu-Au deposits. The latter commonly have distinctive high-sulfidation sulfide mineral assemblages, which have been found in both ancient deposits and on the modern seafloor (e.g., enargite-luzonite chimneys in the Eastern Manus Basin and subseafloor sulfosalt mineralization in the Aeolian arc: Petersen et al. 2014; Dekov et al. 2016). However, normal mid-ocean ridge black smokers typically do not show any of these trace element enrichments or mineral assemblages, implying unique sources of ore fluids or other enrichment processes in the Au-rich systems.

Gold-rich seafloor hydrothermal systems fall into five broad categories: Cu-Au-rich deposits that are common in the calderas of arc-front volcanoes (Sunrise, Brothers); large Cu-Zn deposits in early-stage arc rifts (Eastern Manus Basin); Zn-Cu-Pb deposits at rifted continental margins (Hakurei deposit, Okinawa Trough); ultramafic-hosted Cu-Au mineralization at slow-spreading mid-ocean ridges (Logatchev and Ashadze deposits on the Mid-Atlantic Ridge); and large-tonnage, low grade brine-pool deposits (Atlantis II Deep of the Red Sea). The range of different deposit types highlights different metal sources and a range
of different conditions suitable for Au enrichment. Does source rock matter? Mercier-Langevin et al. (2011) noted that the most Au-rich deposits in Archean and some Paleoproterozoic greenstone belts are associated with transitional to calc-alkaline intermediate to felsic volcanic rocks, which may reflect a particularly fertile geodynamic condition and/or timing of mineralization (e.g., early arc rifting and/or a role for crustal contamination). The simplest explanation is that certain magmas are produced under these conditions that are better suited than others for the genesis of Au-rich VMS deposits. However, the enrichment of Au in a wide range of volcanic host rocks on the modern seafloor, from felsic volcanic rocks in rifted continental crust to ultramafic rocks at slow-spreading ridges (e.g., German et al. 2016), confirms that Au may be sourced from almost any magma type.

Most of the Au in VMS deposits has been mined from large-tonnage massive sulfide deposits with remarkably uniform Au grades, including such giant deposits as LaRonde-Penna and Horne. About 5% of VMS deposits in the geological record qualify as Au-rich giants, containing more than ~1 million ounces. They include very different deposit types, ranging from bimodal-mafic Cu-Zn deposits (LaRonde-Penna, Horne) to large-tonnage, Zn-rich felsic-siliciclastic deposits (La Zarza), Cu-Au-rich magmatic-hydrothermal systems (Mt. Morgan), and small high-grade epithermal-like deposits (Eskay Creek). Yet some classic VMS deposits (e.g., Kidd Creek) are notably gold poor. In this case, strongly reduced hydrothermal fluids may have been unable to transport gold along with the other metals or gold may have been lost to contemporaneous sediments, for example, contributing to regionally extensive Au-enriched black shales.

Only two large “Au-rich” deposits have been found on the modern seafloor: the Solwara 1 deposit in the Eastern Manus Basin and the Hakurei deposit in the Okinawa Trough. They also occur in very different settings and represent very different styles of mineralization. The largest known accumulation of Au on the modern seafloor is in the metalliferous sediment of the Atlantis II Deep of the Red Sea. The metalliferous muds contain ~45 tonnes of Au, but here the gold occurs in ultrafine arsenian pyrite and in non-sulfide diagenetic phases, including clays (Laurila et al. 2015), bearing little resemblance to VMS mineralization.

3 Plumbing versus priming

Predicting Au grade in VMS systems is complicated by the fact that the Au is a trace constituent of the ores. Highly variable grades reflect system dynamics, including phase separation, conductive cooling, subsurface entrainment of seawater, leaching of pre-existing gold, and inputs of magmatic volatiles. Several (or even all) of these may contribute to Au enrichment at a variety of different scales, from an individual ore lens (or chimney) to entire districts.

Sampled fluids from seafloor hydrothermal vents are often close to or oversaturated with Au (Table 1). In some cases, the concentrations are as high as in geothermal fluids from magmatic systems associated with large-tonnage Au deposits (e.g., Simmons et al. 2016). These data indicate there is no shortage of Au in sea floor hydrothermal systems. Instead, the major controls on Au

![Figure 1. Au grade distribution in massive sulfide deposits of the Eastern Manus Basin (data are shown for samples from 8 deposits, including Solwara 1: GEOMAR database)](image)

<table>
<thead>
<tr>
<th>Location</th>
<th>Temp °C</th>
<th>Depth (m)</th>
<th>Host Rock</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mid-Ocean Ridges, e.g. EPR (n=6)</td>
<td>350</td>
<td>2500-2600</td>
<td>MORB</td>
<td>1061</td>
<td>6735</td>
<td>31</td>
<td>3.6</td>
<td>0.08</td>
</tr>
<tr>
<td>Vienna Woods, Western Manus (n=3)</td>
<td>285</td>
<td>2485</td>
<td>BABB</td>
<td>286</td>
<td>1877</td>
<td>62</td>
<td>2.7</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Pacmanus, Eastern Manus (n=13)</td>
<td>358</td>
<td>1700</td>
<td>Felsic</td>
<td>16774</td>
<td>39589</td>
<td>3191</td>
<td>42.8</td>
<td>0.94</td>
</tr>
<tr>
<td>SuSu Knolls, Eastern Manus (n=11)</td>
<td>325</td>
<td>1190-1500</td>
<td>Felsic</td>
<td>14616</td>
<td>3662</td>
<td>705</td>
<td>20.7</td>
<td>0.61</td>
</tr>
<tr>
<td>Reykjanes Deep Fluid 2007 (n=3)</td>
<td>314</td>
<td>1350-1500</td>
<td>MORB</td>
<td>15467</td>
<td>14433</td>
<td>227</td>
<td>55.3</td>
<td>2.90</td>
</tr>
<tr>
<td>Reykjanes Deep Fluid 2014 (n=3)</td>
<td>302</td>
<td>1575-1600</td>
<td>MORB</td>
<td>2267</td>
<td>12933</td>
<td>1017</td>
<td>63.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Ladolam Deep Fluid (n=3)</td>
<td>&gt;275</td>
<td>1350-1500</td>
<td>Felsic</td>
<td>4450</td>
<td>185</td>
<td>23</td>
<td>6</td>
<td>16.0</td>
</tr>
<tr>
<td>Broadlands-Ohaaki (Br+47)</td>
<td>290</td>
<td>1600</td>
<td>Felsic</td>
<td>&lt;10</td>
<td>330</td>
<td>18</td>
<td>to 8</td>
<td>to 1.5</td>
</tr>
<tr>
<td>White Island (magmatic vapor)</td>
<td>345</td>
<td>0</td>
<td>Felsic</td>
<td>27</td>
<td>375</td>
<td>81</td>
<td>0.2</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Data sources: Hannington et al. (2016), Craddock (2009), Simmons et al. (2016)
enrichment appear to be the timing and mechanism of fluid release from Au-enriched reservoirs (geothermal or magmatic) and the focusing of those fluids into favorable depositional sites. Recent data from deep drill holes at Reykjanes suggest that Au-enriched reservoirs are possibly more common than previously thought and may be progressively enriched over time until the fluids are tapped and discharged to the seafloor (Hannington et al. 2016). In the case of the deep liquids from Reykjanes, at least part of the Au load is likely present as nanoparticles, allowing very large quantities of Au to accumulate in subseafloor reservoirs.

Some of the highest gold grades in black smoker vents are found in the summit calderas of arc volcanoes (e.g., Sunrise, Brothers). These systems are characterized by frequent explosive eruption of magma followed by intense but short-lived, high-temperature hydrothermal activity. Gold sourced from the magmatic volatiles is deposited in high-temperature Cu-rich chimneys, but there is relatively little accumulation of massive sulfide. High-intensity but short-lived venting results in the loss of significant Au to the black smoker plumes (e.g., Gartman et al. 2014). In contrast, low-temperature Zn-rich chimneys (i.e., white smokers or “diffusers” with high surface area) capture the Au by direct precipitation or by entrapment of Au nanoparticles (e.g., Craddock 2009).

4 A more important role for boiling

While direct magmatic contributions have been invoked to explain the Cu-Au ores in some deposits, in many cases there is little or no evidence of a magmatic input in terms of other trace elements, alteration, or isotopic systems. Often, the variations in Au grade are too localized to be explained by magmatic pulses or large-scale zone refining. New data from seafloor hydrothermal vents suggest that transient phases of boiling are far more common than previously thought and have a major impact on grade distribution. Direct observation of steam venting and large variations in vent fluid chlorinity have now been documented at dozens of different sites, both on mid-ocean ridges and in arc-backarc systems (Monecke et al. 2014). The boiling temperatures range from a few hundred degrees at shallow water depths (1,000 m) to more than 400 °C in the deep ocean. Flashing of the vent fluids is common, and at water depths close to the boiling point of seawater the phase separation is highly localized. This can lead to spectacular Au grades, with a strong Cu-Au association at the deepest vents or a Zn-Au association at shallower vents. Distinctive banding of chalcopyrite, sphalerite, galena and gold is evidence of pulsed phase separation at the highest pressures and temperatures (e.g., Hardardottir et al. 2010). But just a few meters from boiling vents, the hydrothermal venting may be occurring at much lower temperatures owing to mixing and cooling in some fracture networks and not in others. Thus, Au grades may be developed over very short distances, caused by sealing in one place, cracking in another, and the migration of phase separation across a vent field over time.

5 Implications for exploration

A wide range of different processes and metal sources contribute to Au enrichment in VMS deposits (Table 2). Recognizing that such complexity exists, and that gold enrichment may be attributed to different processes in different deposits (or even in different parts of the same deposit), has important implications for exploration, resulting in many potential targets. Most Au-rich deposits have one or more attributes, apart from their high Au contents, that distinguish them from other “Au-poor” deposits in the same district. New data from the seafloor are highlighting some of the processes that are responsible for those differences.

Acknowledgements

Financial support for this work was provided by GEOMAR Helmholtz Centre for Ocean Research Kiel and a NSERC Discovery grant to M.H.

<table>
<thead>
<tr>
<th>Au-Enrichment Process or Source</th>
<th>Example</th>
<th>Exploration Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-temperature cooling &amp; zone refining</td>
<td>TAG, MIR, Alvin Zones</td>
<td>Zn-Au association</td>
</tr>
<tr>
<td>Low-temperature boiling (shallow water)</td>
<td>Axial Seamount</td>
<td>Zn-Au-Ag-As-Sb-Hg-Tl association</td>
</tr>
<tr>
<td>High-temperature boiling (deep water)</td>
<td>Reykjanes</td>
<td>Low sulfidation Cu-Au association</td>
</tr>
<tr>
<td>Arc-related magmatic contributions</td>
<td>Sunrise, Solwara, Brothers</td>
<td>High sulfidation Cu-Au association</td>
</tr>
<tr>
<td>Enriched continental crustal sources</td>
<td>Okinawa Trough, Palinuro</td>
<td>Zn-Au-Ag-As-Sb-Hg-Tl association</td>
</tr>
<tr>
<td>Enriched mafic-ultramafic mantle sources</td>
<td>Logatchev</td>
<td>Low sulfidation Cu-Co-Ni-Au association</td>
</tr>
<tr>
<td>Brine pool dynamics &amp; diagenetic enrichment</td>
<td>Atlantis Deep Red Sea</td>
<td>Auriferous sedimentary pyrite</td>
</tr>
</tbody>
</table>

Table 2. Examples of different types of Au enrichment in seafloor hydrothermal systems.
References


Hannington MD, Scott SD (1989a) Gold mineralization in volcanogenic massive sulfides: Implications of data from active hydrothermal vents on the modern sea floor. Econ Geol Monogr 6:491–507


Epithermal ore deposits: first-order features relevant to exploration and assessment

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Abstract. The general features of ore deposits in the epithermal environment are influenced by their tectonic, magmatic and geologic associations. Geologic variability means that there is a wide variation in features associated with individual districts, deposits, and prospects. In this presentation we review some of the first-order features relevant to exploration and assessment of epithermal deposit targets. Our recommendations combine knowledge from traditional and recent geologic and genetic models with personal lessons from exploration and published exploration case studies. These recommendations provide a framework for investigation and documentation of key features such as genetic models and deposit classification, depth of formation, alteration mineralogy and zoning, and ore and gangue assemblages and textures, among others. Use of this framework for the design and later interpretation of geochemical and geophysical surveys will assist greatly in the development and testing of epithermal precious- and base-metals exploration targets.

1 Introduction

The general features of ore deposits in the epithermal environment are influenced by their tectonic, magmatic and geologic associations (Sillitoe and Hedenquist 2003). While highly variable, alteration and ore minerals plus textures and zonation patterns have defining characteristics (Arribas 1995; Hedenquist et al. 2000). These characteristics have implications for the assessment of prospects during mineral exploration.

Waldemar Lindgren recognized nearly a century ago (Lindgren 1933) that the group of ore deposits he termed epithermal formed within the upper km or so of Earth's surface. He and his colleagues appreciated that geothermal hot springs and volcanic fumaroles are the active surficial expression of hydrothermal systems that formed epithermal deposits. Lindgren realized that the epithermal group has characteristic styles of deposits, and he distinguished several deposit groups on the basis of metal association, gangue and alteration assemblages, based on relative contents of Au, Ag, base metal (Zn, Pb, and/or Cu) sulfide minerals and the abundance of Se or Te. Here we use three precious- and base-metal epithermal deposit groups, Au-Ag, Ag-Au±base metal sulfides (bms), and Au-Ag-Cu-As (Table 1). The first two groups have gangue and alteration minerals indicative of near-neutral pH fluids, whereas the alteration halos of the latter deposit style indicate an initial fluid with an acidic pH, related to volcanic emanations (Ransome 1907). These three endmembers correlate with low-, intermediate-, and high-sulfidation epithermal deposit types, respectively (Hedenquist et al. 2000).

The Ag-Au±bms and Au-Ag-Cu-As deposits may be spatially associated with one another (Hedenquist et al. 2000; Sillitoe and Hedenquist 2003), and either or both occur in association with (and centered on) subvolcanic porphyritic intrusions, which, within districts, can be hosts to more deeply formed (~1.5-3 km) porphyry Cu-Au deposits (Sillitoe 2010). These epithermal deposits are typically associated with intermediate-composition, oxidized magmas and hydrothermal fluids of moderate- to high-sulfidation state in volcanic arcs. By contrast, Au-Ag deposits (with very low base metal contents) commonly form in zones of crustal extension, typically in back-arc rifts, and are associated with more reduced and low sulfidation-state bimodal rhyolite-basalt magmatism (John et al. 2001; Einaudi et al. 2003). Volcanic rocks most commonly host all epithermal deposit styles, but all rock types, particularly sedimentary basement, can be potential hosts, especially where the ore body form is strongly influenced by structures and veins have a large vertical interval.

The low sulfide-content Au-Ag deposits in rifts typically contain arsenopyrite or pyrrhotite plus Fe-rich sphalerite, indicating a reduced and low-sulfidation state, in addition to pyrite; chalcopyrite and other intermediate sulfidation-state sulfides can be present in minor quantities, caused by sharp cooling (due to boiling). By contrast, the more sulfide-rich Ag-Au±bms veins contain chalcopyrite, tennantite/tetrahedrite, galena and low-Fe sphalerite, as well as local hematite and pyrite, defining a more oxidized and intermediate sulfidation state, related to more oxidized magmas in volcanic arcs. Enargite in Au-Ag-Cu-As deposits, also located in volcanic arcs, define these deposits as high sulfidation state, along with fine pyrite, covellite and locally native S; the early residual quartz and advanced argillic stage of alteration in these deposits is typically barren and associated with coarse pyrite. The high sulfidation state of these is related to cooling of an intermediate sulfidation-state fluid and the lack of any buffering capacity of the residual quartz host rock (Einaudi et al. 2003). In these deposits, the Au stage mainly follows the Cu stage, and is associated with chalcopyrite, tennantite/tetrahedrite and low-Fe sphalerite.
Veins of Ag-Au±bms (intermediate sulfidation-state sulfides) have local high sulfidation-state assemblages proximal to the feeder zone, and there can be local halos of advanced argillic alteration, consistent with the close genetic association of these two sulfide-rich (up to several wt% base metals) deposit styles.

2 Depth of formation

The Ag-Au±bms and Au-Ag-Cu-As deposits form as deep as ~1+ km (Table 1), with vertical ore intervals of ~100 up to 600 m; the top of ore may be 100-300 m below paleosurface. By contrast, Au-Ag deposits form at a shallower depth, and the top of ore veins may lie a few tens of meters below the paleosurface, capped by silica sinter, with a surficial blanket above the groundwater table of steam-heated acid sulfate water (pH~2.5) and kaolinite-alunite alteration. Temperature at the paleosurface was a maximum of ≤100°C, whereas temperature increases along the boiling point-for-depth curve to ~300°C at 1000 m depth (Fig. 1). This temperature-depth relation controls the distribution of temperature-sensitive alteration minerals (Fig. 2).

3 Alteration minerals and zonation

Alteration mineralogy is controlled largely by temperature as well as pH (Hedenquist et al. 2000). In Au-Ag deposits, their shallow depth of formation (Table 1) means that the paleotemperature was low, typically <230°C at paleodepths <300 m (Fig. 1). At this temperature the alteration is dominated by illite next to the vein, plus local adularia and silicification. At distal positions or depths <150 m (<200°C), interstratified illite-smectite and then smectite are the stable clays. The Ag-Au±bms deposits typically form at greater depths and hence higher temperature, to about 1 km and ~300°C. Above ~250°C the white mica in the alteration halo is crystalline (muscovite) with illite and lower temperature clays in distal positions or shallow depths over ore veins.

By contrast, Au-Ag-Cu-As deposits are proximal to intrusive centers, hosted by early-formed hypogene advanced argillic alteration (Hedenquist and Taran 2013). Core zones of residual quartz (locally vuggy in texture), closest to feeder zones, form by acidic condensates of magmatic vapor (pH~1). Alteration halos flare outward as depth decreases and consist of an inner zone of quartz-alunite-dickite that grades outward and upward to quartz-kaolinite, then to clays. Where a structure intersects a horizon of lithologic permeability, a lithocap of advanced argillic alteration can form where the acidic condensate flows laterally (Sillitoe 2010), with this lithocap typically being offset from (on the shoulder of) the deep source intrusion (Hedenquist and Taran 2013). Pyrophyllite ± diaspore is common in the high-temperature feeder zones, and similar alteration may occur in proximal positions along structures that are subsequently reopened by quartz Ag-Au±bms veins of a later system, with deep halos of white mica.

4 Gangue minerals and textures

Deposits of Ag-Au±bms and Au-Ag-Cu-As commonly have sulfate minerals such as barite and anhydrite as gangue, which indicate relatively oxidized fluid. By contrast, Au-Ag deposits do not have sulfate minerals, and the pyrrhotite, arsenopyrite plus Fe-rich sphalerite indicate a reduced fluid.
Both Au-Ag and Ag-Au±bms veins are dominated by quartz, with subsidiary adularia, carbonates (bladed calcite, indicative of boiling) and in Ag-Au±bms veins only, Mn carbonates ± rhodochrosite (Table 1). Crystalline quartz occurs in the deeper, higher temperature Ag-Au±bms veins, commonly with banded or crustiform textures, whereas finer quartz and calcedony occur at the shallower depths (and lower temperatures) of Au-Ag veins. Colloform textures are present where boiling and vapor loss of an ascending liquid, accompanied by sharp cooling (Fig. 3), results in boiling and vapor loss of an ascending liquid, which deposits as a gel, locally banded (Fig. 3, inset). Gold saturation from a bisulfide complex – dominant in epithermal systems – is strongly driven by boiling due to the loss of H₂S to the vapor phase (Hedenquist et al. 2003). The presence of such colloidal features in banded quartz veins and breccia fills are evidence of boiling and potentially gold precipitation. Indeed, high gold grades in all styles of epithermal deposit are commonly associated with such colloform or laminated colloidal features (also seen in banded quartz veins of porphyry Au deposits, again due to vapor loss).

![Figure 3. Silica solubility vs temperature for quartz, cristobalite and amorphous silica. Boiling and equilibrium vapor loss (red lines) results in the cooling liquid to shift from quartz to amorphous silica (sinter or colloid) deposition; non-equilibrium vapor loss (e.g., during sharp depressurization; dashed red line) can cause silica colloids to form with relatively small temperature decreases. Mixing of any deep liquid with a shallow groundwater (cool or steam-heated) will never cause amorphous silica to form. Inset: dendritic Au overlain by colloform bands of colloidal silica (Sleeper, NV, photograph by J Saunders; 2 mm width).](image)

### 5 Exploration implications

Ideally, exploration for epithermal prospects begins with knowledge of the tectonic setting (e.g., arc vs rift), such that the style of deposit and the nature of alteration and geochemical signature can be predicted and utilized to develop working exploration models. Assessment of prospects, once identified, will benefit from an understanding of the depth of erosion; paleosurface features such as silica sinters (or laminated colloidal silica formed in acidic lakes) and steam-heated alteration as well as the calcedony blankets formed at the paleowater table (Fig. 1) indicate little erosion (Sillitoe 2015). Zonation of alteration mineralogy (Hedenquist et al. 2003), and increasingly mineral chemistry (Chang et al. 2011), provide powerful tools to assist in the location of the feeder conduit(s) close to the main upflow center(s). Patterns of temperature-dependent alteration mineralogy and mineral composition can be mapped, assisted by SWIR (short wave infrared spectral methods). Appreciation that residual vuggy quartz and advanced argillic minerals commonly have zoning asymmetric to the feeder zone, and are typically barren of Au-Ag-Cu-As (Hedenquist et al. 2000), is essential since, where mineralized, feeder zones of lithocaps typically have higher metal grades.

In this manner, knowledge of the tectonic, magmatic and geologic setting, and documentation in plan view as well as cross- and long-section of the temperature-dependent alteration mineralogy, ore and gangue assemblages, structures and lithological information, and other potential district- or deposit-scale relevant features (such as ore and mineral textures, mineral composition, etc.) provide a framework for the design and interpretation of geochemical and geophysical surveys. For example, the nature of a geochemical anomaly (anomalous suite as well as threshold of anomaly, etc.) can be highly variable between districts and hence requires orientation surveys to provide confidence in interpretation of stream, soil and rock results. Clay halos (low resistivity zones) can vary in width depending on permeability of host rock, whereas residual quartz (particularly lithocaps) will provide high resistivity anomalies. Sulfides in narrow veins typically do not provide chargeable anomalies, whereas sulfides in lithocaps and disseminated at shallow levels of porphyry deposits do (unless supergene oxidized). Where alteration halos are sufficiently wide around veins, etc. (particularly under cover), magnetic lows may indicate extent of alteration and/or structural corridors to assist in mapping efforts. Among others, these observations will assist in the development and testing of epithermal exploration targets.

### References


Table 1: Characteristics of end-member ore deposit styles in the epithermal environment

<table>
<thead>
<tr>
<th>Deposit style (tectonic setting)</th>
<th>Depth to ore top, m (vertical interval)</th>
<th>Alteration, proximal to distal</th>
<th>Host, gangue with ore</th>
<th>Sulfide minerals</th>
<th>Ag:Au ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Ag (rift)</td>
<td>&lt;50 to 400 m (&lt;100-300 m)</td>
<td>il±ad, il, il-sm, sm</td>
<td>qz vein host, ad, cc</td>
<td>asp, po, high-Fe spl (low sulf’dn), py, Se, Mo, rare cp</td>
<td>~20:1 to &lt;1:1</td>
</tr>
<tr>
<td>Ag-Au±bms (arc)</td>
<td>100 to 800+ m (150-500+ m)</td>
<td>white mica (ms), il-sm, sm</td>
<td>qz vein host, ad, rhod, ba, an</td>
<td>py, td/tn, low-Fe spl, cp, Te (intermediate sulf’dn)</td>
<td>10-25:1 to &gt;100:1</td>
</tr>
<tr>
<td>Au-Ag-Cu-As (arc)</td>
<td>100 to 900 m (100-600+ m)</td>
<td>al, ka-dk±pi-ds, (ms), il-sm, sm</td>
<td>residual qz host, ba, an</td>
<td>py, en (lz, fa) (high sulf’dn), tn/td, low-Fe spl, cp, Te, Mo</td>
<td>~1:1 to ~100:1</td>
</tr>
</tbody>
</table>

Abbreviations: bms, base metal sulfides; sm, smectite; il, illite; il-sm, interstratified il-sm; ad, adularia; ms, muscovite; ka, kaolinite; dk, dickite; pi, pyrophyllite; ds, diaspore; cc, calcite; rhod, rhodochrosite; ba, barite; an, anhydrite; qz, quartz; asp, arsenopyrite; po, pyrrhotite; py, pyrite; spl, sphalerite; td/tn, tetrahedrite/tennantite; cp, chalcopyrite; en, enargite; lz, luzonite; fa, famatinite; Se, selenides; Te, tellurides; Mo, molybdenum anomalies; sulf’dn, sulfidation state (Einaudi et al., 2003). Arc-related deposits have variable anomalies of Bi, Sn, Cd (due to magmatic affiliation; Hedenquist et al., 2000; Sillitoe and Hedenquist, 2003)
Gold metallogeny of Greenland

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Abstract. Over half of Greenland is underlain by Archean and Paleoproterozoic rocks. Orogenic gold deposits dominate the gold metallogeny of these eras. Of those, only the Paleoproterozoic Nalunaq deposit produced gold (10.7 t). Mesozonal orogenic gold occurrences are present in Archean and Paleoproterozoic terranes, but are only poorly understood. Most of the Archean and Paleoproterozoic rocks are at high-metamorphic grade and consequently host hypozonal orogenic gold mineralization in western Greenland. The Størø gold deposit close to the capital Nuuk hosts indicated resources of 3 t Au. Other shear zone-hosted gold mineralization is of unknown origin. Epithermal gold mineralization is associated with Tertiary felsic intrusions in eastern Greenland that also host Mo-porphyry mineralization. The main identified gold resource of Greenland is hosted in the Tertiary Skaergaard gabbro intrusion and estimated at 178 t of gold. The limited amount of gold resources identified to date in Greenland is at odds with its highly favorable geology for both orogenic and epithermal-porphyry systems. This likely reflects a lack of targeted exploration and applied research in Greenland, which hampers the development of more efficient exploration models and vectors adapted to the local geological context.

1 Introduction

Understanding the distribution and potential of gold resources in a country has, important impact on its economy. The ice-free coastal area of Greenland has a similar size to Sweden or Paraguay, and contains a variable geological record spanning from some of the oldest rocks on Earth to contemporaneous glacial erosion (Fig. 1).

We review the geology of Greenland with respect to its potential to host different types of gold mineralization associated with recognised global epochs of endowment. More than half of Greenland is underlain by Archean and Paleoproterozoic rocks (Fig. 1), which host most of orogenic gold, iron-oxide copper gold (IOCG) and gold-rich volcanogenic massive sulfide (VMS) deposits. Greenlandic Proterozoic to Phanerozoic basins are under-studied in terms of gold endowment, as is the Caledonian Orogen. The Tertiary is characterized by intense magmatism due to continental break-up, and an important era for epithermal gold and gold-rich porphyry deposits.

2 Orogenic gold mineralization

Although Archean and Paleoproterozoic rocks host important orogenic gold resources globally, Greenland had only very little gold production, all coming from the ca. 1780-1760 Ma Nalunaq gold mine in South Greenland (Bell et al. 2017).

2.1 Archean orogenic gold

One reason to explain the limited Greenland gold production may be that only few occurrences belonging to the classical Archean granite-greenstone belt-hosted mesozonal orogenic gold deposits are currently known. The western part of Greenland is underlain by two Archean cratons, the Rae Craton in the north and the North Atlantic Craton (Nain) in the south. These are separated by a Paleoproterozoic orogen (Fig. 1; Kolb et al. 2016).

The Ataa gold province in the Aasiaat Domain located in the southern Rae Craton is characterized by gold mineralization in quartz-carbonate veins with a mesozonal quartz, ankerite, fuchsite, biotite, chlorite, actinolite, titanite, tourmaline, pyrrhotite, pyrite, chalcopyrite, arsenopyrite, gold and scheelite alteration assemblage (Kolb et al. 2016; Stendal at al. 1999). Auriferous veins and breccia zones are hosted by shear zones in greenstone belts and contain as much as 15.1 ppm Au over 2.8 m thickness. The extent of gold mineralization along strike and at depth has not systematically been tested.

The Godthåbsfjord and Tartoq gold provinces of the North Atlantic Craton comprise mesozonal orogenic gold occurrences at Isua and in the Tartoq area (Kolb et al. 2013; Evans and King 1993). At Isua, the poorly explored gold mineralization grading as much as 110 g/t is hosted in shear zones in amphibolite and Eoarchean tonalitic gneiss of the Isukasia terrane. Auriferous quartz veins and breccia contain hydrothermal chlorite, quartz, pyrite and chalcopyrite. Microthermometry indicates PT conditions of 420-460°C and 3.3-4.4 kbar, consistent with peak metamorphic conditions.

The Tartoq gold province is situated in the Mesoarchean greenstone belts to the north and south of the Sermiligaarsuk fjord. Since 1856, several companies have explored the area based on a gold-rich VMS model.
Gold is, however, hosted by quartz-carbonate veins in shear zones that form a complex system of 40 km strike extent. The hydrothermal alteration assemblage is dominated by quartz, ankerite, chlorite, tourmaline and pyrite, a characteristic mesozonal alteration assemblage. Locally in ultramafic wall rocks, serpentine, talc and chlorite are the hydrothermal alteration minerals. As much as 50 ppm Au is reported in grab, chip, channel and drill core samples. The ore assemblage is pyrite, arsenopyrite, pyrrhotite, chalcopyrite, tennantite and gold. The mesozonal orogenic gold mineralization of likely Mesoarchean age has never been systematically explored.

Most of the North Atlantic Craton is characterized by granite-gneiss terranes at amphibolite facies or higher metamorphic grades (Kolb et al. 2013). Consequently, most of the orogenic gold occurrences have hypozonal alteration assemblages. The Godthåbsfjord gold province comprises four main Neoarchean occurrences at Qilangaarsuit, Bjørneøen, Storo and Qussuk that cluster along the Neoarchean Ivinguit Fault. The host rocks are high-metamorphic grade greenstone belt-equivalents of ages ranging from Meso- to Neoarchean. The orogenic gold mineralization is controlled by quartz veins hosted in shear zones and fold structures. The Storo deposit has inferred resources of 885 kt at 3.4 g/t Au (3 t Au), whereas all other occurrences are not systematically explored. The hypozonal alteration assemblage consists of quartz, garnet, biotite, hornblende, pyrrhotite, arsenopyrite, chalcopyrite, gold and, locally löllingite. The estimated PT conditions for hydrothermal mineralization are 530-630°C and 4-6 kbar, which relate to Neoarchean retrogression in the shear zones that control terrane exhumation.

The Tasiusarsuaq gold province includes small Neoarchean occurrences with similar hypozonal quartz veins and hydrothermal mineral assemblages (Kolb et al. 2013). In the southern part, the ca. 2740 Ma Sermilik occurrence contains up to 6.4 ppm Au in quartz veins. The hydrothermal alteration assemblage of biotite, garnet, K-feldspar, hornblende, quartz and pyrite formed at approx. 660°C and 7.5-8 kbar, unusually high pressures.

The Mesoarchean, amphibolite facies Bjørnesund greenstone belt hosts a couple of gold occurrences in quartz-carbonate veins controlled by a Mesoarchean basal thrust (Kolb et al. 2013). The hydrothermal alteration assemblage consists of quartz, biotite, garnet, muscovite, sulfides and, locally, clinopyroxene. This assemblage is consistent with regional peak metamorphic PT conditions at 580-630°C and 4-6 kbar.

The Paamiut gold province is located farther to the south and extends for approx. 40 km inland (Kolb et al. 2013). The gold occurrences are only poorly explored although there have been reports of as much as 12 g/t Au in hydrothermal alteration zones, and as much as 4 g/t Au in quartz veins and stream sediment samples. Fieldwork in 2010 has identified four gold occurrences in a complex thrust and ramp system of unknown age. The auriferous quartz veins are generally 2 to 20 cm-wide, although a few reach 20 m in width. The wall rocks are amphibolite, tourmaline and pyrite, a characteristic mesozonal orogenic gold mineralization formed on the retrograde path during late ENE-trending folding at ~350-400°C and 3-6 kbar.

The Rae Craton in eastern Greenland is one of the least explored areas in Greenland, but auriferous quartz veins of up to 2.7 g/t Au have been identified in the Kangerlussuaq Fjord area (Kolb et al. 2016). The veins are up to 10 m-wide and have a mesozonal alteration halo of actinolite, clinopyroxene, muscovite, titanite, arsenopyrite, löllingite, pyrite, gold and minor chalcopyrite and scheelite. The hydrothermal gold mineralization formed on the retrograde path during late ENE-trending folding at ~350-400°C and 3-6 kbar.

Figure 1. Schematic geological map of Greenland showing known gold occurrences of different type. The shaded colors in the centre reflect extrapolation of geology beneath the Inland Ice.

2.2 Paleoproterozoic orogenic gold

Large areas of north, central and south Greenland are underlain by Paleoproterozoic orogens (Fig. 1). However, orogenic gold mineralization is only known from the Ketilidian Orogen in South Greenland, where the Nalunaq gold deposit is situated (Steenfelt et al. 2016).

The Nalunaq gold deposit produced 10.7 t of gold between 2004 and 2013. The 0.8-2 m-wide gold-quartz veins are controlled by a shear zone system in amphibolite
2.3 Caledonian orogenic gold

Three gold occurrences are known from the Caledonian Orogen in eastern Greenland (Fig. 1; Kolb et al. 2016), but have never been explored further. The gold occurrences are located close to a major N-S-striking décollement in the Ketilidian Orogen. The orogenic gold mineralization is widespread in Archean gabbro-anorthosite complexes throughout Greenland (Kolb at al. 2016). Most of these complexes are poorly known and mainly explored for their Cr-Ni-PGE-contents.

Eastern Greenland hosts numerous intrusions and thick plateau basalts that are related to the opening of the Atlantic Ocean in the Tertiary and the Iceland Plume (Fig. 1; Kolb et al. 2016). The world-famous, 56.0 Ma Skaergaard intrusion is situated at the mouth of the Kangerlussuaq Fjord. In 2013, Platina Resources Ltd. estimated indicated and inferred resources at 203 Mt of ore with 0.88 g/t Au and 1.33 g/t Pd with a cut-off grade of 1 g/t Au equivalent, with the potential for even larger resources of more than 285 t Au in adjacent orebodies. The layered Skaergaard intrusion is approx. 11 x 7 km in outcrop and crystallized under closed conditions from a ferrobasalt parental magma (Nielsen et al. 2015). The dominant sulfides are chalcocite, bornite and digenite. Gold mineralization is hosted in a series of mineralized layers and dominated by tetra-auricupride (AuCu). The mineralization likely formed by in-situ fractionation of interstitial melt in the solidifying cumulate. Sulfur saturation in melt of mush zones resulted in formation of immiscible sulfide droplets that scavenged precious metals. The droplets were subsequently dissolved in immiscible Fe-rich melt that transported the precious metals to the intrusion floor. The sequence of processes was repeated in the floor mush. Gold was deposited in stratified proto-macrolayers from upward migrating mush melt. A possible equivalent to contact mineralization of the Bushveld and Duluth complexes has recently been described from the northern contact of the intrusion. Less studied orthomagmatic Au-PGE occurrences are the 47.3 Ma Kap Edvard Holm Complex and the ca. 48 Ma Kruuse Fjord Gabbro Complex. The former contains 2.2 g/t Au over 1.6 m in a stratiform reef hosting 1 to 25 µm sized Ag and Cu alloys. The latter contains 293 ppb Au in grab samples in the form of native gold.

The ~55 km-long Miki Fjord and the shorter Togeda macrodikes are located ~2-20 km northeast of the Skaergaard intrusion and host Cu-PGE-Au mineralization. The mineralization contains chalcopyrite, pyrrhotite and magnetite disseminated or as stringers. Gold mineralization of up to 0.16 g/t Au is formed by <60 µm bismuthinides, tellurides and stannite group minerals as inclusions in chalcopyrite. The mineralization formed by sulfide liquid immiscibility of the basalt magma due to sulfur assimilation from the wall rock.

3 Orthomagmatic gold mineralization

Orthomagmatic Cr-Ti-V-Ni-PGE-Au mineralization is widespread in Archean gabbro-anorthosite complexes throughout Greenland (Kolb et al. 2016). The Tertiary intrusions of eastern Greenland host some Mo-porphyry deposits that are spatially associated with
epithermal veins (Kolb et al. 2016). The 39.6 Ma Flammefjeld igneous complex is situated between Kangerlussuaq Fjord and Andrup Fjord (Fig. 1). It consists of an intrusion breccia and younger quartzfeldspar porphyry and aplite. Quartz-carbonate veins with fluorite and barite, and mineralization of 0.45 g/t Au, 135 g/t Ag, 0.58 wt% Cu, 5.81 wt% Pb and 1.35 wt% Zn in hand specimen occur in the 5 km periphery of the complex. Float samples return maximum 38.4 g/t Au and in-situ grab samples up to 7.5 g/t Au. The ore mineralogy is pyrite, galena, sphalerite, chalcopyrite, tetrahedrite, arsenopyrite, electrum and minor magnetite and hematite. The generally <1 m-wide veins have colloform, crustiform or cockade structures and druses. Regional argillic alteration is common around the veins.

5 Other gold mineralization types

The Paleoproterozoic orogens in Greenland hold some of the characteristics for IOCG mineral systems (Fig. 1; Kolb et al. 2016). However, no focused investigation has been carried out to validate the occurrences. In the Kettilidian Orogen, IOCG-style mineralization is resembled by Au-Bi-Ag-As-W-Cu-Mo-bearing quartz veins in hydrothermal iron-oxide - albite alteration zones in diorite and gabbro north of Sondre Sermilik Fjord and Cu-Ag-Au hydrothermal vein mineralization at Kobberminebugt. The Josva Mine in Kobberminebugt produced ~60 t Cu, ~50 kg Ag and 0.5 kg Au from 1905-1914. The shear zone-hosted Cu-Ag-Au mineralization occurs in veins, breccias and foliation-parallel stringers, surrounded by an early albite alteration. This early alteration is overprinted by a proximal garnet-calcite-(epidote-diopside-actinolite-apatite-titanite) assemblage and a distal hornblende-biotite-epidote assemblage. The ore assemblage is bornite-chalcocite-ilmenite-magnetite-hematite-chalcopyrite(-wittichenite-electrum-pyrite-galena). The mineral assemblages indicate hydrothermal mineralization at temperatures between 475 and 660°C. The origin of the hydrothermal fluids and the timing of mineralization are, however unresolved.

In the north-eastern part of Inglefield Land, North-West Greenland, the Inglefjeld Cu-Au belt hosts numerous fault- and breccia-hosted hydrothermal alteration zones with sporadic Cu-Au mineralization in Paleoproterozoic host rocks. The Cu-Au mineralization can be followed along strike for several meters and up to 5 km in mylonite and cataclasite. The hydrothermal alteration zones consist of biotite, quartz, muscovite, graphite and chlorite. Sulfide lenses are up to 20-30 m-long and 0.1-0.5 m-wide with 30-90 vol.% sulfides, containing pyrrhotite, pyrite, chalcopyrite, cubanite, graphite and locally magnetite. The mineralization contains up to 0.4 wt.% Cu and 8.6 ppm Au. The model for Cu-Au mineralization implies hydrothermal fluid migration in shear zones and retrograde replacement of peak metamorphic mineral assemblages in alteration zones. These alteration zones have been associated with either a magmatic-metamorphic fluid source or deep-penetrating basin brines from formerly overlying, now eroded Paleozoic rocks, but a conclusive model is lacking.

6 Conclusions

The identified gold resources of Greenland are restricted to ~14 t of gold in orogenic gold deposits and 178 t of gold in one orthomagmatic deposit. The summary of the gold metallogeny shows that Greenland is underexplored and research efforts to unravel gold mineral systems are still in their infancy. Although Greenland is characterized by large areas of Archean and Paleoproterozoic terranes that host known orogenic gold occurrences, their detailed genesis is often unknown. Additionally, mineral exploration has largely been non-systematic and not been able to identify resources. The same is true for the other important class of deposits, such as epithermal gold deposits.

Western Greenland has a complex orogenic history in the Archean and orogenic gold occurrences formed in Mesozoic and Neoarchean systems at meso- and hypozonal conditions. Paleoproterozoic orogeny at the Archean craton margins is related to important meseozonal orogenic gold mineralization in South Greenland and shear zone-hosted Cu-Au mineralization of unknown origin. The Caledonian Orogen has some gold occurrences, which are neither studied nor explored. The opening of the Atlantic Ocean and the Iceland mantle plume control epithermal-porphyry and orthomagmatic systems in eastern Greenland.

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References


How can fluid inclusion studies better constrain orogenic gold deposit models: case studies from the Superior Province and Meguma terrane, Canada

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Abstract. Fluid inclusions provide the means to track the evolution of hydrothermal ore deposits, including orogenic gold deposit settings. Here examples are used to indicate that processes such as fluid cycling are preserved as evidenced by the presence of decrepitated inclusions. In addition, overpressuring of these systems is also recorded, as predicted by models for these deposits quantified using isochores for fluid inclusions. The use of evaporate mounds is presented as a means to show that chemistry of fluid inclusions is more complicated than the generally used wt. % equiv. NaCl. It is suggested that a more complete evaluation of fluid inclusions is needed to better characterize the nature of fluids and processes within orogenic gold deposits.

1 Introduction

Fluid inclusions (FI) provide the only direct means of sampling mineralizing fluids related to hydrothermal ore deposits. As such they are invaluable in terms of being able to reconstruct not only the chemistry of the ore fluid, but also the PT conditions attending the mineralizing event. For this reason FI have for many years been an integral part of ore deposit studies (e.g., Roedder 1984; Bodnar et al. 2014). In this context orogenic gold deposits (OGD) have been studied as much as any other hydrothermal ore deposit type. Compilations of the latter work (Ridley and Diamond 2000; Bodnar et al. 2014) reveal that in general the dominant fluid in OGD is aqueous-carbonic with $X(CO_2) = 0.05-0.15$ and of low salinity (i.e., 5-10 wt. % equiv. NaCl). In some studies fluid unmixing is suggested to have occurred, in which case more carbonic- and saline-rich fluids are present as a result of the immiscibility process. Also noted is the variable presence of other volatiles species, CH$_4$ and N$_2$ being the most common and potentially significant in gold precipitation. These aforementioned generalities have led to the perception of a global gold fluid having the attributes just described (e.g., Goldfarb et al. 2005). Whereas the latter has credibility, it is also worth noting that this fluid is shared with other hydrothermal ore deposits, such as skarn and granite hosted Sn-W, LCT-type pegmatites, reduced intrusion related gold (RIRG), and in some cases even porphyry copper deposits (e.g., Butte). In addition, it is noted that many gold barren metamorphic veins also share the same fluid chemistry. Thus, whereas this fluid may in fact be common to many OGD settings, it is clearly not unique to this ore environment.

The most recent summary of FI data for OGD deposits (Bodnar et al. 2014) presents results for homogenization temperatures (Th), salinities (wt. % equiv. NaCl) and $X(CO_2)$. Missing from this dataset is more specific and insightful compositional data that might provide useful in assessing the origin of the fluids, nature of the mineralizing environment, and discriminating among OGD and gold other deposit types (e.g., RIRG). In contrast, the latter summary presents LA ICP-MS data for many porphyry Cu-Mo-Au deposits. Thus, the absence of such information for OGD prevents a more definitive characterization and thus discrimination of the fluid chemistry for this deposit type. A second point worth noting is there is rarely if ever any consideration given to the textural attributes of fluid inclusions. This aspect is of particular relevance given the generally accepted model of seismic pumping for these deposits which involves repeated overpressuring of the environment. It has been known for some time now that the latter leaves its mark on FI as it induces textural re-equilibration due to changing P(fluid) (e.g., Sterner and Bodnar 1989; Diamond and Tarantola 2015). Thirdly, but not least, is the adherence to a rigorous classification scheme for FI which incorporates stringent guidelines. Although proposed for some time now, the fluid inclusion assemblage approach (FIA; Goldstein and Reynolds 1994; Bodnar 2003a) for FI classification, which provides the means to properly recognize and isolate fluid entrapment events, seems not to have been widely adopted, integrated and applied to ore deposits, including OGD studies.

In this paper we address some of the outstanding issues of FIs as they relate to OGD deposit settings 1) timing of fluid inclusion entrapment; 2) textures of fluid inclusions and their implications; 3) evidence for pressure cycling during vein formation; 4) the nature of the solute composition of FIs as inferred from evaporate mound chemistry. These latter aspects of FIs collectively imply that some of the fundamental conclusions made based on FI studies should be reconsidered and going forward a different approach be used.

2 A new approach to fluid inclusion studies of orogenic gold systems

For a FI study to have merit, to be useful and have long lasting application, it is argued that certain aspects be addressed which are then incorporated into the interpretation. Included in this would be recognition of all the FI types present a demonstrated and established relationship of each of these FI types to each other and more importantly to the gold event(s), and documentation
of the PTX for each FI type where X is NOT wt. % equiv. NaCl, but a more quantitative establishment of fluid chemistry. These aspects are further explored below with specific examples that are used to illustrate the usefulness of the proposed approach.

2.1 Timing of fluid inclusion entrapment

Discerning the timing of FI entrapment is not without challenges, particularly in OGD where a long-lived fluid-flow system has produced samples that are in general inundated with FI such that recognition of FIA is not without challenges. This does not however mean that use of the terms primary (P), secondary (S) and pseudosecondary (PS) should not be strictly adhered to. In this regard, it is the term P that is most often misused. The use of P implies a demonstrated trapping of a FIA on a growth surface, as can be observed in other settings (e.g., epithermal, porphyry). The commonly inferred use of P for the isolated 3 dimensional array (3DA) of FI is considered, therefore, an inappropriate use of the term, Roedder (1984) himself having commented on such perils decades ago and suggesting that "the safest presumption is that an inclusion is secondary until proven primary" (p. 21). Instead, the term indeterminate, as suggested by Bodnar (2003a), would be appropriate for this and FIA which do not fit easily into the P, S, or PS categories.

The application of cathodoluminescence (CL) to FI studies has provided much insight, the case of porphyry deposits perhaps illustrating this best (Pennistom-Dorland 2001; Landtwing et al. 2005). Now widely used in the latter settings, it remains to make an impact in OGD. An example of such application is shown in Figure 1, a typical quartz vein from the Meguma terrane of NS, Canada; the CL image clearly shows two stages of quartz. The significance of image relates to FI being present in the CL dark quartz which suggests the FI are therefore secondary. In contrast, the disregard of stringent use of the term P and instead application of the 3DA term would have these FI classified incorrectly.

![Figure 1. CL images of two areas from the same quartz sample hosted as part of a bedding-concordant type vein in the Caribou gold deposit, Meguma terrane of Nova Scotia. The images show the vein quartz is characterized by bright and dull CL zones. Whereas the former represent the signature of the primary quartz and has distinct CL zones related to growth features, the latter dull zones correspond to areas inundated with fluid inclusions.](image1)

A further example of the perils of FI classification relates to the presence of neonates (Fig. 2), these annual arrangement or halo of FI produced during re-equilibration of a parent inclusion induced by either ΔP or ΔT (see Diamond and Tarantola 2015), hence they are secondary with respect to their host quartz. These FI types are discussed in more detail below, but what is important here is that such inclusions would fit the 3DA classification note above and thus provide incorrect PTX information about the system. Kontak et al. (2016) suggest that in fact such inclusions are common in OGD samples due to frequency of P cycling during vein formation.

![Figure 2. Quartz-hosted FIs in sample of ore-grade vein material from the 144 Gap Zone deposit, West Timmins area. Left: Abundant decrepitated FI in clear quartz with no subgrain development. Middle: Close-up of previous image showing neonates forming haloes around central parental inclusions. Note that the types of FI in the haloes vary, which suggests these FI experienced different ΔPT conditions when decrepitated. Right: Close-up of neonate FI showing their CO2-rich nature.](image2)

2.2 Fluid inclusion textures and implications

Textures reflect a process, a case in point being bladed calcite in epithermal settings, which is well known as a proxy that can be used in the field for fluid boiling (e.g. Moncada et al. 2012). Although the shapes of FI vary considerably, which are due in part to variable deviatoric stresses, these textural features are rarely discussed let alone interpreted in the context of a process despite their relevance having been discussed for some time (e.g., Sterner and Bodnar 1989; Kontak 2002; Bodnar 2003b; Diamond and Tarantola 2015; Kontak et al. 2016). In fact, the popular seismic pump model for vein formation in OGD (Sibson et al. 1988) predicts that re-equilibration of FI should occur. It is not surprising to note therefore that in fact our studies of FI in 100s of samples from numerous OGD settings all show evidence of decrepitation! Two settings illustrate this - the intrusion hosted 144 Gap Zone from the Archean Timmins West deposit area (Fig. 2) and one of the many Lower Paleozoic Meguma deposits (Fig. 3; see Kontak et al (2016) for other examples). Two aspects are important in the context of such FI: 1) the quartz hosting the decrepitated FI do not in general record subgrain development; and 2) there are abundant equant FI present in the same areas as the decrepitates (Fig. 3). The latter observation relates to the fact that it is large macro-FI, generally >100 μm size, that record re-equilibration.

2.3 Evidence for pressure cycling

Fluid inclusions provide the means to document the
cyclicty of fluid over pressuring during the formation of orogenic veins, a process which is generally well accepted in the formation of these deposits based on, for example, the nature of the veins (Goldfarb et al. 2005). Here results of several studies that document evidence for this process are reported. Firstly, the presence of decrepitate textures, which are common for FI in many settings (Kontak 2002), are an affirmation of changing fluid pressure. Examples of these textures are shown in very different settings: an intrusion-hosted setting in the Archean of Ontario (Fig. 2), the Meguma OGD of Nova Scotia (Fig. 3), and the Archean Red Lake setting of Ontario (Fig 4). In all these cases abundant modified inclusions record decrepitate textures due to FI re-equilibrating to new PT conditions. In a detailed study of this process, Behuniak (2016) reported detailed measurements of densities and related isochores for FIA in single samples from five deposits in the Red Lake area. The results for one of these is shown in Figure 5 where the data indicate ΔP varied by about 3 kbars during vein formation and, by inference, ore forming process. Importantly the measurement of homogenization of the pure carbonic inclusions (i.e., the L CO2-V CO2-phases) in the neonates enveloping the central parental inclusions record very different densities, such as shown for an example in Figure 4, which indicates they record equilibration to new conditions. Similar results, with up to ΔP of up to 2.5 kbars, have also been recorded for several deposit settings in the Meguma terrane of Nova Scotia (Kontak et al. 2016; Choquette 2017). Thus this process is considered to be more widespread than generally considered and typical for many OGD, but just not reported as part of in FI studies.

2.4 Nature of solute chemistry in fluid inclusions

The solute chemistry of fluid inclusions is commonly reported as wt. % equiv. NaCl based on FI studies and is based on the ice melting temperature. As the latter does not discriminate for the presence of the multiple cations and anions that are likely present, unless first melting ore eutectic temperatures are noted, this is an over simplification and precludes a full characterization of the fluid chemistry of these systems and contrasts with the quantification of fluid chemistry for porphyry deposits. The use of evaporate mound chemistry (e.g., Kontak 2004) provides a simple means to characterize FI chemistry and thus provide a method to improve on the standard used past and present of wt. % equiv. NaCl, which does the discriminate among the many any solutes potentially present in vein- and ore forming fluids. The application of this method for many ore deposit many settings, including gold (Kontak et al. 2014), indicates that in fact the solute chemistry is complicated (e.g., Na-K-Ca-Mg-Fe-S-F-Cl). Thus the use of this method has the potential to improve the current characterization of fluids in OGD settings. Two examples of the application of this method are shown in Figure 6, one for a Meguma deposit and the other for an Archean intrusion-hosted setting in Timmins, Ontario. For
the Meguma ODG deposit, the data are considered to reflect equilibration of the vein fluid, originally Na-rich and Ca-poor, with the host metasediments which contributed both Ca and K to the fluid with time. For the Timmins sample, three distinct fluids are indicated, including one that is F- and S-bearing (not shown). Whereas the Ca-rich fluid is late stage with regards the quartz vein formation, it was not possible to discriminate the other two fluids thermometrically. It is also noted that in our work F and S are commonly seen in mound analysis of other gold deposits, thus they are not unusual. In addition, it is noted that whereas Ca may be inferred from low fist melting or eutectic temperatures from microthermometric studies of FI, the same cannot be said for many other elements identified in mound analyses (K, Fe, Mn, Ba, As, F, S). Thus, this simple method of providing semi-quantitative chemistry for FI provides the means of assessing the different types of fluids in OGD types for camps and districts and to track the role of processes, such as fluid:rock reactions, in these systems.

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References


Multiple sulfur isotopes monitor fluid evolution in MIF-S-bearing orogenic gold deposit

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Abstract. Recent developments in in-situ isotope analysis offer a tremendous opportunity to investigate the nature of the most important ligand for gold transport in orogenic systems: sulfur. While δ34S is able to track changes in the evolving primary nature of ore-forming fluids, a second tracer Δ33S is virtually indelible and can uniquely fingerprint sulfur derived from Archean sediments. Here, we apply measurements of δ34S and Δ33S from spatially constrained samples across a gold lode and its alteration halo located in the Eastern Goldfields, Australia. By combining both the δ34S and Δ33S tracers to a detailed multi-sulfide petrogenesis, we demonstrate 1) the presence of mass independent fractionated sulfur (MIF-S; Δ33S = +0.4‰) in the ore fluid and 2) an evolution toward increasingly light δ34S values (from +1‰ to -8‰) through time at constant Δ33S. These results indicate that sulfur (and potentially Au) is at least partially derived from Archean sediments. Further, in delineating the unchanging source of sulfur (as constant Δ33S), we were able to monitor the evolution of the ore fluid, capturing a change in oxidation state related to Au precipitation. Rapid changes in pressure control oxidation of the fluid, highlighting the importance of fault-valve cycles in some orogenic gold deposits.

1 Introduction

Orogenic gold deposits have formed along the margins of lithospheric blocks throughout Earth’s Mesoarchean to present history. However, because all orogenic deposits are separated from their source, the source of the fluid is commonly difficult to interpret and locate, leading to debate surrounding fluid and/or metal sources that may involve mantle, magmatic or metamorphic reservoirs (Goldfarb and Groves 2015). What is recognised is the temporal and spatial overlap between gold mineralisation and crustal growth (e.g., Frimmel 2008), indicating the link between tectono-magmatic processes and mineralising systems.

Sulfur cycling between geochemical reservoirs plays an important role in the Earth’s evolving geosphere. As such, tracing the pathway of sulfur from one reservoir to another has the potential to illuminate global-scale processes linked to crustal growth. Mass independent fractionation of sulfur (MIF-S) is an isotopic signature unique to a single reservoir, the Archean sedimentary record (Farquhar et al. 2000). Tracing this distinctive signature has highlighted the importance of lithospheric-scale volatile recycling at craton margins (LaFlamme et al. In review) and in the formation of orogenic gold deposits (Selvaraja et al. 2017a), where hydrothermal fluid migration transports Au as bi- or tri-sulfide complexes (e.g. Loucks and Mavrogenes 1999; Pokrovski and Dubrovinsky 2011).

Investigation of mass dependent fractionation of sulfur (monitored as δ34S) may lend insight into the geochemical reservoir(s) from which sulfur is sourced (Alt et al. 1993). However, δ34S alone may not be sufficient to comprehensively image dynamic mineral systems where chemical processes such as dissolution, precipitation, fluid phase unmixing and redox reactions are parameters that regulate metal mobilisation, transport and deposition (Palin and Xu 2000). By contrast MIF-S, quantified as Δ33S, is a chemically conservative tracer representing the deviation from mass dependent fractionation processes in the Archean sedimentary rock record. Recycled Δ33S may only be diluted but it is not affected by dynamic chemical processes. The combination of Δ33S and δ34S in a mineral system thus allows us to discern changing sulfur reservoir inputs and evolving chemical parameters (e.g. pH, fO2, f/S2). This is critical, as changing chemical parameters of the Au-bearing fluid is key to understanding the processes governing Au precipitation (Ohmoto 1986), and by inference predicting their location.

Debate surrounds wide-ranging δ34S in orogenic gold deposits, and has been attributed to different source fluids (Goldfarb et al. 2005), rapid changes in pressure (fault-valve kinematics; e.g., Hodkiewicz et al. 2009), input of granitic magmas (e.g., Hagemann and Cassidy 2000), and/or fluid-rock interaction (e.g., Sangster 1992). Recently, both δ34S and Δ33S have been applied to Archean orogenic gold deposits, proving to radically change the understanding of source reservoirs by establishing that a component of sulfur (and potentially Au) is commonly derived from Archean sedimentary rocks (Selvaraja et al. 2017b; Agangi et al. 2016). Here, we further these observations by monitoring MIF-S throughout the mineralising evolution of an orogenic gold deposit, to discriminate between changes in source reservoir versus fluid processes that control Au precipitation.

To address source and chemical controls on mineralization, we present a multi-scale (deposit- to grain-scale) in-situ multiple sulfur isotope study of the multi-sulfide paragenetic sequence that defines the Waroonga orogenic gold deposit of the Yilgarn Craton. Here, we assess how δ34S relates temporally to Δ33S in space and time, to monitor the chemical evolution of a Au-bearing fluid.

2 The Agnew orogenic gold camp

The Waroonga deposit is located in the Agnew district,
forming part of the Eastern Goldfields region of the Yilgarn Craton. The Agnew district is located within a 7 km thick basal greenstone pile, being dominantly composed of tholeiitic basalt, high-Mg basalt, ultramafic rock, gabbro and gabbro-pyroxenite peridotite sills and minor interbedded sedimentary layers (Platt et al. 1978; Hayman et al. 2015). The greenstone was intruded by the ca. 2666-2655 Ma granitoids, as well as numerous sill complexes (Squire et al. 2010).

Unconformably overlying the greenstone pile are two sedimentary basins. In the vicinity of the Waroonga deposit, the Scotty Creek Formation comprises mafic-ultramafic conglomerate and polymeric volcanic conglomerate suggesting local sourcing from the underlying greenstone pile. Further up section the Scotty Creek Formation becomes a quartzofeldspathic sandstone that was deposited in a shallow fluvial depositional environment and has a maximum depositional age of ca. 2664 Ma (Squire et al. 2010).

2.1 The Waroonga deposit

Mineralisation at the Waroonga deposit is structurally controlled and hosted in the Emu Shear Zone which cuts across the Scotty Creek Formation. The shear zone is characterised by actinolite-biotite alteration and is associated with laminated and brecciated quartz veins. Regionally, shearing is associated with ca. 2636 Ma oblique collision during the Kalgoorlie Orogeny (e.g., Duuring et al. 2012).

Mineralisation occurs within distinct ore shoots, the largest identified being the Kim lode. Within the Kim lode, Au is intimately associated with up to 5 m wide laminated quartz breccia. Mineralisation is thought to have developed late in the shearing history and is characterised by arsenopyrite + chalcopyrite + galena + pyrrhotite + tetrahedrite. + Au. Sulfide-bearing samples were selected from the Waroonga deposit to represent a spatially-constrained cross section through the Kim lode (Fig. 1).

![Figure 1. Spatially-controlled sampling for multiple sulfur isotope analysis at the Waroonga deposit Kim lode.](image)

3 Methods

Characterisation of <50 μm sulfides by Energy-dispersive X-ray spectroscopy (EDS), and identification of fractures, inclusions and zoning by backscatter electron (BSE) imaging occurred using a FEI Verios 460 XHR SEM under conditions of 15 kV with a focused 6.0 nA beam at the CMCA, University of Western Australia (UWA).

Multiple sulfur isotopic ratios were determined using a CAMECA IMS1280 large geometry ion microprobe located at CMCA-UWA, following the procedures defined in LaFlamme et al. (2016). Briefly, mounts (25 mm diameter) were made by coring puck (3.2 mm in diameter) of rock and casting in epoxy. After polishing, mounts were coated with 30 nm of Au and loaded with a standard block into the sample chamber. A 3.7-4.6 nA focused Cs+ primary beam interacted with the sample at 20 keV. The beam, in Gaussian mode, bombarded the sample surface to create a 15 μm analytical pit.

Isotopes $^{33}$S, $^{34}$S and $^{35}$S were simultaneously detected by three Faraday Cuts using amplifiers with $10^6 \Omega$ (L1/2), $10^{11} \Omega$ (L1), and $10^{10} \Omega$ (FC2 or H1) resistors. Data were collected over 123 s of acquisition time in 20 integration cycles. Measurements were interspersed with Sierra pyrite $(\delta^{34}S = +2.17‰, \Delta^{33}S = -0.02‰)$ to correct for drift and monitor internal sample repeatability. As well, analyses of matrix-matched reference material were used to calibrate isotope ratios for chalcopyrite (Nifty-b: $\delta^{34}S = -3.58‰, \Delta^{33}S = +0.06‰$), pyrrhotite (Alexo: $\delta^{34}S = +5.23‰, \Delta^{33}S = -0.96‰$), and arsenopyrite (in house ASP200: $\delta^{34}S = +1.50‰, \Delta^{33}S = -0.50‰$). Measurement error (2σ) on $\delta^{34}S$ is equal to about $-0.4‰$ and on $\Delta^{33}S$ is $-0.25‰$.

4 Petrogenesis and sulfur isotope results

Detailed petrographic observations and chemical analysis demonstrate an evolving mineralising event. Chalcopyrite and pyrrhotite are early in the mineral assemblage and restricted to the wall rock and brecciated fragments of wall rock in the laminated quartz breccia. Equant arsenopyrite is prevalent throughout mineralisation. Free Au and galena are associated with arsenopyrite within the laminated quartz but not with arsenopyrite within the silicified clasts of wall rock that together form the breccia.

To monitor the ore fluid evolution in the system, in-situ multiple sulfur isotope analysis targeted three sulphide phases (pyrrhotite, chalcopyrite, arsenopyrite) as well as cores and rims of arsenopyrite (Fig. 2). All phases yield $\Delta^{33}S$ values that range from $+0.1‰$ to $+0.6‰$ with a mean of $+0.3\pm0.2‰$ (2SD on the mean). Chalcopyrite and pyrrhotite (within the wall rock) yield $\delta^{34}S$ values that range from $+0.7‰$ to $+2.9‰$. Arsenopyrite from the wall rock yields $\delta^{34}S$ values that range from $-1.8‰$ to $+0.8‰$. 
Detailed BSE imaging of arsenopyrite in laminated quartz vein highlights cores and rims, rims being associated with gn and Au (Fig. 3). Cores yield δ34S values that cluster at -0.5 ± 0.4‰ (2SD on the mean) whereas rims yield a large spread in δ34S values from -7.6‰ to +0.5‰.

Figure 3. Multiple sulfur isotope results from cores and rims of arsenopyrite (apy) associated with Au. Rims are associated with Au and galena (gn).

5 Combined in-situ Δ33S and δ34S to monitor fluid evolution

Sulfur isotope datasets from hydrothermal systems often report a spread in δ34S space (e.g., Hodkiewicz et al. 2009), due to its sensitivity to both changing input of sulfur reservoirs and changing thermochemical fluid conditions. Here, we apply spatial and temporal controls to in-situ measurements which include two independent sulfur isotope tracers, Δ33S and δ34S, in order to place multidimensional constraints on the mineralising fluid evolution. The spatial and temporal dimensions are controlled by assessing sulfide phases throughout the petrogenetic mineralisation sequence within and distal to the Au-hosting laminated breccia.

Our results show an anomalous and unchanging Δ33S throughout the evolution of mineralisation from chalcopyrite + pyrrhotite to arsenopyrite cores to arsenopyrite rims associated with galena and Au (Fig. 3). However, in contrast δ34S shifts to increasingly light values throughout the fluid evolution, and the lightest (most negative) values being associated with the precipitation of arsenopyrite rims in equilibrium with Au.

Shifts to increasingly lighter δ34S in hydrothermal systems have previously been attributed to the incorporation of oxidised magmatic fluids associated with coeval granite emplacement (Cameron and Hattori 1987) and/or ore fluid reactions with host rock. Deeply seated magmatic fluids did not interact with an oxygen-poor atmosphere and therefore have Δ33S = 0 (Labidi et al. 2013). Their incorporation would produce a significant dilution of the observed Δ33S signal during the evolution of the ore fluid. Wall rock sulfidation or carbonation would also change Δ33S with respect to δ34S, which is sensitive to changes in HSO₄ to H₂S proportions.

Rather our results demonstrate an invariable Δ33S, precluding changes of the sulfur reservoir source through time. This implies that a single, ubiquitous ore fluid is responsible for mineralisation and that increasingly light δ34S reflects sensitivity to the fluid oxidation state. To explain the progressive oxidation of the ore fluid which (in this instance) is critical to Au precipitation, we invoke the theory that rapid fluid-pressure fluctuations during fault-valve cycles led to phase separation, as previously proposed by Hodkiewicz et al. (2009). During phase separation reduced gases are preferentially partitioned into a vapour phase, which increases the ratio of SO₄ to H₂S in the residual ore fluid (Ohimoto 1986). The oxidised ore fluid destabilises Au-sulfide complexes. At the large-scale, fault valve cycles are related to shear failure and dilation attributed to seismicity at plate boundaries (Cox 2016).

6 Fingerprinting a unique sulfur reservoir

The multiple sulfur isotope results from the Waroonga orogenic gold deposit yield a significant MIF-S signature, typically equal to Δ33S = +0.2–0.5‰. Although measurement error on each analysis is similar to the Δ33S value, the MIF-S is consistently positive for all 282 analyses demonstrating that sulfur in the mineral system is at least partially derived from the Archean sedimentary rock record. Positive Δ33S values are preserved in Archean carbonaceous sediments. This signature is unique to the
Archean sedimentary record, forming in the Archean oxygen-poor atmosphere.

The mineralising system at Waroonga preserves a ubiquitous positive $\Delta^{34}S$ signature that in early mineralisation (pyrrhotite + chalcopyrite) has a $\Delta^{33}S/\delta^{34}S = -0.7$. This initial ratio is important because in $\delta^{34}S$-$\Delta^{34}S$ space, the primary Archean sedimentary record preserves an array, known as the Archean reference array, equal to about $\Delta^{33}S/\delta^{34}S = -0.7$, that is consistent throughout the Archean (Thomassot et al. 2015 and references therein). Therefore, we argue that the source of sulfur at the Waroonga deposit is at least partially derived from devolutilisation of carbonaceous shales, evidence to further the ideas proposed by Tomkins (2013). As carbonaceous shales are known to locally contain elevated Au concentrations (Large et al. 2011), we argue that they may be important to the formation of orogenic gold deposits.

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Multi-stage hydrothermal processes and diverse metal associations in orogenic gold deposits of the Central Lapland greenstone belt, Finland

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Abstract: Results of systematic U-Pb dating of hydrothermal monazite and xenotime by LA ICP-MS method together with other geochronological data suggest that formation of gold deposits took place during the accretion-collision (~1.91 Ga) and the late-/post-orogenic (~1.80-1.77 Ga) stages of the tectonic evolution in the Central Lapland greenstone belt. The same crustal structures channelled multi-stage fluid flow events, and sulphur isotope data together with the trace element compositions of sulphide minerals indicate that episodic involvement of fluids from local sources in the regional circulation of metamorphic fluids led to the variation in the base metal contents of orogenic gold deposits in this belt.

1 Introduction

The Paleoproterozoic Central Lapland greenstone belt (CLGB) covers a ca. 40 000 km² area in northern Finland and it is one of the most important orogenic gold metallogenic provinces in Europe. In this belt, the Kittilä Mine (Agnico-Eagle Ltd.) at the Suurikuusikko deposit (Fig. 1) is currently the largest primary gold producer (177,374 oz in 2015) in Europe and there are numerous, although smaller past-producers (e.g. Saattopora and Pahtavaara deposits) and gold occurrences still under intense exploration. In the CLGB, gold deposits show rather diverse metal associations and some of them contain significant concentrations of copper, cobalt and nickel in addition of gold (Fig. 1). For testing the hypothesis that multiple hydrothermal pulses with different fluid and metal sources were involved in the formation of orogenic gold deposits with diverse metal associations in the CLGB, we applied in situ multi-, and single-collector LA ICP-MS analytical techniques with high spatial resolution for U-Pb dating of hydrothermal monazite and xenotime, as well as for sulphur isotope and trace element characterization of sulphide minerals.

2 Regional geology and tectonic evolution

The CLGB consists of a supracrustal sequence of mafic-ultramafic metavolcanic rocks, mafic dikes and sills, quartzites, phyllites and graphitic schists. Metamorphism and deformation of these rocks took place during the Svecofennian orogeny (1.92-1.80 Ga). The protoliths of these rocks were deposited during the elongated and repeated rifting of the Archaean Karelian craton (Fig. 1).

Calc-alkaline intermediate-felsic volcanism and deposition of clastic sediments (Salla Group) was followed by accumulation of komatiitic-tholeitic volcanic rocks and terrestrial to shallow marine sedimentary units (Kuusamo and Sodankylä Group) during the early stages of intracratonic or cratonic margin rifting between 2.44 and ca. 2.2 Ga. Komatiites-picrites and high-Mg basalts erupted and shallow to deep marine sediments were accumulated during the re-activation of rifting between ca. 2.2 – 2.05 Ga (Savukoski Group; Fig. 1). The continental break-up commenced at around 2.05 Ga and extensive komatiitic and basaltic lavas, as well as turbiditic and carbonaceous material rich deep marine sediments (Kittilä Group; Fig. 1) were deposited in the oceanic basin(s). The closure of the oceanic basin(s) led to accretion of the Kola, Karelia and Norbotten microcontinents between 1.92 and 1.87 Ga, followed by continental extension (from ca.1.88 to 1.85 Ga), continent-continent collision (1.85-1.79 Ga) and final orogenic collapse and stabilization between 1.80-1.77 Ga (Lahtinen et al 2003). Syn-orogenic (Vuotsa Complex, 1.91 Ga) and late/post-orogenic (Nattanen Suite, 1.81-1.77 Ga) granitoids intruded the northern part of the CLGB (Fig. 1D). Other felsic complexes with less known relationships to orogenic stages also occur in the CLGB.

The main D1 ductile and D2 brittle-ductile deformation in the CLGB took place in conjunction with the SW-vergent thrusting of the Inari Granulite Belt and northward-oriented thrusting along the south-dipping Sirkka Line (Fig. 1 A) during accretion of microcontinents. The NE oriented major strike-slip fault zones were also formed during this tectonic stage. However, the timing of D3 is a bit ambiguous and local tectonic features also support its placement into the later tectonic stages. Late brittle (D3) deformation features are connected to the late-to post-orogenic tectonism (<1.82 Ga). The mid-greenschist facies peak metamorphism in the middle part of the CLGB was reached during the early stages deformations. The metamorphic grade increases up to mid-to upper amphibolite facies along the southern, western and northeastern boundaries of the CLGB and in the vicinity of the granitoid intrusions.

3 Gold deposits in the CLGB

The occurrences of gold only deposits in the CLGB, including the Suurikuusikko deposit, are mostly confined to the zones of NE-SW oriented strike-slip faults (e.g. the
Apart of mafic-ultramafic metavolcanic rocks and felsic plutonic rocks, stratigraphic units older than the Savukoski group are not differentiated from the Archaean basement.

**a** major structures and districts of gold only and gold-base metal deposits.

**b** distribution of mafic-ultramafic metavolcanic rocks.

**c** distribution of metasedimentary units containing carbonaceous material rich sulphidic formations.

**d** distribution of felsic plutonic rocks.

Kiistala Line), whereas the Au-(Co)-Cu deposits are preferably located along the WNW-ESW oriented thrust faults (e.g. the zone of the Sirkka Line; Fig.1). Gold mineralization along the Kiistala Line is hosted by the volcanic and sedimentary rocks of the Kittilä Group. The 1.91 Ga felsic porphyry dikes intruding the Kittilä Group are also mineralized. The gold deposits along the Sirkka Line are hosted by the ultramafic-mafic and sedimentary units of the Savukoski Group or they are located in the contact zone of the Savukoski and Kittilä Groups. Locally, 2.2-2.0 Ga mafic dikes and 2.0 Ga felsic porphyry dikes also occur in the host rock assemblage.

We selected the Suurikuusikko and Iso-Kuoisko gold only deposits along the Kiistala Line and the Saattopora and Levijärvi Au-Cu deposits along the Sirkka Line for the purpose of the current comparative studies in the CLGB (Fig. 1). The different host rocks in these deposits show similar hydrothermal alteration with early barren albitionization and superimposing quartz-albite-carbonate and carbonate-quartz(-tourmaline)-sulphide veining with pervasive carbonate alteration and localized biotitization and sericitization.

The gold ore at the Suurikuusikko deposit is refractory and gold is almost exclusively hosted by the structure of arsenopyrite and pyrite occurring in disseminations or in quartz-carbonate stockworks. Apart of pyrrhotite and minor amount of stibnite, other sulphide minerals are very rare in this deposit. The euhedral grains of auriferous pyrite and arsenopyrite are deformed and show well observable zoning. The Iso-Kuoisko deposit also contain subordinate amounts of an early stage refractory gold ore similar to the gold mineralization at the Suurikuusikko deposit. However, the major amount of gold is confined to late fractures in the form of free native gold grains associated with native bismuth, maldonite, galena, and altaite. These fractures cut massive pyrrhotite filling up open spaces in earlier formed quartz-carbonate veins or net-textured pyrrhotite masses infiltrating altered host rocks.

Visible gold in the Saattopora deposit is confined to late carbonate-quartz-tourmaline veins and matrixes of hydrothermal breccias. The veins and breccias cut strongly albitized metasedimentary and metavolcanic units. The major sulphide minerals in these veins are pyrrhotite, pyrite, chalcopyrite, arsenopyrite, gersdorffite and pentlandite. Minor amounts of uraniumite often crusted by pyrobitumen are also present in the veins. In the zones of cross-cutting mafic and felsic dikes the disseminated
mineralization also contain abundant magnetite. The mineralogy and texture of visible gold-bearing mineralization at Levijärvi is comparable with the Saattopora deposit, but magnetite-rich zones are absent, and pyrite is very rare in the parageneses of sulphide minerals.

4 Geochronology of hydrothermal processes in the CLGB

Previous geochronological studies obtained an 1916 ± 19 Ma Re-Os isochron age for gold bearing arsenopyrite from the Suurikuusikko deposit (Vyche et al. 2015). Mänttäri (1995) proposed 1.78-1.75 Ga age for the formation of gold bearing veins in the Saattopora deposit on the basis of U-Pb dating of hydrothermal monazite, rutile and tucholite. During our current studies, more than 200 polished thin sections from the selected ore deposits were checked by SEM in order to define textural settings and mineral parageneses of hydrothermal monazite and xenotime grains large enough (e.g. min. 20 μm) for U-Pb dating by

![Figure 2. Results of U-Pb dating of hydrothermal monazite and xenotime from selected ore deposits and comparison of results to the timing of major tectonic, metamorphic and magmatic events in the CLGB. Ages marked by yellow ellipses are from this study, timing of deformation, metamorphic events and ages for magmatism are from Rastas et al. (2001) Hanski and Huhma (2005), Höltschi et al. (2007), Eilu et al. (2007) and Patison et al. (2007).](image)

the applied LA ICP-MS analytical technique (Kurhila et al. 2017). Samples from the Suurikuusikko deposit did not provide monazite and xenotime useful for the purpose of our studies.

Results of our geochronological studies indicate that the zones along the major crustal structures were repeatedly re-activated and mineralized during the ca. 140 Ma long orogenic evolution of the CLGB. The hydrothermal processes were commenced during the early accretional stage of the orogenic evolution at around 1.9-1.90 Ga not only along the Kiistala Line but also along the Sirkka Line (Figs. 1 and 2). However, this stage did not produced gold at the Levijärvi deposit. Regional fluid flow events also took place at around 1.85 Ga: formation of some chalcopyrite rich veins can be connected to this stage at Saattopora, whereas veins with ages at around 1.85 Ga appears to be barren in other deposits. The formation of the magnetite-rich disseminations at Saattopora post-dates this mineralization event and took place at around 1.82 Ga, during a transient extensional stage of the orogenic evolution. Apart of the Suurikuusikko deposit, the late to post-orogenic fluid flow events between 1.8 and 1.76 Ga were the major stages of gold and base metal accumulation in deposits both along the Kiistala Line and the Sirkka Line.

5 Fluid and metal sources: sulphur isotope and sulphide trace element data

Systematic sulphur isotope analyses of pyrite, pyrrhotite and chalcopyrite from the selected ore deposits were performed by multi-collector LA ICP-MS analyses: details of analytical conditions are given in Molnár et al. (2016). Determination of Au, As, Co, Ni, Sb, Sn, Se, Te, Hg, Mo, Pb and Bi contents of these sulphide minerals and arsenopyrite was performed by single collector LA ICP-MS analyses. About 1/3 of trace element analytical spots were placed next to the sites of sulphur isotope analyses in these minerals.

The most common δ34S values for the analysed sulphides are between 0 and +5 ‰ in all deposits (Fig. 3), and generally, there is no correlation between the textural settings of sulphide grains and their sulphur isotope data in most deposits. This feature suggests a common homogeneous or homogenized source of sulphur during the multi-stage, regional scale hydrothermal processes in the CLGB. However, there are significant deviations from the typical range of sulphur isotope data in some samples from the Suurikuusikko and Saattopora deposits: this is exemplified by presentation of data for pyrite on Figure 3. At Saattopora, pyrite from the magnetite-bearing disseminated mineralization is characterized by up to +20 ‰ δ34S values, whereas some coarse-grained hydrothermal pyrite from the metasedimentary host rocks of the gold ore at the Suurikuusikko deposit provided negative δ34S values. These deviations indicate local involvement of metasediment sourced sulphur in certain stages of
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6 Summary and conclusions

The ca. 140 Ma long orogenic evolution of the Paleoproterozoic CLGB is characterized by multi-stage hydrothermal processes along the major structures of the belt. Accumulation of gold is confined to the early accretional stage at around 1.91 Ga and to the late/post-orogenic stages between 1.8 and 1.76 Ga. All of the hydrothermal stages show rather uniform sulphur isotope signatures indicating a large homogeneous or homogenised sulphur source for the hydrothermal processes. However, influence of local sulphur and metal reservoirs is also detectable in the sulphur isotope and trace element data for sulphide minerals. The latter peculiarities appear to be promising to develop methods for predicting types of gold mineralization by systematic analyses of sulphide mineral samples from exploration drillcores and heavy mineral separates from till.

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Gold deposits of the Lesser Caucasus: products of successive Mesozoic and Cenozoic geodynamic settings

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Abstract. Gold deposits were formed during two different geodynamic evolution stages of the Lesser Caucasus, starting with Mesozoic arc construction along the Eurasian margin, and followed by Cenozoic subduction-related to post-collision magmatism and tectonics during final Arabia-Eurasia convergence and accretion. Gold deposits are of the low-, and intermediate- to high-sulfidation type, with the latter ones being associated with porphyry deposits. Some deposits could be analogous to transitional VMS-epithermal systems in the Late Cretaceous Bolnisi district and during nascent Jurassic arc evolution along the Eurasian margin, but require further investigation.

1 Introduction

The Lesser Caucasus extends from the Black Sea to the Caspian Sea, across Georgia, Armenia and Azerbaijan (see inset in Fig. 1). It is a central segment of the Tethys orogenic and metallogenic belt, linking the Anatolian and Iranian tectonic zones. The ore deposits and districts can be assigned to two different geodynamic evolution stages, starting with Mesozoic arc construction and evolution along the Eurasian margin, followed by Cenozoic subduction-related to post-collision magmatism and tectonics. Various types of gold deposits were formed during the different stages and are the subject of this review. More details and references about the gold deposits can be found in Moritz et al. (2016a).

2 Geodynamic context

The Lesser Caucasus consists of three tectonic zones: the Jurassic-Cretaceous Eurasian margin, including the Somkheto-Karabagh belt and the Kapan block, the Amasia-Sevan-Akera ophiolite zone, and the Gondwana-derived South Armenian block (Fig. 1). The Somkheto-Karabagh belt and the Kapan block were formed during NE-verging Jurassic-Cretaceous subduction of a northern branch of the Neotethys beneath Eurasia, followed by Late Cretaceous collision with the South Armenian block, and a jump of the Late Cretaceous-Paleogene subduction zone to the SW of the Turkish Bitlis massif. East-verging subduction of the southern Neotethys branch and Cenozoic convergence of Eurasia and Arabia resulted in an Eocene magmatic climax, followed by Neogene collisional to post-collisional magmatism (Sosson et al. 2010; Rolland et al. 2011, 2012; Moritz et al. 2016b; Rezeau et al. 2016). The timing of Arabia-Eurasia collision is still debated, but a majority of authors favor a late Eocene to Oligocene age (40-25 Ma) for initial collision in the Caucasian-Zagros region (see references in Moritz et al. 2016a,b).

3 Ore formation during Jurassic nascent magmatic arc construction along Eurasia

During Middle and Late Jurassic nascent arc construction, the metallogenic evolution was dominated by subaqueous magmatic-hydrothermal systems. Ore deposits in the two representative districts at Alaverdi and Kapan (Fig. 1) include Cu-rich pyrite bodies, polymetallic lenses and veins, and stockwork-type mineralization. Associated hydrothermal alteration varies from chlorite-epidote-carbonate-dominated to silicification and argillie alteration (Khachaturyan 1977; Achikgiozyan et al. 1987; Calder 2014; Mederer et al. 2014). The deposits were mainly mined for copper, but gold was an important by-product in the Alaverdi district, and is currently the main commodity mined at the Shahumyan deposit in the Kapan district, where it is intimately associated with tellurides. The Jurassic deposits may represent either coeval hybrid VMS-epithermal-porphyry systems, or the juxtaposition of different mineralization styles with different ages, due to rapid changes in local tectonic, magmatic, sedimentary and ore-forming conditions in a nascent magmatic arc setting. The ages of deposits are bracketed between 162 and 148 Ma (Calder 2014; Mederer et al. 2014).
4 Porphyry-epithermal systems formed during Late Jurassic to Early Cretaceous arc thickening along the Eurasian margin

Typical porphyry Cu and intermediate- to high-sulfidation epithermal systems were emplaced in the Somkheto-Karabagh belt during the Late Jurassic to Early Cretaceous, when the arc reached a more mature stage with a thicker crust, and sufficient amounts of fertile magmas were generated by magma storage and MASH processes. Porphyry Cu formation started at 146 Ma at Teghout in the Alaverdi district (Amiryan et al. 1987), and was followed by a major cluster of porphyry Cu and epithermal systems at ~133 Ma in the Gedabek district (Babazadeh et al. 1990; Hemon et al. 2012), laterally extending to the Gosh and Chovdar epithermal deposits (Fig. 1; Moritz et al. 2016a). The epithermal deposits are characterized by argillic alteration, intense silicification, local vuggy silica, and opaque assemblages, including enargite, chalcocite, covellite, tellurides, sulfosalts and base metal sulfides. The deposits are both structurally and lithologically controlled (Moritz et al. 2016a). The Gedabek district experienced major uplift and denudation during the Early Cretaceous (Sosson et al. 2010). It is still unclear how the epithermal deposits were preserved during this tectonic evolution, since such ore deposits are particularly vulnerable to erosion. Porphyry Cu and epithermal style mineralization reported in the Mehma district (Fig. 1; Mederer et al. 2014) could possibly be roughly contemporaneous with the porphyry-epithermal systems at Teghout and Gedabek. However, because of poor age constraints, further studies will be necessary to verify this.

5 Epithermal and transitional-type ore formation during final Late Cretaceous subduction of the northern Neotethys

The Late Cretaceous Bolnisi district (~87-71 Ma) is the last major metallogenic event before the South Armenian block was accreted with the Eurasian margin (Fig. 1). It documents hinterland migration of the active magmatic arc, attributed to a flatter subduction geometry (Rolland et al. 2011). Mineralization is stratigraphically controlled, one group is hosted by Turoonian to early Santonian volcanic and volcano-sedimentary rocks (Madneuli deposit; Tsiteli Sopeili, Kveno Bolnisi and David Gareji prospects), and a second group (Sakdrisi deposit; Darbazi, Imedi, Beqtakari, Bnelikhevi and Samgreli prospects) is hosted by Campanian volcanic and volcano-sedimentary rocks (Gugushvili, et al. 2014). Genetic models are consistent with a submarine magmatic-hydrothermal system (i.e., transitional VMS-epithermal setting with a potential porphyry system at depth; Migineishvili 2005; Gialli et al. 2012; Gugushvili et al. 2014). A vertical distribution of mineralization styles is recognized in several ore centers (e.g., Madneuli, Sakdrisi, Kveno Bolnisi, David Gareji) with Cu-rich ore bodies at depth grading upwards into sphalerite, galena and barite veins, vertical breccia and stratiform ore-bodies, and gold-bearing epithermal mineralization at shallow levels (Gialli et al. 2012; Gugushvili et al. 2014). The low-sulfidation Beqtakari precious and base metal system is controlled by a stratiform breccia sequence (Lavoie et al. 2015).

6 Cenozoic gold deposits: witnesses of final subduction of the southern Neotethys and collision between Arabia and Eurasia

Abundant Cenozoic magmatic rocks outline the accretionary boundary and suture zone between the Gondwana-derived South Armenian block and the Jurassic-Cretaceous Eurasian margin. This major collision zone coincides with the dextral Pambak-Sevan-Sunik fault system, and controls a number of significant epithermal-porphyry mining districts described below (Fig. 1).

The Zangezur-Ordubad district is a major ore producer of the Lesser Caucasus (Fig. 1). Spatially associated porphyry and epithermal systems are hosted by the major Meghri-Ordubad pluton (Fig. 1) and associated volcanic rocks (Karamyan 1978; Amiryan 1984; Babazadeh et al. 1990; Moritz et al. 2016a, b). Dextral strike-slip tectonics initiated during oblique Arabia-Eurasia plate convergence controlled Eocene ore deposition and magma emplacement. This tectonic system was repeatedly reactivated during Neogene collision and post-collision ore formation and magmatism (Hovakimyan et al. 2017). The Meghri-Ordubad pluton was incrementally assembled during middle Eocene calc-alkaline subduction magmatism, late Eocene-middle Oligocene post-subduction shoshonitic magmatism, and late Oligocene-early Miocene adakitic, shoshonitic to high-K calc-alkaline magmatism (Rezeau et al. 2016). Porphyry Cu-Mo deposits were formed at the end of the middle Eocene subduction event (~44-40 Ma; e.g. Agarak), and the late Eocene-middle Oligocene post-subduction event (~27-26 Ma; e.g. Kadjaran; Moritz et al., 2016a; Rezeau et al., 2016). Precious and base metal epithermal mineralization accompanied late Eocene and late Oligocene magmatism as evidenced by K-Ar ages (37.5 ± 0.5 and 38.0 ± 2.5 Ma at Tey-Lichkvaz; 24 ± 1 Ma at Atkis near Kadjaran; Bagdasaryan et al. 1969). The epithermal systems consist of veins and stockworks hosted by volcanic and intrusive rocks affected by silicification and sericite-carbonate-argillic (kaolinite) alteration (Moritz et al. 2016a). An early Miocene epithermal event is documented by 20.5 Ma Cu veins overprinting the ~27-26 Ma Kadjaran porphyry deposit (Re-Os molybdenite age; Rezeau et al. 2016).

The low-sulfidation epithermal Zod/Sotk gold deposit is hosted by the Jurassic-Cretaceous Sevan-Akera ophiolite complex along the easternmost part of the South Armenian block (Fig. 1). Local felsic dikes and stocks, overprinted by ore-related hydrothermal alteration, are interpreted as late Eocene, Oligocene and Miocene (e.g., Leviran 2008).
Therefore, mineralization is reported as Oligocene to Miocene in age, which is at variance with respect to a K-Ar whole rock alteration age of 43 ± 1.5 Ma (Bagdasaryan et al. 1969). Thus, it is open to question whether the Zod/Sotk deposit coincides with Eocene subduction-related magmatism or with Neogene collision to post-collision tectonic and magmatic evolution.

The recently discovered Amulsar prospect (Fig. 1) is hosted by late Eocene to early Oligocene volcano-sedimentary rocks affected by silicification and argillic alteration, including alunite. Mineralization is lithologically and structurally controlled. The main ore structure consists of a multiply folded central zone, segmented by late oblique normal faults (Lydian International 2016). Small magmatic intrusions yielded a 34-33 Ma K-Ar age (Bagdasaryan and Ghukasian 1985), which suggests a link with Neogene collision evolution.

The Meghradzor-Hanqavan ore district occurs along the northern part of the Pambak-Sevan-Sunik fault system (Fig. 1). The Meghradzor low-sulfidation epithermal deposit is hosted by middle Eocene andesite and tuff, and consists of ~EW-oriented quartz-chalcedony-carbonate-sericite veins and breccia zones containing sulfides, tellurides and native gold (Amiryan 1984). K-Ar dating on sericite from altered host rocks yielded an age of 41.5 ± 1.0 Ma (Bagdasaryan et al. 1969). The adjacent Hanqavan porphyry Cu-Mo prospect dated at 29.34 ± 0.12 Ma by Re-Os molybdenite geochronology (Moritz et al. 2016a) is hosted by a 33.3 ± 3 Ma old tonalite (K-Ar whole rock dating, Bagdasaryan et al. 1969). The Eocene to Oligocene ore-forming and magmatic events are reminiscent of the long-lasting metallogenic evolution of the Meghri-Ordubad region (see above). Therefore, the ore deposit potential of this district merits further attention.

7 Intrusion-related deposit in the South Armenian block: witness of south-verging subduction of the northern Neotethys?

The Toukhmanouk prospect occurs in the Tsaghkuniat massif along the easternmost part of the Gondwana-derived South Armenian block, next to the Meghradzor-Hanqavan district (Fig. 1). The Toukhmanouk prospect consists of ~NE-oriented, subvertical quartz-carbonate-sulfide vein swarms crosscutting Jurassic and Cretaceous volcanic and intrusive rocks (Wheatley and Acheson 2011), and a Proterozoic trondhjemitite. The main sulfides are sphalerite, galena, pyrite and arsenopyrite, and the
valuable commodities are gold and silver. Re-Os molybdenite dating yielded an age of 146 Ma (Moritz et al., 2016a). Recently, Hässig et al. (2015) suggested the existence of a SW-verging Jurassic-Cretaceous subduction zone along the eastern margin of the South Armenian block. If we accept such a geodynamic setting, it could explain the particular location of the Toukhmanouk deposit, and it would open up new exploration avenues.

8 Conclusions

The Lesser Caucasus offers an excellent potential for high-sulfidation epithermal deposits associated with porphyry Cu systems in the Late Jurassic to Early Cretaceous subduction setting of the Somkheto-Karabagh belt. Abundant low- to high-sulfidation epithermal deposits and prospects were formed during the Cenozoic evolution of the Lesser Caucasus, and can be locally associated with porphyry Cu-Mo deposits. Their link with either Eocene subduction or Neogene collision to post-collision settings is still open to question. The transitional nature of epithermal systems with VMS-type mineralization in the Late Cretaceous Bolnisi district and during nascent Jurassic arc evolution along the Eurasian margin requires further investigation.

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Carlin-style gold-silver mineralization at the Cove deposit in Nevada, USA: possible missing link between Carlin-type gold deposits and magmatic-hydrothermal systems

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Abstract. Magmatic-hydrothermal models for Carlin-type deposits have been criticized because of the lack of zoning and evidence for high-temperature mineralization. Ongoing exploration and research at the Cove deposit has identified Carlin-style mineralization in which both gold and silver occur in arsenian pyrite in appreciable amounts. The mineralization is spatially associated with an Eocene intrusive center. The Carlin-style mineralization clearly post-dates Au+Ag-bearing polymetallic sulfide-rich mantos in Triassic carbonates. The overprint occurs mainly as narrow rims on polymetallic-stage sulfides. In siliciclastic rocks below and above the carbonates, polymetallic mineralization occurs as Au+Ag-bearing polymetallic sulfide-quartz veins. The Ag/Au ratios in Carlin-style gold mineralization, decrease steadily away from a high of >12 underneath the previously mined pit, where Ag concentrations in arsenian pyrite are as high as 1.8 wt%, to <0.5 within 3 km, where Ag is below detection limits in pyrite. The age of mineralization is bracketed by a U-Pb date on zircon of 38.0±1.2 Ma from a weakly mineralized, altered felsic dike and a 40Ar/39Ar date of 34.22±0.06 Ma on sandine from an unaltered ignimbrite that unconformably overlies mineralization in the pit.

1 Introduction

Controversy remains over whether Carlin-type gold deposits in Nevada are distal products of magmatic-hydrothermal systems (Sillitoe and Bonham 1990; Muntean et al. 2011) or whether they solely form from meteoric and/or metamorphic fluids (Seedorff 1991; Ilichik and Barton 1997; Large et al. 2011). The Cove gold-silver deposit has both polymetallic and Carlin-style mineralization that is spatially related to an Eocene intrusive center. Cove has been termed a "distal-disseminated" deposit, a classification that is meant to distinguish such deposits from the large Carlin-type gold deposits in Nevada (cf. Hofstra and Cline 2000). Johnston et al.'s (2008) detailed study of Cove demonstrated the two styles were spatially distinct, and they proposed that Cove represents an example of a continuum between magmatic-hydrothermal systems and Carlin-type gold deposits in Nevada. Here we present new data from recent deep drilling below the previously mined Cove deposit that supports such a continuum.

2 Geology of the Cove deposit

Gold and silver mineralization at Cove and the nearby McCoy deposit is centered on an Eocene intrusive system (Fig. 1). Past production at Cove amounted to 3.3 Moz of gold and 108 Moz of silver from both open pit and underground mining. Mineralization at Cove occurs mainly along the hinge zone of a northwest-trending, southeast-plunging anticline. McCoy, which occurs 1.6 km southwest of Cove, is a garnet-pyroxene skarn Au-Ag deposit, spatially and temporally related to the Brown stock. Much of the gold at McCoy is associated with retrograde skarn and quartz+adularia+pyrite alteration (Brooks et al. 1991). Felsic dikes extend from the Brown stock to Cove, where they are typically altered to quartz-sercite-pyrite and contain only anomalous gold and silver. Previously mined polymetallic mineralization at Cove occurs as disseminations and crustiform to banded quartz+pyrite+arsenopyrite+sphalerite+galena, Au-Ag-bearing veins with late calcite and Mn-bearing carbonates (typically <0.1 m widths) with illicite-bearing envelopes in siliciclastic rocks and mantos in carbonates. Gold typically occurs as electrum, whereas silver occurs as acanthite, in galena, and in various sulfosalts, mainly tetrahedrite-tennantite.

Figure 1. Simplified pre-mining map of the Cove-McCoy area. From Johnston et al. (2008). Brown stock is in southwest corner of map.
Banding textures and sulfosalts in veins and disseminations decrease in abundance with depth until they are absent.

3 Carlin-style mineralization at Cove

Carlin-style mineralization mainly occurs in silty carbonate-rich sections of the Triassic section, preferably in limestone. The carbonates are variably ferroan. Gold occurs in arsenian pyrite and is invisible using a SEM. Presumably, the gold occurs as Au⁺ occurs in the lattice of pyrite, similar to the Carlin-type deposits in the Nevada. The carbonates are decarbonatized and variably silicated, and silicate minerals are argillitized to illite. Mineralized zones are commonly strongly carbonaceous. Late veinlets and pods realgar±stibnite±orpiment with late calcite were common in the previously mined mineralization, but are absent in the deeper mineralization currently being drilled.

3.1 Spatial and temporal relationships between Carlin-style and polymetallic mineralization

Carlin-style mineralization was encountered in carbonate units from the pre-mining surface down to the limits of the previous drilling and mining (<500 m deep). Polymetallic mineralization mainly occurred from depths of 200 to 500 m. Gold-bearing jasperoids, which are also commonly Mn-bearing, were common at shallow depths in the open pit. It was unclear whether they were related to Carlin-style and/or polymetallic mineralization. The current deep drilling has encountered Carlin-style mineralization in the previously under explored Home Station and Panther Canyon dolomite members of the Augusta Mountain Fm. and especially the underlying limestone of the Favret Formation at depths of 350 to 650 m. Below the Favret, polymetallic mineralization in basal conglomerate of the basal Triassic Dixie Valley Formation occurs at depths of 550 m to 750 m in a zone referred to as the 2201 (Fig. 2). Three zones of Carlin-style mineralization are currently being explored (Fig. 2). The CSD zone occurs below and alongside Carlin-style mineralization that was previously mined underground. The Helen zone is located northwest of the open pit, and CSD Gap occurs in between. The deep Carlin-style mineralization has a strong spatial relationship with mafic sills, many of which are strongly altered and locally mineralized.

Though the previously mined mineralization contained zones of spatially overlapping polymetallic and Carlin-style mineralization, no definitive cross-cutting relationships between the two styles were documented. The recent deep drilling, however, has clearly demonstrated the Carlin-style mineralization post-dates the polymetallic mineralization. Where the overprint occurs, polymetallic sulfide mineralization appears to have an etched appearance as if it had been dipped in acid. The overprint is expressed in thin sections by thin rims of arsenian pyrite that are enriched in Au, Ag, Tl, Hg, and Sb, as detected with the SEM and quantified with electron microprobe analyses (Fig. 3).

3.2 Zoning in Carlin-style mineralization

Carlin-style mineralization shows strong zoning in Ag/Au ratios and in pyrite textures and chemistry away from the CSD zone towards the Helen zone. Figure 4 shows a decrease in Ag/Au ratios in Carlin-style mineralization (without polymetallic mineralization) from >12 in the CSD zone to <0.5 in the Helen zone in a distance of <3 km. Arsenian pyrite associated with Carlin-style mineralization in the CSD is coarser grained (typically 10-50 µm), euhedral to subhedral crystal with well-defined arsenic zoning, contains up to 6 wt% As, and has detectable Ag and Au (SEM and microprobe). In contrast arsenian pyrite in the Helen zone occurs as irregular “fuzzy” <10 µm grains that contain only up to 2.1 wt% As, and no detectable Au and Ag. The overall gold grades in areas of Carlin-style mineralization increase from the CSD to the Helen zone, from mostly <3 ppm in the CSD zone to mostly 4-10 ppm in the CSD Gap and Helen zones.

4 Geochronology

Five new U-Pb SHRIMP dates on zircons from the four mapped phases of the Brown stock overlap. The ages range from 37.4 Ma to 38.9 Ma at 1σ uncertainties, which overlap with a ⁴⁰Ar/³⁹Ar date of 38.24±0.24 Ma (2σ) on adularia in the McCoy skarn deposit (Groff et al. 1997). At Cove, a new U-Pb SHRIMP date of 38.0±1.2 Ma was obtained from zircons from an argillically altered sample of the Gold Dome dike. Elsewhere, the Gold Dome dike is cross-cut locally by polymetallic veins. A mafic sill from Cove was dated at 40.8±0.8 Ma (1σ); however, only three zircons were analysed. Illite from the altered Bay dike at Cove was dated at 39.37±0.23 Ma by ⁴⁰Ar/³⁹Ar by Johnston et al. (2008), which overlaps slightly with U/Pb age on the Gold Dome dike. The isochron plot of the illite sample showed minor excess argon (⁴⁰Ar/³⁹Ar=299±3).
Figure 3. (top) core photo from PG14-23 showing Carlin-style alteration overprinting polymetallic mineralization in the CSD zone, (middle) an SEM image from a sample in this interval showing polymetallic-stage pyrite overprinted by Carlin-style mineralization expressed as late As- and Ag-rich rims, (bottom) and BSE images from the same sample showing quantitative results from electron microprobe analysis.

5 Discussion

5.1 Cove-McCoy polymetallic mineralization

Geochronology and mapped geology strongly suggest the Au+Ag-bearing polymetallic mineralization at Cove and McCoy are related to the same magmatic-hydrothermal systems associated with an Eocene intrusive system. The highest temperature, exposed part of the system is the skarn mineralization associated with the Brown stock at McCoy.

Dikes coeval with the Brown stock extend from McCoy to Cove. Homogenization temperatures of fluid inclusions in polymetallic veins from Cove range from 250° to 370°C, with most between 275° and 325°C and salinities of 2-7 wt% NaCl eq (Johnston et al., 2008). δD and δ18O data on illite are consistent with magmatic water with minor amounts of meteoric water, and δ34S of polymetallic sulfides ranges from 2.2 to 3.3‰ (Johnston et al. 2008). Cove ore fluids could have been sourced from Brown stock and moved laterally and cooled toward Cove, or more likely as suggested by Johnston et al. (2008), fluids were sourced from a cupola zone underlying Cove.

5.2 Transitions to Carlin-style mineralization

The overprinting of polymetallic mineralization by Carlin-style mineralization, could be the result of a separate later hydrothermal system. More likely it evolved from a single system. Strong support of a single system comes from the gradual decrease in Ag/Au ratios away from the Cove, caused by both increasing Au grades and decreasing Ag grades. The decreases in Ag/Au and Ag grades are reflected by decreasing Ag concentrations in arsenian pyrite rims. This may be related to cooling and fluid mixing, decreases in salinity, and deposition of most of the remaining silver prior to sulfide complexes becoming the predominant transporting agent. In addition, δ34S values of late stibnite and realgar range from 1.6 to 4.5‰, slightly heavier than the values for the polymetallic sulfides.

The Kinsley Carlin-style gold deposit in eastern Nevada has many similarities to the Cove system in that it is spatially and temporally related to an Eocene intrusive system where mineralization zones outward from W-(Mo)-bearing skarn adjacent to an Eocene granitic stock to polymetallic quartz veins and mantos to jasperoids to Carlin-style gold mineralization that is ~3 km from the stock (Hill 2016). The pyrites associated with Carlin-style mineralization show a zonation in textures and

Figure 4. Zonation of Ag/Au ratios of Carlin-style mineralization without polymetallic mineralization in limestone of the Favret Fm.
compositions similar to Cove. For example, ore-stage pyrites in the previously mined main pit in the Cambrian Dunderberg Shale, 3 km from stock, typically form subhedral to euhedral zoned arsenian grains (up to 3 wt% As) that are <20 μm that have fuzzy narrow rims. They locally have inclusions of sphalerite and galena. They contain up to 530 ppm Au and 90 ppm Ag based on microprobe analyses. These pyrites are analogous to the pyrites associated with Carlin-style mineralization in the Helen zone at Cove. In contrast, pyrites 2 km from the stock in stratigraphically lower Cambrian Secret Canyon Shale, at the Secret Spot target, are zoned euhedral grains up to 500 μm, where As increases outward to the rim (up to 6 wt% As). Early stibnite and Ag/Zn-bearing tennantite–tetrahedrite inclusions locally occur in the pyrite. They contain up to 9.1 wt% Ag and <100 ppm Au (Hill 2016). These pyrites are analogous to the pyrites associated with Carlin-style mineralization in the CSD zone at Cove.

5.3 Implications to understanding Carlin-type gold deposits

The new research presented here on Cove and Kinsley points to a continuum between Carlin-style mineralization and polymetallic magmatic-hydrothermal systems. In both localities Carlin-style mineralization is distal to skarns. It clearly overprints polymetallic mineralization at Cove, whereas inclusions of base metal sulfides in the arsenian pyrite at Kinsley suggest the styles overlapped in time. Muntean et al. (2011) stressed the lack of zoning in minerals and metals the large Eocene Carlin-type deposits in Nevada, which led them to a magmatic-hydrothermal model where the magmatic source of hydrothermal fluids was deeper than typical porphyry systems, allowing spatial separation of Carlin-type mineralization from much deeper polymetallic mineralization. Though current drilling and mining in the large Carlin-type deposits has locally been to depths of ~2 km, no Ag-rich Carlin-style, polymetallic, or skarn mineralization has yet been encountered, perhaps just out of reach of the drilling.

Alternatively, the zoning at Cove and Kinsley is simply telescoped. Both Cove and Kinsley have slightly younger unaltered Eocene volcanic rocks covering or flanking the polymetallic and Carlin-style mineralization. In the Cove pit, an unaltered ignimbrite and thin section of underlying volcaniclastic sediments unconformably overlie mineralized Triassic strata. Sanidine from the ignimbrite was dated at 34.22±0.06 Ma using 40Ar/39Ar (John et al. 2008). This date, along with the dates reported above, constrains the age of polymetallic and Carlin-style alteration to be between ~39.2 and 34.3 Ma. The minimum amount of uplift and/or erosion between mineralization and emplacement of the ignimbrite can be estimated from the homogenization temperatures and salinities of fluid inclusions in quartz in polymetallic veins at Cove reported by Johnston et al. (2008). Assuming a homogenization temperature of 300°C, a salinity of 5 wt% NaCleq, no CO2, and trapping along the liquid-vapor curve, fluid inclusions from deepest sample (665 m) had a trapping pressure of 83.2 bars and density of 0.767 g/cm³ (Hass 1971). The calculated estimated depth is 1015 m, requiring 350 m of erosion prior to the emplacement of the ignimbrite. However, the fluid inclusions at Cove show no evidence of boiling; therefore, depths could have been significantly deeper requiring greater erosion. Ongoing mapping and thermochronology at both Cove and Kinsley should better constrain the age and amount of uplift.

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References


Geochemistry of marine shales in the West Rand and Central Rand groups of the Mesoarchaean Witwatersrand Basin: implications for sedimentary gold endowment

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Abstract. New mineralogical and geochemical data on low-grade metamorphosed Mesoarchaean marine shales of the West Rand and Central Rand groups, Witwatersrand Supergroup, reveal changes in the general Au and PGE flux from the Archaean hinterland over the time of sedimentation. Local mineralogical variations are attributed to alternating micro–laminae and varying heavy mineral content, including sulfides and oxides. The West Rand Group shales contain, on average, 0.12 % Corganic, 0.42 % S, and ~5 ppb Au, those from the Central Rand Group on average, 0.2 % total Corganic, 0.09 % S, and ~6 – 9 ppb Au. The Au background values, which exclude any potentially hydrothermally modified domains, are significantly higher than those given for the upper continental crust. A lack of strong correlation of Au with other elements suggests that its distribution is largely independent of the presence of other specific minerals and Au was concentrated into the basin’s embayments largely by sedimentary processes. A peak in syn–sedimentary Au–enrichment at Central Rand times correlates with the period of maximum gold concentration in fluvial to fluviodeltaic conglomerates and indicates coeval elevated Au flux off the Archaean hinterland.

1 Introduction

The <2.98–2.78 Ga Witwatersrand Supergroup situated in the central portion of the Kaapvaal Craton of South Africa (Fig. 1) is one of the best–preserved records of marine and fluvial sedimentation on an Archaean continent. The supergroup represents the fills of two different basins, namely the West Rand and the Central Rand basins, which were stacked on top of each other. The West Rand Group has contributed less than 5 % while the Central Rand Group’s share is more than 80 % of a total of >53 000 t gold produced so far from Witwatersrand mines. The process of gold–enrichment remains contested. Mechanical concentration of gold that had precipitated from Archaean meteoric waters is the prevailing hypothesis (Frimmel 2014). Nevertheless, there is evidence of post–depositional hydrothermal mobilization of gold. Though there have been many studies on the Witwatersrand gold–bearing rocks, such as quartz–pebble conglomerates, and finer grained siliciclastic rocks, aiming to decipher the origin of the gold, little information is available on background Au and platinum group element (PGE) concentrations and associated minerals in intercalated shale units.

The geochemical characteristics of different intrabasinal, regionally persistent marine shale units of the Witwatersrand Supergroup, which represent major changes in provenance and basin architecture over Mesoarchaean times, should provide clues on gold accumulation processes. The Roodepoort Formation is the stratigraphically highest major marine shale unit in the relatively gold–poor West Rand Group, whereas the Booyssens Formation is, by far, the most important marine shale unit within the gold–rich Central Rand Group.

Figure 1. Surface and subsurface distribution of the main Archaean stratigraphic units of the Kaapvaal Craton. The Witwatersrand basin fill comprises the West Rand and Central Rand groups (modified after Frimmel 2014).

This study evaluates the mineralogy and geochemistry of shales from the above formations in order to test whether there was an elevated Au flux into the marine...
depositories at the time and whether secular changes in this flux existed.

2 Geological framework

The Witwatersrand Supergroup preserves a record of terrigenous clastic rocks and gold palaeo–places in an intracratonic basin. The original depository probably covered an area of more than 50 000 km² on the Kaapvaal Craton and is now preserved in two structural basins, the West Rand and the Central Rand basins. Sedimentation of the West Rand Group, the lower portion of the Witwatersrand Supergroup, commenced after 2.985 ± 0.014 Ga (youngest detrital zircon age in basal sandstone; Kositcin and Krapez 2004). Deposition of the West Rand Group occurred mainly in marine or intertidal environments in a semi–restricted basin, with only minor fluvial deposition. The West Rand Group is subdivided into the Hospital Hill, Government and Jeppestown subgroups (SACS 2006). Its minimum areal extent is approximately 42 000 km² and the group attains a maximum thickness of 5 150 m in the Klerksdorp Goldfield.

The Roodepoort Formation of the Jeppestown Subgroup, reflecting a major tectonic change from the West Rand to the Central Rand basin, reaches a maximum thickness of approximately 500 m in the Klerksdorp and Welkom goldfields but thins in an easterly direction towards the East Rand goldfield to <150 m. The lower Roodepoort Formation has a distinct east–west lithofacies variation from graded wackestone and ripple cross–laminated siltstone in the west to magnetic shale in the east. Its lithology includes stripy sandstone of the lower quartzite unit, overlain by massive grey sandstone, wackestone, non–magnetic siltstone–shale and magnetic siltstone–shale. Unlike many other magnetic shale units of the West Rand Group, this unit is composed of black, green and white bands, which represent laminae composed of black magnetic shale, green non–magnetic shale and white quartz–epidote sand lenses. A dolerite sill occurs in the upper half of the Roodepoort Formation.

Deposition of the Central Rand Group sediments ended between 2.840 ± 0.003 Ga (youngest detrital xenotime; Kositcin and Krapez 2004) and 2.780 ± 0.003 Ga (authigenic xenotime; Kositcin et al., 2003). The Central Rand Group is subdivided into the Johannesburg and Turfontein subgroups (SACS 2006) and consists mainly of low–grade metamorphosed greywacke, conglomerate and sandstone. It is preserved over a minimum area of 10 000 km² and attains a maximum thickness of 2 880 m near the centre of its present area of distribution (Fig. 2). The younger lithostratigraphic units of the Central Rand Group were affected, at least along the basin margin, by syn–depositional folding and thrusting, attesting to syn–orogenic sedimentation with respect to collisional tectonic activities towards the north and west.

The Booyens Formation of the Johannesburg Subgroup is the only unit within the Central Rand Group that consists predominantly of laterally extensive marine shale. It is thickest in the Western Areas (West Rand Region) and Carletonville goldfields (~300 m) but decreases in thickness in westerly, southerly and easterly directions to <100 m.

3 Results

A total of 238 unmineralised, partly silty shale samples, free of evidence of hydrothermal overprint (such as quartz and/or carbonate veins) from the Roodepoort Formation of the West Rand and the Booyens Formation of the Central Rand groups (Fig. 2) were selected for mineralogical and geochemical analysis from borehole cores and underground working areas in the Witwatersrand Supergroup. Out of these, 121 samples were assayed for Au and PGE concentrations.

Figure 2. Simplified geological map of the Witwatersrand Supergroup, also showing the main goldfields (modified after Frimmel et al. 2005).

Major and trace element, including rare earth element (REE), concentrations were determined by XRF, ICP–OES and ICP–MS, whereas the shale mineralogy was determined by XRD and EMPA. Whole–rock concentrations of Au and PGE were analysed by fire assay and acid–digestion ICP–OES/MS with detection limits of 0.5 ppb for Au and 1 ppb for PGE. LECO analysers were used to determine total Corganic and sulfur content. All of this was preceded by petrographic analyses.

3.1 Mineralogy

The sample suite studied is made up mainly of convolute–laminated, dark grey to black shale, the latter in many places being interstratified with layers of carbonate. Most of the samples are also well–laminated on a thin–section
scale. In places, silty and muddy layers are interlaminated. The silt-size fraction comprises quartz, microcline, and very rarely plagioclase. Pyrite is the most abundant sulfide and occurs in various forms that include detrital, syngentic, diagenetic and epigenetic types. The abundance of pyrite varies with respect to the stratigraphic position but is generally low in these marine deposits. The Roodepoort Formation shale consists of quartz, magnetite, amphibole, chlorite, ankerite, muscovite and biotite. The Booyens Formation shale is composed of quartz, chlorite-muscovite mixtures, pyrite, carbonate, and rutile. These mineralogical assemblages are similar to those reported by Wronkiewicz and Condie (1987), Guy and Beukes (2010) and Phillips and Powell (2015). XRD analysis revealed that hydromuscovite and magnesian chlorite are the principal sheet silicates. No free gold particles were observed.

3.2 Geochemistry

The post–Archaean Australian shale composite (PAAS, Taylor and McLennan 1985) was used as reference to normalise the geochemical data. Element concentrations with distinct differences between arithmetic and geometric mean values, which are an indication of the log-normal distribution of the data, were averaged using geostatistical Napier’s constant inverse log. The observed high variations in element contents reflect variable degrees of dilution by carbonate and quartz. The distribution of trace elements is controlled by shale mineralogy. Figure 3 shows patterns of trace elements plotted relative to PAAS.

Large ion lithophile elements (Rb, Sr, U, and Th): The Roodepoort Formation shales are depleted in Rb (15.5–135 ppm, \( \bar{x} = 48 \) ppm), Sr (10.2–213 ppm, \( \bar{x} = 64 \) ppm), Ba (132–834 ppm, \( \bar{x} = 412 \) ppm), and U (0.98–1.4 ppm, \( \bar{x} = 1.14 \) ppm) relative to PAAS. The Booyens Formation shale is enriched in Ba (711–761 ppm, \( \bar{x} = 742 \) ppm) relative to PAAS, depleted in Rb and Sr and its U content varies with stratigraphic position and geographic location. The concentrations of MnO and Th in the Booyens Formation are highly variable with stratigraphic depth.

REE: The studied Witwatersrand shales’ absolute concentrations of REE are similar to those of PAAS. There are, however, clear stratigraphic variations in REE content. Highly siderophile elements (HSE): The Au content of the Roodepoort Formation shale is highly variable, both vertically and laterally, and averages 6.57 ± 1.76 ppb. The Pd and Pt concentrations in the same samples average 4.2 ± 0.02 and 3.97 ± 0.02 ppb, respectively, and are less variable, both vertically and laterally. The Au content of the Booyens Formation shale is distinctly higher with significant differences between different goldfields: it is on average 9.85 ± 1.29 ppb in the Welkom goldfield and 5.18 ± 0.03 ppb in the Western Areas goldfield. The Pd content in the Booyens Formation shale in the Welkom goldfield and the Western Areas goldfield averages 4.16 ± 0.02 and 10.68 ± 0.02 ppb, respectively, that of Pt averages 3.89 ± 0.01 ppb and 6.12 ± 0.04 ppb, respectively. Other HSE, i.e. Ir, Os, and Rh are below the lower limit of detection, although spikes of Os above the detection limits were observed in some of the samples. The Au and PGE values are higher than the averages of upper continental crust (Fig. 4). No positive correlation between total organic carbon, sulfur and gold in the studied samples was observed.
4 Discussion

The samples studied show highly variable chemical compositions within and across stratigraphic units. The relative variation in REE content of both the West Rand and Central Rand shales is attributed to silty material corroborated by grain size variation and the presence of quartz and carbonate minerals. The lower La/Ba ratio in the studied shales is interpreted to be the result of particles settling to the floor of the open ocean, and marine productivity during the deposition the Roodepoort and Booyensens sediments. The higher Rb/Cs ratios indicate preferential Rb ion association relative to Cs onto clay minerals. The distribution of Cr, Ni, V, and Co and other relatively immobile trace elements (Zr, Hf, Ba, and Pb) reflects changes in provenance from West Rand Group sedimentation to that of the Central Rand Group.

The elevated Cr and Ni values in the studied Witwatersrand shales reflect a greenstone provenance. Variation was not only observed in the above provenance tracers but also in the background concentrations of Au, Pd and Pt. Although regional geographic variations in Au and PGE contents were observed in the Booyensens Formation, this unit is more enriched in background Au and PGE than the Roodepoort Formation shale. Inter-element correlations suggest that carbon does not play a major role in hosting significant concentrations of Au, PGE, base and transition metals in the studied shales. There is a weak correlation between gold and PGE in the Roodepoort and Booyensens shales, which may indicate that it's distribution is not solely determined by its siderophile affinity. A weak correlation between Pt and Pd is suggestive of decoupling, which is a factor of varying geochemical behaviour in the upper crustal environment.

5 Conclusions

There are clear differences in background Au and PGE concentrations between West Rand and Central Rand Group marine shale units. The Central Rand Group shales show strong Au-enrichment relative to average upper continental crust (1.5 ppb Au). The lack of direct regional correlation between Au and C and S is interpreted as an indication that the gold is not chemically bound to specific elements and mineral phases within the intracratonic shale units of the Witwatersrand Supergroup. Therefore, the fractionation of gold in the studied Witwatersrand shales can be explained by the depositional environment, rate of sedimentation, effectiveness of extraction ofAu from seawater, adsorption capacities for Au during diagenesis, relic metal leaching–fixation mechanism, and oxygen fugacity in the sea floor.

The lack of particulate gold in the studied shales is interpreted as a function of marine depofacies and sedimentary sorting. Gold accumulation was mainly controlled by mechanical sedimentary processes which involved breaking down gold particles into finer discrete particles. Assuming that most of the gold was dissolved in Mesoproterozoic meteoric waters (Frimmel 2014), precipitation of gold that was later mechanically disintegrated could have been triggered by redox reactions with hydrocarbons and cyanobacteria (Frimmel and Hennigh 2015). The Central Rand Basin architecture provided sufficient catchment area and efficient sedimentary (i.e. fluvial) processes for gold accumulation in embayments, such as estuaries, thus explaining why the rich goldfields are located along the edge of the basin.

Acknowledgements

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Controls of BIF-hosted gold mineralization, Musselwhite mine, Superior Province, Ontario, Canada

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Abstract. The Musselwhite gold deposit is hosted in polydeformed amphibolite facies banded iron formation (BIF) of the Mesoarchean North Caribou greenstone belt, northwestern Superior Province. The deposit consists of narrow sub-vertical orebodies hosted along second- and third-order high strain zones that intersect strongly reactive, silicate-rich BIFs. Gold precipitation is facilitated by the BIF’s layered anisotropy and specific rheology acting as a structural trap. Pyrrhotite replacement and “silica-flooding” of the iron formation constitute the typical high grade ore, and gangue minerals include almandine garnet, grunerite, ferro-tschermakite, ankerite, and hedenbergite. Alteration haloes around the ore zones consist in distal potassic and proximal carbonate alteration. Gold positively correlates with Cu, Ag, Se and Te. Structural crosscutting relationships indicate that gold mineralization is syn- to late-D2 deformation and subsequent strain resulted in local remobilization of sulfides and gold. The bulk of gold mineralization is pre-peak metamorphism, which is dated at 2660 Ma based on U-Th-Pb monazite data. Garnet-biotite geothermometry suggests an equilibration of metamorphic and alteration minerals composition after gold deposition. Consequently, a thorough characterisation of the structural and tectonometamorphic evolution is critical for exploring for BIF-hosted gold mineralization in complex polyphase tectonic settings.

1 Introduction

Banded iron formation-hosted gold deposits are structurally controlled stratabound deposits that represent one of the main targets for gold exploration in the northern part of the Precambrian Canadian Shield as demonstrated by past and current producers and recent discoveries (Dubé et al. 2015).

The Musselwhite mine is part of few BIF-hosted gold deposits currently in production in Canada. Our research aims at understanding the structural, lithological and geochemical controls on the formation and distribution of the BIF-hosted gold mineralization, as well as defining the geochemical footprint of the hydrothermal system to improve geological and exploration models (Dubé et al. 2015).

2 Regional context

The Goldcorp Musselwhite mine is located in the North Caribou greenstone belt (NCG), western Superior Province (Fig. 1; Thurston et al. 1991), which comprises 3.05-2.87 metavolcanic-dominated assemblages and <2.89 Ga metasedimentary-dominated assemblages. It is surrounded by the 2.87-2.84 Ga tonalite-trondhjemite-granodiorite batholiths of the North Caribou pluton and the Schade Lake gneissic complex, and by the 2.73-2.72 Ga Southern batholith (Fig. 1C, D) (Biczok et al. 2012; Kalbfleisch 2012). Three major phases of regional deformation are recognized (Piroshco and Shields 1985; Breaks et al. 2001; Oswald et al. 2015a). The map structural pattern is dominated by NW-trending D2 structures showing a strong SW-NE strain gradient. Late-D2 regional metamorphism ranges from mid-greenschist to mid-amphibolite facies (Breaks et al. 1985; Hall and Rigg 1986; Otto 2002).

The Musselwhite deposit host succession consists of calc-alkaline, intermediate to felsic volcanic rocks of the South Rim assemblage and the structurally underlying tholeiitic, mafic volcanic and sub-volcanic rocks, and tholeiitic, komatiitic basalts and ultramafic volcanic rocks of the Opapimiskan-Markop assemblage (OMA; Oswald et al. 2015b). Two main BIF sequences are intercalated within the OMA (Moran 2008): the Northern iron formation (NIF), which hosts most of the economic gold mineralization, and Southern iron formation (SIF; Fig. 1E). The succession is folded by a NW-trending, F2 synform-antiform pair.
Geochronological and structural data show that the Musselwhite succession was previously overturned by a megascopic recumbent F₁ syncline, and structurally overlies the younger Zeemel-Heaton assemblage (ZHA, Fig. 1D; Oswald et al. 2015a; McNicoll et al. 2016). The combination geological and structural data also suggests this F₁ fold was associated with a major thrust fault (Figs. 1D, E; Oswald et al. 2015c). Documentation of polymictic conglomerates along this boundary suggests it may be an activated unconformity.

### 3 Ore mineralogy

The bulk of the Musselwhite ore is hosted in silicate-rich BIF and occurs as zones of strata-bound pyrrhotite replacement and associated “silica flooding” and discordant quartz-pyrrhotite veins. The ore zones are associated with D₂ high-strain zones concentrated within shallowly NW-plunging F₂ fold hinges, as well as along strongly attenuated limbs (Fig. 2A; Biczok et al. 2012; Oswald et al. 2015a,b).
metasomatic mm- to cm-scale layering marked by abundant coarse-grained red almandine garnet porphyroblasts, intergrown with fine- to medium-grained, bladed grunerite, green hornblende/ferro-tschermakite, reddish brown biotite, iron carbonates, and locally hedenbergite (Figs. 2A, B; 3). Gold is associated with sulphide minerals consisting almost exclusively of disseminated to semi-massive pyrrhotite with minor chalcopyrite and trace pyrite, sphalerite and arsenides. Pyrrhotite also occurs as fracture-fill within garnet porphyroblasts and in necks of boudinaged quartz veins. Visible gold occurs as small inclusions in quartz, hedenbergite, amphiboles or biotite, as well as in garnet fractures.

Figure 3. Gold grain associated with pyrrhotite and silicates in high grade silicate-BIF ore.

4 Hydrothermal alteration

The metamorphosed hydrothermal alteration at Musselwhite is characterized by distal and proximal zones, with no clear intermediate zonation. The overall lateral extent of alteration is limited and strongly dependant on rock type compositions. In mafic volcanic rocks, distal potassic alteration (i.e., biotite) grades into a proximal carbonate alteration with quartz-calcite ± sulfide veins in the ore zone. The distal alteration of BIF is either marked by biotite in clastic-rich bands or grunerite replacing chert and magnetite in poorly-reactive oxide bands. Proximal alteration is characterized by iron carbonates, Ca- and Al-bearing amphiboles replacing grunerite, and pyrrhotite-replacement of magnetite and Fe-silicates (Fig. 4). Conversion of carbonates to pyroxenes during subsequent metamorphism weakened the signature of carbonate alteration.

Geostatistical analysis of the lithogeochemical data (e.g. binary plots, principal component analysis) shows that, in addition to being correlated with total-sulfur and loss-on-ignition components, gold is also associated with Ag, Se, Te, and Cu (Oswald et al. 2015b).

5 Structural and metamorphic overprint

Various relationships at mine-scale (e.g., semi-massive Po vein in an ore zone), sample-scale (remobilised Po; axial planar visible gold in deformed quartz veins), and microscopic features (ore-related minerals affected by $S_2$; sulfide remobilization textures; Fig. 5) show that $D_2$ deformation was still active after the main stage of gold mineralization. Annealing texture of sulfides, continued crystallisation of coarse almandine garnet, and local conversion of amphibole to pyroxene support an interpretation that $M_2$ tectonometamorphism outlasted most of gold mineralization.

<table>
<thead>
<tr>
<th>Silicate BIF</th>
<th>Regional</th>
<th>Distal</th>
<th>Proximal</th>
<th>Ore</th>
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<td>Chert</td>
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<td>Garnet</td>
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<td>Biotite</td>
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<td>Calcite</td>
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<tr>
<td>Fe-carbonates</td>
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<tr>
<td>Pyroxene(s)</td>
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<tr>
<td>Pyrrhotite</td>
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<td>Qtz vein</td>
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<td>$S_2$-flooding</td>
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Figure 4. Synthetic chart showing the variations in abundance and origins of the mineral paragenesis of the silicate-BIF; from that of regional-scale metamorphism to those of alteration- and ore-related assemblages (modified from Oswald et al. 2015c). Ca-amphiboles = Hornblende, Ferro-tschermakite. Pyroxene(s) = Hedenbergite, Ferrosilite. Variations in line thickness reflect mineral abundance (as well as grain size for garnet).

Figure 5. Clast of $S_2$-foliated silicate matrix isolated in remobilized pyrrhotite, high grade ore sample.

Metamorphic mineral assemblages in pelitic samples (e.g., Garnet-Biotite-Sillimanite, absence of kyanite) suggest that peak pressure conditions reached around 3.3-5 kbar (Tinkham et al. 2011). Garnet-Biotite geothermometry on barren and gold-bearing pelitic samples using FeMg and FeMgAlTiCaMn systems (Ferry and Spear 1978; Holdaway 2000) gives temperature calculations between 610 and 630°C, which are in agreement with petrographic observations. This suggests an equilibration of metamorphic and alteration minerals composition after the
bulk of gold deposition.

Constraints on the timing of gold mineralization comprise a Sm-Nd model age on garnet, interpreted to be of hydrothermal origin, at 2690 ± 9 Ma (Biczok et al. 2012). A U-Th-Pb analysis of a late-M2 monazite has yielded an age of ca. 2660 Ma (Oswald et al. 2015b), providing a minimum constraint for the timing of regional D2 metamorphism/deformation to which the gold mineralizing event is associated.

6 Implications for exploration

The first-order tectonic boundary between the North Caribou terrane and the Island Lake Domain, the early stage unconformity and/or thrust fault at the contact between the OMA and the adjacent ZHA, and the documented presence of polymictic conglomerate in the upper stratigraphic sequence (Fig. 1D; Oswald et al. 2015c) are all critical features typically found in greenstone-hosted orogenic gold districts (e.g., Robert et al. 2005). They provide targets for exploration throughout the greenstone belt, especially where associated with second- or third-order D<sub>2</sub> structures affecting highly reactive BIF units.

The style and nature of the hydrothermal alteration in BIF-hosted gold deposits varies depending on BIF facies. The timing and peak conditions of metamorphism, and the tectonic events also influence the footprint of the hydrothermal alteration. Their thorough characterisation is instrumental in exploring for BIF-hosted gold mineralization in granite-greenstone belts.

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Gold-rich mineralisation in fore-arc setting at ODP site 786B: evaluation of magmatic input into oceanic crust hydrothermal system

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Abstract. Gold and other metals variably enriched in volcanogenic massive sulphide (VMS) deposits are mobilised in the oceanic crust by two main processes: hydrothermal alteration of the oceanic crust's lower sheeted dykes and exsolution of metal-rich fluids into the hydrothermal system from differentiating magmas. The extent to which each process contributes to metal enrichment in VMS deposits, and the style of mineralisation produced varies between different tectonic settings. Oceanic Drilling Program (ODP) Hole 786B recovers the upper oceanic crust of a supra-subduction zone including a 30 m-wide mineralised transitional zone at the base of the hole which shows evidence for magmatic fluid input. This study uses in-situ trace element, S-isotope analyses in sulphide minerals and whole-rock data to characterise the metal endowment of the mineralised zone, the sources of the trapped metals and the specific signature of magmatic fluid inputs in the hydrothermal system. Magmatic fluid exsolution most likely provided most of the Au, Se, S, Mo, Bi and Te enriched in the transitional zone whilst As, Sb could have been mobilised by rock-buffered hydrothermal alteration. Little base metal mobilisation occurred in Hole 786B leading to significant metal fractionation and promoting Au-rich mineralisation.

1 Introduction

The metals enriched in volcanogenic massive sulphide (VMS) deposits, hydrothermal ore deposits forming in extensional tectonic settings on, or very near, the seafloor, are commonly considered to come from two main sources: hydrothermal alteration zones in the lower sheeted dyke section of the oceanic crust (Alt 1995; Patten et al. 2016), and exsolving magmatic volatiles (Moss et al. 2001; Yang and Scott 2002). The metal budget of VMS deposits is extensive with many precious metals (Au, Ag) and semi-metals (As, Sb, Te, Se, Bi, Tl, Cd) being enriched alongside base metals (Monecke et al. 2016). It has been suggested that enrichments of the precious and semi-metals such as Au, As, Se, Mo, Ag, Sb, Te, and Bi in Au-rich VMS deposits indicates significant input of magmatic volatiles into the hydrothermal system (Sillitoe et al. 1996; Yang and Scott 2002). This suite of metals, however, is also mobilised by hydrothermal alteration reactions in the lower sheeted dyke section of the oceanic crust (Patten et al. 2016; Patten et al. 2017). Constraints of the trace element signature of magmatic volatile input in hydrothermal systems would aid understanding of the causes for the variable metal budgets in Au-VMS deposits and could be an important tool in development of localised exploration strategies.

Oceanic drilling program (ODP) Hole 786B in the Izu-Bonin forearc is one of the only deep drill holes into supra-subduction oceanic crust recovering over 700 m of basement rocks from the volcanic section to the upper sheeted dyke complex, including a conspicuous 30 m thick transitional zone in the lowermost section of the core (Alt et al. 1998). This mineralised zone includes a 5 m-thick zone at 815-820 mbsf containing pyrite, chlorite and sericite alteration, which based on negative δ34S values and acidic conditions of alteration has been interpreted to have been formed by hydrothermal fluids rich in magmatic volatiles (Alt et al. 1998). The mineral paragenesis and the trace metal endowments have not been previously investigated but may provide insight into the trace metal signature of a magmatic volatile-rich submarine hydrothermal system. The objectives of this study are to characterise the mineralisation and the associated trace metal endowment and to determine the signature of magmatic volatiles input in the hydrothermal system at Hole 786B. The results of the study provide insight into the signature of magmatic fluid input in the oceanic crust hydrothermal system, into the fluxes of metals in arc-related oceanic crust and into the controls of Au enrichment VMS deposits.

2 Methodology

In-situ trace element analyses by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) of the sulphide population of Hole 786B transitional zone was carried out at Göteborg University using a NWR213 nm laser coupled to a Agilent 8800QQQ mass spectrometer.
Figure 1. Depth profile of whole-rock data in Hole 786B. Gold, As, Sb and Se are from this study and S, Cu, Zn and Pb are from Arculus et al. (1992) and Alt et al. (1998). Crosses are volcanic section samples and triangles are mineralised samples.

Spot size of 20 μm was used with a laser pulse frequency of 5 Hz and a laser energy density of 4.65 J.cm⁻². Analyses of 179 points were carried out on pyrite, chalcopyrite, sphalerite, marcasite and bornite. Reference materials MASS-1, Po727 T1 SRM and Sph-Upp were used for calibration and monitoring. In-situ S isotope analyses on pyrite were performed using a Nu Plasma HR multicollector ICP-MS together with a Photon Machine Analyte G2 laser microprobe at the Geological Survey of Finland in Espoo. Spot size of 30 μm was used with a laser pulse frequency of 5 Hz and a laser energy density of 2.2 J.cm⁻². Pyrite reference materials PPP-1 and an in-house standard Py1 were used for calibration and monitoring. Whole-rock Au analyses were carried out at Stockholm University using a Thermo XSeries 2 ICP-MS following the ultra-low detection limit method described in Pitcairn et al. (2006). The 3σ method detection limit calculated from blank digests is 0.027 ppb. Arsenic, Sb and Se analyses were carried out by hydride generation atomic fluorescence spectrometry (HG-AFS), using a PSA 10.055 Millennium Excalibur instrument. The 3σ method detection limits are 0.059 ppb, 0.081 ppb and 0.039 ppb for As, Sb and Se respectively. Reference materials TDB-1, WMS-1 and CH-4 were used to control analytical precision and accuracy.

3 Results

The transitional zone in ODP Hole 786B, extending from 800 to 830 mbsf (Fig. 1), is characterised by an increase in alteration temperature (≥150 °C), change in secondary minerals and increase in sulphide proportion relative to the volcanic section (Alt et al. 1998). The mineralised zone is significantly enriched in Au, As, Sb, Se and S but does not show enrichment in base metals (Fig. 1). The mineralised zone can be subdivided into the upper alteration zone (UAZ, 799-815 mbsf) and the lower alteration zone (LAZ, 815-830 mbsf) based on secondary minerals and sulphide paragenesis (Fig. 1).

3.1 The upper alteration zone

The UAZ is characterised by alteration to corrensite, smectite and albite, with common veins of quartz and
carbonate (Alt et al. 1998). Sulphide mineralisation is mostly associated with quartz and carbonate veins and consists of pyrite with accessory sphalerite, marcasite, chalcopyrite and trace galena. Whole rock data and in-situ pyrite analyses suggest that the UAZ is preferentially enriched in As, Ag, Au, Hg, Zn, Cu, and Pb relative to the LAZ (Fig. 2). Pyrite grains in veins from the UAZ have δ^{34}S values ranging between 1.5 ‰ and 10.4 ‰ with an average of 5.9 ‰ δ^{34}S.

The LAZ is characterised by alteration to Mg-rich chlorite, mixed layer chlorite-smectite, quartz, albite, sericite and K-feldspar (Alt et al. 1998) giving a white, bleached appearance to the rock. The LAZ contains the greatest sulphide abundance of Hole 786B, dominated by pyrite with rare occurrences of chalcopyrite and sphalerite inclusions. Sulphide proportion decreases in the lower part of the LAZ (820-830 mbsf) concomitant with trace appearances of bornite and covellite associated with chalcopyrite. Whole-rock data and in-situ pyrite analyses suggest that the LAZ is preferentially enriched in S, Se, Mo, Te and Bi relative to the UAZ (Fig. 2). Disseminated pyrites from the LAZ have negative δ^{34}S values, ranging from -8.9 to -0.6‰ and averaging -3.3 ‰.

4 Discussion

4.1 Alteration and mineralisation patterns in the transitional zone of Hole 786B

The secondary mineral assemblage and the pyrite-sphalerite-chalcopyrite-galena paragenesis of the UAZ is interpreted to have form by alteration at moderate temperature (150-200 °C) and under reduced and near neutral pH (Alt et al. 1998). The positive δ^{34}S pyrite signature of the UAZ (5.9±2.9 ‰) suggests that fluids were dominated by seawater. These alteration conditions are similar to the upper parts of mineralised zones encountered in mid-oceanic ridge transitional zones such as ODP Hole 1256D and ODP Hole 504B, which also show preferential enrichments in As, Hg, Zn, and Pb (Alt et al. 2010; Patten et al. 2016).

The LAZ shows a distinctly different alteration pattern to the UAZ. Secondary mineral assemblage and the pyrite-chalcopyrite-bornite-covellite paragenesis is interpreted to have formed at higher temperature (~250 °C) and under
oxidised and acidic conditions (Alt et al. 1998). The negative $\delta^{34}$S pyrite signature of the LAZ (-3.3±2.1 ‰) is interpreted to have resulted from magmatic SO$_2$ disproportionation during mixing with seawater, which imply a strong magmatic component to the hydrothermal system. These alteration conditions are similar to those encountered in high sulphidation systems which also show preferential enrichments in Se, Mo, Te and Bi (Sillitoe et al. 1996; Hannington et al. 1999).

4.2 Sources of the metals

Two possible sources can account for the metals enriched in the transitional zone: the lower sheeted dyke section, where metals are leached during hydrothermal alteration, and magmatic bodies which release metals during magmatic fluid exsolution. Concentration of least-altered samples from the volcanic section suggests that the primitive oceanic crust in ODP Hole 786B was enriched in Sb, As and Pb, had similar Cu, Au and Zn concentrations and was depleted in Se relative to MORB (Fig. 3). This suggests that the primitive crust had high fertility for As, Sb and Pb and that these elements could easily have been mobilised during hydrothermal alteration of the lower sheeted dyke section (Fig. 3; Patten et al. 2016). The Hole 786B crust, however, had poor fertility for Au and Se and it is more likely that the high enrichment of these elements resulted from significant magmatic input into the hydrothermal system (Fig. 3). In the LAZ, the specific enrichment in Se, Mo, Te and Bi of pyrite grains with negative $\delta^{34}$S (Fig. 2) also strongly suggests that these elements were mobilised by magmatic volatiles. Although the Au present in Hole 786B transitional zone is likely sourced from magmatic volatiles it is mostly enriched in the UAZ where the alteration is seawater dominated (Fig. 1). We suggest that this distribution is a function of zone refining where Au (and also Cu, and Zn Fig. 1) is remobilised from the central alteration zone within VMS deposits (Hannington et al. 1999). The upper zone of the LAZ is heavily dominated by recrystallised pyrite and show significant depletion of Cu and Zn (Fig. 1) associated with acidic alteration suggesting that zone refining occurred in Hole 786B transitional zone. It is thus likely that Au was remobilised within the transitional zone from the LAZ to the UAZ during zone refining.

4.3 Metal fractionation and implications for Au-rich VMS formation

The mineralisation in Hole 786B transitional zone displays many of the characteristics of Au-rich VMS mineralisation with relatively high Au to base metal ratios (up to one) and enrichments in Se, Mo, Te and Bi. Gold-rich VMS deposits commonly occur in arc-related settings, but VMS mineralisation in these settings are not always Au-rich. Fractionation of Au from base metals is a critical factor in the formation of Au-rich VMS mineralisation and is most commonly suggested to occur either through input of Au-rich magmatic volatiles or through sub-seafloor boiling (e.g. Moss et al. 2001). Investigation of the mineralisation in the Hole 786B transitional zone suggests that Au enrichment is associated with significant input of Se, Mo, Te and Bi, characteristic of magmatic volatile input into the hydrothermal system as suggested by in-situ pyrite $\delta^{34}$S. Additionally, minor base metal mobilisation whether by magmatic degassing or by rock-buffered hydrothermal alteration, indicates that significant metal fractionation can occur during fluid migration throughout the oceanic crust.

Acknowledgements

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Sillitoe RH, Hannington MD and Thompson JF (1996) High sulfidation deposits in the volcanogenic massive sulfide environment. Econ Geol 91: 204-212

Abstract. Preliminary observations ranging from geological and structural mapping to smaller scale petrographic study have been used in order to document possible controls on gold mineralisation at the world-class Callie deposit in Northern Territory, Australia. The Callie gold mine is located 650 km NW of Alice Springs within the Granites-Tanami Orogen. It is characterised by visible, high-grade, gold mineralisation (commonly returns intervals around 100 g/t Au) occurring within sheeted quartz veins that cut across a plunging folded sequence of medium to fine-grained Paleoproterozoic meta-sediments. Whereas the vein system is highly continuous, the high grade gold distribution is restricted to specific finely laminated stratigraphic horizons. This paper presents an integrated study of the mineralisation and associated alteration within a broader tectono-stratigraphic context.

2 Geological setting

The Callie deposit is hosted within the Paleoproterozoic Granites-Tanami Orogen (GTO) located approximately 650 km NW of Alice Springs in the Northern Territory. The GTO is a poorly exposed Paleoproterozoic terrane that is part of the North Australian Craton (NAC). The GTO comprises of folded Paleoproterozoic sediments of the Tanami Group and volcanic units metamorphosed to greenschist to amphibolite facies that are intruded by granitic rocks and dolerite sills and dykes. The Tanami Group is described as a succession of turbiditic sediments which is divided into two main formations, the Dead Bullock Formation and the conformably overlying Killi Killi Formation (Bagas et al. 2014). The Tanami Group hosts important occurrences of gold, of which the Callie deposit is the largest.

The Callie underground mine is hosted within Dead Bullock Formation. Four deformation events are affecting the Dead Bullock Formation and were described by Voulgaris and Emslie (2004). The first
deformation event (D1) is expressed by tight folds moderately plunging about 40° to the east-south-east. Callie main-stage gold mineralisation occurred during the second deformation event (D2) and is manifested as visible gold constrained within sheeted quartz veins trending sub-parallel to an S2 cleavage. These continuous veins, range from 1 to 30 mm in size and trend 030° to 070° and dip approximately 70° towards the southeast. The veins cross-cut the main east-plunging F1 folds and are interpreted to be associated with similarly trending high-strain zones with a reverse movement (Tunks and Cooke 2007). During the third deformation event (D3) folds and mineralised vein corridors were affected by a system of reverse faults trending approximately N-S. Voulgaris and Emslie (2004) correlate this deformation event with emplacement of calcite, quartz, ± ankerite and minor base-metal sulphides. A fourth deformation (D4) event was also delineated by Voulgaris and Emslie (2004) and involved dextral strike-slip faulting with a minor normal component.

As described above, Callie gold mineralisation occurs as visible gold hosted within centimetre-scale sheeted veins. However, whereas the vein system is highly continuous, the gold distribution is restricted to specific finely laminated stratigraphic horizons within the Dead Bullock Formation (the Middle Callie Beds, the Callie Laminated Beds and the Lintilla Beds). These units are fine- to medium-grained laminated siltstones, with graded bedding. They mainly comprise quartz, biotite, chlorite and are also characterised by the presence of abundant ilmenite. The three known host units are slightly more finely laminated than the surrounding rocks, and richer in ilmenite; however, they are not obviously different from the other sedimentary rocks that surround them (Bagas et al. 2014). Thus, the reason for preferential occurrence of mineralised veins in the Middle Callie Beds, Callie Laminated Beds and Lintilla Beds is not obvious. A previous study of the mineralisation conducted within the Callie Laminated Beds by Bigelow (2005) demonstrates that visible gold occurs when the vein intersects an ilmenite-rich lamination and therefore that alteration of ilmenite into rutile was involved in gold deposition.

3 Methods

3.1 Pit mapping, logging and sampling

Systematic open-pit face mapping was completed on all accessible ramps of the open-pit deposits at Dead Bullock Soak. Detailed logging was undertaken on drill holes chosen to include the main structural, lithological, and mineralogical variations observed in the deposits. Petrographic data reported in this paper results from study of selected drill core samples.

3.2 Petrography and mineral chemistry

Approximately 50 polished thin sections were studied using optical microscopy at the Centre for Exploration Targeting and scanning electron microscopy (SEM) at the Centre for Microscopy, Characterisation and Analysis, UWA. Backscattered electron (BSE) imaging, mineral chemical analyses and element maps were performed using a Tescan Vega3 XM SEM equipped with an Oxford instrument X-Max 50 silicon drift Energy-dispersive X-ray spectroscopy (EDS) system with AZtec software Operating parameters for the SEM-EDS include an accelerating voltage of 20 kV, a working distance of 15 mm, a beam current of 1.5 nA, and a detector process time of 4 s.

4 Results

4.1 Vein paragenesis

A study of the different types of veins was undertaken in order to better understand the controls on gold mineralisation. This was mainly conducted on fresh core samples from the Callie deposit and five types of veins were identified. Each vein type is associated with a deformation event.

The first type of vein described (V1) strikes sub-parallel to bedding and is thought to have been emplaced prior to D1. These veins mainly comprise quartz, carbonate and chlorite but locally also contain abundant sulfides depending on the host rock.

The second vein type (V2) are shear veins, striking sub-parallel to S2 cleavage and were emplaced within D2 shear zones. These veins are characteristically boudinaged, and trend from 50° to 100°, and dip from 60° to 80° to the south. This vein type carries most of the mineralisation at Callie as visible gold. Although the main component of this vein type is quartz, the vein composition varies according to the composition of the host rock. The most common minerals associated with gold in V2 are quartz, calcite, K-feldspar, pyrite, galena, chalcopyrite and rutile.

The third vein type (V3), trends E-W to NE-SW, and is interpreted to occur as tension veins. These veins consist of calcite ± quartz and ± ankerite and have the lowest silica content of all vein types. V3 also locally contains chalcopyrite.

A fourth type of vein (V4) is described as stockwork veining. Open-pit mapping suggests that V4 are related to the D4 dextral strike-slip faulting event described by Voulgaris and Emslie (2004). V4 is characterised by a wide halo of sericitisation within the surrounding host rocks. V4 is mainly composed of quartz and calcite but may also include ankerite, pyrite, chalcopyrite, galena and gold. Preliminary petrographic study of these veins from the Callie deposit shows that they also host free gold and locally gold as an exsolution phase within pyrite crystals (Fig. 1).
4.2 A faint mineralisation footprint

The gold mineralisation at Callie is restricted to the veins therefore a thorough study of the veins was undertaken. This study has focused on ore-bearing veins V2 and V4 and preliminary results are presented in this section.

Petrographic observations and element mapping on V2 and V4 veins and their surrounding host rocks have highlighted the presence of selvages around both vein types associated with their emplacement. Selvages around V2 are usually narrow (<5 mm) and rarely visible to the naked eye. Where visible V2 veins selvages are mainly biotite. Element mapping on some of the mineralised V2 veins confirmed that their emplacement is associated with the addition of Al, Fe and Mg to the host rock and a removal of silica (Fig. 2).

Contrary to V2, selvages around V4 veins are conspicuous to the naked eye and widespread spread around the veins (Fig. 3). In addition, biotite surrounding V4 veins is overprinted by sericite. The hydrothermal fluid associated with V4 vein emplacement suggests addition of K to the host rock and removal of Fe and Mg. Therefore there may be two distinct hydrothermal events responsible for gold enrichment within this deposit.

5 Discussion

Study of the vein system at Callie has highlighted the presence of two very distinct mineralised vein types.

The V2 veins are the most important ones as they carry the highest grades of gold in the deposit. The formation of such high grade mineralization remains to be investigated as it may result from multiple fluid pulses during earthquake-induced fault-valve failure as described by Peterson and Mavrogenes (2014).

From cross-cutting relationships and mineral composition, the V4 veins are interpreted to correspond to a distinct structural event from V2. They also result from the input of a very different mineralising fluid as demonstrated by the characteristic alteration halo around the veins. The V4-related deformation event can be interpreted as responsible for additional enrichment of the Callie deposit or for remobilising gold already present in earlier V2 veins, as demonstrated by Fougerouse et al. (2016) study of the Obuasi deposit.

The preliminary results documented in this paper show that two mineralisation events may have occurred in the Callie gold deposit. Each event concomitant with a deformation event, and each contains a distinct alteration footprint.

Further characterisation of the mineralising fluids and fluid/rock interaction in the region is planned in order to understand their role in forming high-grade gold mineralisation observed at the Callie deposit.

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A metasedimentary source for orogenic gold in the Abitibi belt?

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Abstract. The source(s) of metals in Archean orogenic Au deposits is still hotly debated. In this study, we investigate the extent to which Au, As, Sb, Se, Te and Bi are mobilised during prograde metamorphism of metasedimentary rocks in the Neoarchean Abitibi Greenstone Belt, Canada. Samples were collected from the Pontiac subprovince and the Cadillac Group and Porcupine assemblage from the southern Abitibi and were analysed for their metal content using low detection limit methods at Stockholm University, Sweden. Gold concentrations decrease systematically from 4.2 ppb (range 0.25 to 30 ppb) in biotite zone greenschist facies to 0.33 ± 0.1 ppb in sillimanite zone samples. Arsenic and Sb show similar systematic decreases but Se, Te and Bi show no systematic change. Average Au concentrations in Pontiac rocks metamorphosed from greenschist to amphibolite facies. The Pontiac subprovince dips north under much of the southeastern Abitibi and was metamorphosed coevally with orogenic Au deposit formation. Thus, the Pontiac represents a plausible fertile metasedimentary source of metals in the orogenic Au deposits in the eastern Abitibi.

1 Introduction

Orogenic Au deposits are part of a distinctive class of mineral deposit that has been responsible for a very significant part of world gold production. These deposits have formed over more than 3 billion years of Earth history with three main peaks of formation occurring in the Neoarchean (2.7 to 2.5 Ga), Paleoproterozoic (2.1 to 1.8 Ga) and Phanerozoic (<650 Ma) (Goldfarb et al. 2001). The bulk of world Au production has come from Archean aged deposits but some aspects of these deposits remain poorly understood. The different aged deposits are hosted in fundamentally different geological terranes; Archean deposits are hosted in granite-greenstone terranes composed of metavolcanic rocks and granitic plutons whereas Phanerozoic deposits are dominantly hosted in metasedimentary terranes with or without granitic plutons. One of the most critical factors in understanding how these deposits form and in defining genetic models is to identify the sources of fluids and metals.

It is increasingly being shown that the Au in orogenic Au deposits, especially those of Phanerozoic age, is sourced from metasedimentary rocks through metamorphic dehydration reactions. Systematic depletions of Au and related elements in metasedimentary rocks with increased metamorphic grade have been reported from a number of Phanerozoic metasedimentary belts (Pitcairn et al. 2006a; 2015). The suite of elements mobilized during metamorphism matches that enriched in the deposits, and the depletion in the metamorphosed rocks is therefore suggested to represent the source of metals now concentrated in the deposits (Pitcairn et al. 2006a). The depletion of Au occurs due to transition of diagenetic pyrite to pyrrhotite during prograde metamorphism (Pitcairn et al. 2006a; Large et al 2007; Tomkins 2010). Laser ablation mapping of diagenetic pyrite in metasedimentary rocks has shown that pyrite is enriched in Au and the same suite of elements enriched in orogenic Au deposits (Large et al. 2007). These observations are supported by thermodynamic modeling predicting substantial release of Au and related elements in hydrothermal fluids at the greenschist to amphibolite facies transition (Zhong et al. 2015).

The source of the gold accumulated in Archean orogenic Au deposits is one of ore geology’s great debates. For orogenic deposits in Archean terranes there is little consensus on their sources of fluids and metals, and consequently our understanding of the formation of these deposits is severely hindered. Here we test the metasedimentary dehydration model in the Abitibi belt, Canada, one of the world’s classic Archean granite-greenstone terranes that has produced around 5000 t Au (Robert et al. 2005; Dubé and Gosselin 2007).

2 Geological setting

The Abitibi belt is a 700km x 300km granite-greenstone belt occurring in Ontario and Québec, Canada. It is one of the largest and best-preserved greenstone belts on Earth. The belt has been subdivided based on lithological and geochemical associations into the northern volcanic zone (NVZ), the southern volcanic zone (SVZ), the intervening granite-gneiss zone and the Pontiac subprovince to the south. The NVZ is older forming at 2730-2705 Ma, and the SVZ is separated into the western 2703-2698 Ma Blake River segment and the eastern 2714-2701 Ma Malartic
segment (Daigneault et al. 2002; Thurston et al., 2008). The volcanic rocks are predominantly oceanic metabasalts and metakomatiites suggested to resemble modern day oceanic plateaus, and calc-alkaline metavolcanic complexes interpreted to be of island arc origin (Hodgson and Hamilton 1989). The NVC is separated from the SVZ by the Porcupine-Destor fault zone (PDFZ) and the SVZ from the Pontiac by the Larder Lake-Cadillac fault zone (LLCFZ). These fault zones represent major zones of deformation that were active for over 60 Myr showing both dextral strike-slip movement and thrusting (Daigneault et al. 2002; Robert et al. 2005; Bedeaux et al. 2017). Metasedimentary rocks occur in linear belts spatially associated with these fault zones (Powell et al. 1993, Thurston et al., 2008 and references therein). The volcanosedimentary sequences are intruded by granitoids ranging in composition from early calc-alkaline suites (2695-2680 Ma), to late subalkaline to alkaline suites (2685-2670 Ma; Corfu et al. 1989). The volcanosedimentary sequences have been subjected to low-pressure metamorphism at between sub-greenschist (prehnite-pumpellyite) and amphibolite facies (Powell et al. 1993), with higher metamorphic grades occurring in contact aureoles around plutons. Metasedimentary rocks are abundant in the Pontiac subprovince, where metamorphism is Barrovian in style with grades increasing southwards. Contact metamorphism occurred between 2690 and 2650 Ma, whereas regional metamorphism occurred at around 2660 Ma (Robert et al. 2005). The upper crust contains mainly steeply dipping structures whereas the middle crust shown by seismic profiles is moderate to shallowly dipping (Ludden et al. 1993). The age progression and structure are interpreted to indicate accretion of oceanic assemblages onto basement to the north during collision, followed southward migration of an arc-trench system (Kerrich and Ludden 2000).

The Abitibi belt has produced over 5000 t Au (Goldfarb et al. 2001; Robert et al. 2005; Dubé and Gosselin 2007). Deposits occur in specific campus such as Timmins-Porcupine, Kirkland Lake, Rouyn-Noranda and Val-d’Or that are all spatially associated with the two major faults in the area, the LLCFZ and PDFZ. The deposits are hosted by metavolcanic, metasedimentary and plutonic rocks and dominantly occur as arrays of quartz veins containing native gold (Robert et al. 2005). The deposits defined the classic characteristics of orogenic Au deposits with enrichments in Au, As, Sb, W, Sc, Bi and Mo. Most deposits in the SVZ of the Abitibi are hosted in metavolcanic and intrusive rocks of the SVZ, although the Malartic deposit is hosted mainly in metasedimentary rocks of the Pontiac (De Souza et al. 2016). The main phase of gold mineralization occurred between 2680 and 2660 Ma; Robert et al. 2005).

### 3 Sampling and methods

A suite of 120 metasedimentary rock samples were collected from the Abitibi belt and the Pontiac subprovince. The Pontiac samples were collected in north-south transects south of Rouyn-Noranda and Val-d’Or. Cadillac Group samples were collected in a transect northeast of Cadillac, and the Porcupine samples were collected east of Timmins. Most samples were collected from the Pontiac as this area exposes a metamorphic transition from biotite zone greenschist facies in the north down to sillimanite zone amphibolite facies in the south. Care was taken to avoid weathering or mineralisation.

The samples were analysed for major and trace elements at Activation Laboratories, Canada and for Au, As, Sb, Se, Te and Bi using low detection limit methods at Stockholm University. The Au analysis involves multacid digestion of samples, chromatographic separation of Au using an inert resin primed with solvent, and analysis by inductively-coupled-plasma mass spectrometry (ICP-MS) and has a detection limit of 0.02 ppb (Pitcairn et al. 2006b). Arsenic, Bi, Sb and Te analyses were carried out by Atomic Fluorescence Spectroscopy (AFS) using a PSA Instruments Millenium Excalibur with detection limits of between 0.002 and 0.01 ppb. Metamorphic temperatures are estimates based on the bulk assemblages.

### 4 Results

<table>
<thead>
<tr>
<th>Element</th>
<th>Min (ppb)</th>
<th>Max (ppb)</th>
<th>Average (ppb)</th>
<th>Median (ppb)</th>
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</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>0.01</td>
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<td>0.05</td>
</tr>
<tr>
<td>S (%)</td>
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<td>0.38</td>
<td>0.16</td>
<td>0.15</td>
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<tr>
<td>Au (ppb)</td>
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<tr>
<td>As (ppm)</td>
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<td>12.7</td>
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<tr>
<td>Sb (ppb)</td>
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<td>303</td>
<td>205</td>
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<tr>
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<td>110</td>
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<tr>
<td>Te (ppb)</td>
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<td>66</td>
<td>34</td>
<td>31</td>
</tr>
<tr>
<td>Bi (ppb)</td>
<td>63.5</td>
<td>378</td>
<td>181</td>
<td>175</td>
</tr>
</tbody>
</table>

Table 1. Elemental concentrations for biotite zone metasedimentary rocks from the Pontiac subprovince.

Over 60 elements were quantified in the samples but we will focus here on the suite of elements that are typically enriched in OG deposits (Au, As, Sb, Se, Te and Bi) as well as others that are significant for the mobility of Au such as H₂O, C and S. Metal concentrations in biotite zone samples from the Pontiac subprovince are shown in Table 1. Average and median values are relatively similar for all elements, except Au whose average is higher due to 2 samples with 22 and 29 ppb Au, respectively. Of the elements listed in Table 1, only Sb and Te correlate with TiO₂, which is used a proxy of the sedimentary protolith composition. Concentrations of C, Au, As and Sb decrease systematically with increasing metamorphic grade to average values of 0.01 % (all values at detection limit of 0.01 %), 0.33 ± 0.1 ppb, 0.25 ± 0.1 ppm and 75 ppb (range 8.4 to 250 ppb) respectively (Figs. 1 and 2). For these elements the range of concentrations also decreases with increasing metamorphic grade. Sulfur, Se, Te and Bi concentrations show no systematic change with increasing metamorphic grade. A much smaller suite of samples over a shorter range of metamorphic grades was collected from
the Porcupine and Cadillac groups. The range of concentrations from the Cadillac samples generally falls within the range observed in the Pontiac biotite zone samples, and no significant differences between the Cadillac chlorite and biotite zone samples were observed. The Porcupine samples have higher C, As, Sb and Te concentrations than either the Cadillac or Pontiac groups. Average Au concentrations in the Cadillac and Porcupine samples are 1.3 ± 0.6 ppb and 1 ± 0.3 ppb respectively, lower than the biotite zone Pontiac samples (Fig. 1).

![Figure 1](image)

**Figure 1.** Au concentration vs metamorphic temperature for metasedimentary rocks from the Pontiac, Cadillac and Porcupine Groups. Thick line represents the average and the dashed line the median for the Pontiac samples.

![Figure 2](image)

**Figure 2.** Average concentrations of Au, As, Sb, Se, Te, Bi, C, S and H2O vs metamorphic temperature (Met. Temp. °C) for metasedimentary rocks from the Pontiac subprovince.

5 Discussion

5.1 Host minerals for Au

The foundation for the metamorphic dehydration model for the formation of OG deposits is that Au and related metals are mobilised by metamorphic fluids produced primarily from breakdown of chlorite at the greenschist-amphibolite facies transition. The most important mineral reactions in this process that may release metals (in contrast to breakdown of chlorite that produces water) are those involving the sulphides and in particular the transition of pyrite to pyrrhotite (Pitcairn et al. 2006a; Large et al. 2007; Tomkins 2010). This study demonstrates that significant masses of Au, As and Sb were likely removed from the Pontiac subprovince metasedimentary rocks during prograde metamorphism (Figs. 1 and 2). Gold, As and Sb show no correlation with S content suggesting that they are not evenly distributed in the most common sulphide minerals. Selenium, Te, Bi and also Cu do show relatively strong positive correlations with S indicating these elements are more homogenously distributed in sulphides. The most common sulphide in the Pontiac metasedimentary rocks is pyrrhotite. Although still work in progress, we estimate the pyrite : pyrrhotite ratio are 0.3 in the biotite zone samples decreasing to 0.1 in the sillimanite zone samples. This indicates that, assuming pyrite was the main sulphide in the unmetamorphosed protolith rocks, the transition to pyrrhotite has mainly occurred prior to upper greenschist facies conditions. The bulk of Au, As, Sb mobility we observe does not correlate with the pyrite-pyrrhotite transition but with decreasing C and H2O contents (Fig. 2). This may suggest that the pyrite- pyrrhotite transition, which is commonly thought to be the key Au-releasing reaction during metamorphism, does not fully control Au mobility in these rocks. Identification of the mineral reactions responsible for metal mobility is our current aim.

5.2 The Pontiac as a source for metals in the southeastern Abitibi belt

The Pontiac metasedimentary rocks are exposed in the SE Abitibi directly south of the LLCFZ. The rocks are coeval with the majority of metasedimentary rocks of the southern Abitibi (excluding the 2679-2669Ma Timmaskaming sedimentary rocks) being deposited at around 2686 Ma (Davis 2002). The Pontiac metaturbidites are considered to have been deposited from erosion of a continental arc to the north to form a foreland basin and accretionary prism (Davis 2002). The Pontiac metasedimentary rocks dip northwards and are interpreted through seismic profiles to continue northwards under the SVZ of the Abitibi (Ludden et al. 1993). Some workers suggest that the Pontiac may continue northwards under most of the Abitibi (Ludden et al. 1993; Kimura et al. 1993; Davis 2002). The timing of metamorphism of the Pontiac overlaps with the age of OG mineralisation in the Abitibi (Robert et al. 2005).

The average Au concentration in the Pontiac metasedimentary rocks changes from 4.2 to 0.3 ppb (Table 1, Figs. 1 and 2). Assuming a density of 2.7 g cm⁻³, every 1 km³ of biotite zone greenschist facies rock metamorphosed to amphibolite facies would produce over 10 t Au. This indicates that these rocks represent a potential fertile source of Au for the OG deposits in the eastern Abitibi. A section of Pontiac rock 100 km x 50 km x 5 km deep metamorphosed from greenschist to amphibolite facies would mobilise over 250,000 t Au. This
indicates that even at 1% source to sink trapping efficiency, this volume of Pontiac rock could have provided over 2500 t Au, which would account for much of the Au in the eastern Abitibi. This area of source rock could also supply all of the As and Sb enriched in the deposits. The lack of mobility of Se, Te and Bi from the metasedimentary rocks indicates these metals may have been sourced from other rocks such as the metabasaltic rocks, or from magmatic fluids.

5.3 Fertility and endowment of orogenic gold

![Figure 3. Au endowment (t) vs Au mass loss (mg/t) from 4 different orogenic terranes, The Dalradian, Scotland (Dal.), Otago Schists, NZ, Victoria goldfields, Australia, and the Abitibi, Canada. Abitibi mass loss is calculated from the Pontiac samples.](image)

The total Au mass loss from 1km³ of biotite zone greenschist facies rock metamorphosed to amphibolite facies of 10 t Au is considerably higher than the Au mobilised from other terranes where similar mass balance calculations have been carried out such as the Otago and Alpine Schists, New Zealand, The Dalradian metasedimentary terrane, Scotland and the Victoria goldfields of Australia. Figure 3 shows total Au endowment from orogenic gold deposits plotted against protolith to amphibolite facies mass loss for the terranes listed above. The correlation between mass loss and endowment may indicate that the Au concentration of the protolith rock in a metasedimentary terrane may be a primary control on the extent of orogenic gold mineralisation. Although based on limited data at present, the difference in Au concentrations between the Cadillac, Porcupine and Pontiac metasedimentary rocks indicates that different sedimentary packages may have different fertilities at a terrane scale.

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Copper, gold and bismuth behavior in magmatic-hydrothermal systems: fluid-inclusion LA-ICP-MS study

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Abstract. This study compares the elemental composition of fluid inclusions hosted in various co-existing minerals from magmatic-hydrothermal systems. We present data in support of post-entrapment modification of fluid inclusions hosted in quartz, showing that Cu can be enriched up to three orders of magnitude in the S-bearing vapor inclusions when compared to coeval inclusions hosted in topaz and beryl. For analysis of the Au concentrations in natural fluid inclusions, stringent guidelines for cleanliness of LA-ICP-MS systems have to be applied to avoid any contamination that adversely affect low-count signals and detection limits. Detection limits for Au as low as a few ppb have been documented in porphyry-type systems, where inclusions often contain chalcopyrite crystals that fail to dissolve upon laboratory heating at ambient pressure (e.g. Sawkins and Scherkenbach 1981). Re-equilibration experiments on inclusions hosted in natural or synthetic quartz (Zajacz et al. 2009; Li et al. 2009; Lerchbaumer and Audétat 2012) have shown rapid transport and exchange of small (~1 Å) monovalent cations (e.g. H+, Li+, Na+ and Cu+) between the exterior environment and quartz-hosted fluid inclusion. For instance, Cu concentration in the melt and fluid inclusions can increase up to three orders of magnitude if subsequently equilibrated in Cu-bearing solution (Zajacz et al. 2009). The increase in Cu contents is coupled with decrease in Na concentration in samples immersed in Na-free external solution (6–83 % Na loss), or accompanied by H+ diffusion outwards to satisfy the charge balance (Li et al. 2009). The Cu enrichment is more profound in vapor inclusions (increase from 0.3 to 5.7 wt. % Cu), compared to brine inclusions which seemed to be largely unaffected (Lerchbaumer and Audétat 2012). The amount of Cu gained is related to the S content of the inclusion and reaches molar Cu:S ratios ~2 (Seo and Heinrich 2013). By contrast, Au+ cations are expected to migrate, if at all, from the inclusion interior outwards during cooling of typical fluid-saturated rocks (Seo and Heinrich 2013). However, Au+ is a relatively large ion (1.37 Å) which, in contrast to small cations like Li+, Cu+, Na+, is less likely to be transported by change-coupled ion migration through the C-axis channels of the quartz structure (Harris and Waring 1937). These findings have significant implications for interpretation of fluid inclusion data from quartz in various magmatic-hydrothermal settings: while Cu concentrations in vapor inclusions commonly may have increased after inclusion entrapment, Au contents are more likely to represent true or possibly minimum concentrations.

1 Introduction

Evolution of a hydrothermal fluid – the key medium for transport of metals and complexing agents from their source to the site of deposition – is important for the formation of economic metal accumulations. Cooling and decompression of magmatic fluids during upward migration through the Earth’s crust often result in their separation into two coexisting phases: a low-salinity vapor and a high-salinity liquid (brine; e.g. Heinrich et al. 1999). Fluids in hydrothermal systems are generally inaccessible to direct sampling but can be preserved in the form of fluid inclusions trapped in various minerals. Analysis of natural co-existing brine and vapor inclusions and experimental work suggest that Na, K, Mn, Fe, Zn, Rb, Ag, Sn, Cs, W and Pb partition preferentially into the liquid in presence of chlorine, whereas B, As, Pt and Au are concentrated to various extent in the vapor, enhanced by presence of the reduced S (see review by Pokrovski et al. 2013; 2014). The partitioning of Cu between brine and vapor is not as well understood but is likely to be in favor of brine (Seo and Heinrich 2013; Pokrovski et al. 2014). Systematics of the element partitioning between vapor and brine helps explain the distribution and variability of magmatic-hydrothermal ore systems such as porphyry, epithermal and greisen mineralization.

Most information about natural magmatic fluid composition comes from analyses of fluid inclusions. However, fluid inclusions hosted in quartz – an abundant gangue mineral – may suffer from post-entrapment modification of their original chemical composition as a result of ion migration of elements between the inclusion, the host and the surrounding environment. Water loss and change in salinity or exchange of protons has been well documented in porphyry-type systems, where inclusions often contain chalcopyrite crystals that fail to dissolve upon laboratory heating at ambient pressure (e.g. Sawkins and Scherkenbach 1981). Re-equilibration experiments on inclusions hosted in natural or synthetic quartz (Zajacz et al. 2009; Li et al. 2009; Lerchbaumer and Audétat 2012) have shown rapid transport and exchange of small (~1 Å) monovalent cations (e.g. H+, Li+, Na+, Ag+ and Cu+) between the exterior environment and quartz-hosted fluid inclusion. For instance, Cu concentration in the melt and fluid inclusions can increase up to three orders of magnitude if subsequently equilibrated in Cu-bearing solution (Zajacz et al. 2009). The increase in Cu contents is coupled with decrease in Na concentration in samples immersed in Na-free external solution (6–83 % Na loss), or accompanied by H+ diffusion outwards to satisfy the charge balance (Li et al. 2009). The Cu enrichment is more profound in vapor inclusions (increase from 0.3 to 5.7 wt. % Cu), compared to brine inclusions which seemed to be largely unaffected (Lerchbaumer and Audétat 2012). The amount of Cu gained is related to the S content of the inclusion and reaches molar Cu:S ratios ~2 (Seo and Heinrich 2013). By contrast, Au+ cations are expected to migrate, if at all, from the inclusion interior outwards during cooling of typical fluid-saturated rocks (Seo and Heinrich 2013). However, Au+ is a relatively large ion (1.37 Å) which, in contrast to small cations like Li+, Cu+, Na+, is less likely to be transported by change-coupled ion migration through the C-axis channels of the quartz structure (Harris and Waring 1937). These findings have significant implications for interpretation of fluid inclusion data from quartz in various magmatic-hydrothermal settings: while Cu concentrations in vapor inclusions commonly may have increased after inclusion entrapment, Au contents are more likely to represent true or possibly minimum concentrations.
Our study attempts to compare composition of fluids trapped simultaneously in different coeval minerals typical of magmatic-hydrothermal systems including quartz, topaz, and beryl. Vapor and brine inclusions hosted in co-punctuated minerals, trapping the same hydrothermal fluid, represent ideal materials to address the preservation of fluid composition and to unravel the peculiar behavior of Cu, Au and other elements. The Au and S analysis bring various analytical challenges (Schlöglova et al. 2017) which are addressed by using recently developed highly sensitive sector-field laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) at ETH Zürich. By trying to push the limits of detection to very low values, we recognized analytical limitations. We can explain the exceptionally low Au contents of fluids generating small but high-grade granite-related gold deposits with the help of a thermodynamic model for the Bi–Au system of coexisting fluid and metal melts.

2 Sample selection

Fluid inclusions used in our study occur as petrographically well-constrained assemblages of pseudosecondary or secondary, high-salinity (28–39 wt. % NaCl eq.), low-density (~0.2–0.3 g·cm⁻³) vapor contamination in the LA-ICP-MS transport system, we quartz, and 20 Hz for topaz and beryl. To avoid 10 Hz was used for ablation of standard materials and downstream from the sample chamber. Repetition rate of duration). For the carrier gas, we used 1.0 L·min⁻¹ of 6.0 grade He, merged with 0.75–0.95 L·min⁻¹ of 6.0 grade Ar downstream from the sample chamber. Repetition rate of 10 Hz was used for ablation of standard materials and quartz, and 20 Hz for topaz and beryl. To avoid contamination in the LA-ICP-MS transport system, we used all-glass cell of ~1 cm³ volume, fluorinated ethylene propylene (FEP) tubing (Rotilabo®, Carl Roth GmbH, Germany) between the LA and the ICP-MS, and skimmer and sampler cones made of Ni, cleaned with HF (for details see Schlöglova et al. 2017). Samples and all glass parts of the instrumentation were cleaned by aqua regia and rubbed in 1-µm alumina suspension (Struers, Denmark). The sampling of fluid inclusions was done using an iris aperture for gradual opening, assuring complete ablation of the targeted inclusion, and also allowing pre-ablation of the sample surface by laser ablation. We used a small element menu, with a dwell time of 20 ms for ¹¹B, ²³Na, ²⁹Si, ³⁴S, ³⁹K, ⁶⁵Cu and ¹³³Cs, and 200 ms for ¹⁹⁷Au. The LA-ICP-MS signals were treated with SILLS (Guillong et al. 2008). The limits of detection were calculated based on Pettke et al. (2012).

4 Results

4.1 Post-entrapment modification of quartz-hosted fluid inclusions and metal partitioning

We analyzed 570 individual vapor or brine inclusions from coeval minerals at four localities. The minimum, maximum and median concentrations for most analyzed elements are overlapping at all localities thus confirming that the sampled inclusions do represent coeval fluids (Fig. 1). The B, Na, K and Cs show consistent concentrations in inclusions hosted in different minerals. However, the Cu concentrations in the quartz-hosted vapor inclusions span a range between ~3 ppm and 50 000 ppm, with median near 5000 ppm (Fig. 1). By contrast, the Cu concentrations of the vapor inclusions in topaz and beryl are in the range of ~20–2000 ppm, with the median value of ~200 ppm being one order of magnitude lower than that in quartz-hosted vapor inclusions. Gold has been detected in few inclusions only, in all host minerals (Fig. 1).

Figure 1. The B, Na, S, K, Cu, Cs and Au concentration ranges in brine (solid bars) and vapor (open bars) inclusions hosted in quartz, topaz and beryl. Bars cover minimum to maximum range with median value indicated (outliers and values below the detection limit have been removed). Note different scale for Au.
Apparent element partition coefficients between vapor and brine ($K_{V/L}$) were calculated from the median concentrations of the inclusion assemblages found in each mineral at every locality. The apparent partition coefficients of Cu in the quartz-hosted fluids are greater than 10 (Fig. 2), suggesting apparent preference of Cu into the vapor. However, the partition coefficients of Cu from the topaz- and beryl-hosted fluids are lower than 1. The latter are consistent with experimental results from S-bearing systems (e.g. Pokrovski et al. 2013) yielding $K_{V/L} = 0.005–0.6$ for density ratio of interest in this study ($\rho_V/\rho_L = 0.38$). By contrast, the $K_{V/L}$ of Cu for the quartz-hosted fluids are higher than those from any experiments. The partition coefficients of Au are consistent for fluids entrapped in all minerals and reach 5.5–8.5, i.e. suggesting a distinct preference of Au for the S-rich vapor phase albeit at very low concentrations in both fluid phases (Fig. 2).

Figure 2. Partitioning of Cu and Au between vapor and brine (log $K_{V/L}$) based on the fluid density contrast (log $\rho_V/\rho_L$). Experimental data and corresponding references are compiled in Pokrovski et al. (2013).

4.2 Gold partitioning between bismuth-rich melt and aqueous fluid

The extremely low Au concentrations recorded in the vapor and brine inclusions in this study require a very efficient mechanism of Au sequestration during hydrothermal processes. The very low Au abundances can be achieved by saturation with another phase that strongly partitions Au even at trace levels. Tooth et al. (2008) document removal of Au from hydrothermal fluids during precipitation of native Bi in the liquid metallic form, which may precipitate directly from hydrothermal fluid above 241 °C. In order to test this hypothesis we evaluate attainment of Bi saturation by comparing our measured Bi concentrations in fluid inclusions (locality Gold) with thermodynamic calculation of Bi solubility over a range of temperature, pressure and oxygen fugacity.

Solubility of liquid bismuth Bi (l) was calculated in the Bi-O-H-Na-K-Cl system using the thermodynamic data of Holland and Powell (1998), Shock et al. (1997), Tooth et al. (2008), Tooth et al. (2013), and Etschmann et al. (2016). Based on these experiments we consider an Na-K-Cl fluid with $\text{Bi}^{3+}$, $\text{BiOH}^{2+}$, $\text{Bi(OH)}_2^+$, $\text{Bi(OH)}_3^+$, $\text{Bi(OH)}_4^-$, $\text{BiCl}_3$ and dissolved species and metallic Bi as condensed pure phase. We performed two sets of calculations of Bi (l) solubility for oxygen fugacity at the hematite-magnetite (HM) or quartz-fayalite-magnetite (QFM) buffer. The pH was controlled by coexisting K-feldspar, quartz and muscovite or andalusite. The thermodynamic calculations were carried out from 200 to 700 °C, at saturated vapor pressure and along a constant $P-T$ gradient continuing from the critical point of H$_2$O to 700 °C and 1013 bar for coexisting vapor and brine (Driesner and Heinrich 2007). Our vapor (3 wt. % $\text{NaCl}_{eq}$) and brine (32 wt. % $\text{NaCl}_{eq}$) inclusions are expected to coexist along this gradient at 530 °C and 600 bar.

Calculated solubilities and measured concentrations of Bi are compared in figure 3. The Bi solubilities in vapor versus brine remain nearly identical at all conditions. This demonstrates that the speciation is dominated by Bi-OH species as opposed to Bi-Cl complexes, as suggested by Tooth et al. (2013) and Etschmann et al. (2016). Oxygen fugacity has major effect on the Bi solubility owing to the equilibrium: $\text{Bi} (l) + 3/4 \text{O}_2 + 3/2 \text{H}_2\text{O} = \text{Bi(OH)}_3 (aq)$. As oxygen fugacity increases from QFM to HM, the solubility of Bi (l) rises by four orders of magnitude (Fig. 3). The Bi concentrations measured in this study: $\sim 10 \text{ ppm (5·10^{-5} molal)}$ and $\sim 140 \text{ ppm (7·10^{-4} molal)}$ in vapor and brine, respectively, are reproduced at $\text{O}_2$ one log unit below the hematite-magnetite buffer (HM-1 ± 1). These redox conditions are plausible and documented by the presence of magnetite in cassiterite-bearing hydrothermal veins and replacement of ilmenite by hematite and rutile in the W-bearing topaz-quartz greisen. Our model illustrates that the coexisting vapor and brine at the locality Gold were saturated with Bi (l) at plausible redox conditions.

Figure 3. Solubility of Bi (l) at hematite-magnetite (HM) and quartz-fayalite-magnetite (QFM) redox buffers, $T = 200–700$ °C.
The efficiency of Bi precipitation for Au sequestration was evaluated with a thermodynamic model for Au partitioning between hydrothermal fluid and Au-bearing Bi alloy in the Au-Bi-Na-Cl-O-H-S system (Tooth et al. 2008, Fig. 4). In aqueous fluid, \( \text{Au(HS)}^2^- \) controls the incorporation of Au in the Bi-Au liquid as follows: 4 \( \text{Au(HS)}^2^- + 4 \text{H}^+ + 2 \text{H}_2\text{O} = 4 \text{Au} \text{(alloy)} + 8 \text{H}_2\text{S (aq)} + \text{O}_2 \). Using the concentration 0.18 wt.% Au in the Bi alloy at the locality Gold (Pettke et al. 2012), the corresponding Au concentration in aqueous fluid is 0.1 to 0.01 ppb, well below the analytical capabilities of current LA-ICP-MS systems. Our analytical study provides confirmation that precipitation of Bi occurred and was responsible for very efficient removal of Au from hydrothermal fluids.

![Figure 4](image)

Figure 4. The Au partitioning between Bi-rich melt and aqueous fluid under various \( P-T-X \) conditions, after Tooth et al. (2008). The Au concentration in Bi melt is a median value calculated from LA-ICP-MS data (locality Gold) in Pettke et al. (2012).

5 Conclusions

We demonstrate that quartz-hosted S-bearing vapor inclusions suffer post-entrapment modification and bear Cu concentrations up to three orders of magnitude higher than the coeval vapor inclusions hosted in topaz and beryl. Topaz and beryl might therefore be more reliable hosts for studies involving elements present as small univalent charged ions (e.g., Cu'). In Bi-bearing mineral systems, Au partitions preferentially to the Bi-rich melt, being nearly all scavenged from the hydrothermal fluid, therefore not detectable by any modern ICP-MS instruments with improved detection limit as low as a single ppb.

Acknowledgements

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References


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Fruta del Norte, Ecuador: a completely preserved Late Jurassic epithermal gold-silver deposit

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Abstract. The Fruta del Norte gold-silver discovery in southeastern Ecuador displays key aspects of low- and intermediate-sulphidation style mineralization, including an overlying siliceous sinter horizon. Base metal-poor, quartz-adularia-calcite veins are spatially related to a distinctive feldspar quartz porphyry whereas Mn carbonate- and base metal-rich quartz veins dominate the deposit in andesite to the south and at depth. Both vein styles are succeeded upwards by silicic ore consisting of disseminated marcasite in chalcedonic silicification, veins and breccia. The low-sulphidation veins in the north are partly hosted by the feldspar quartz porphyry (160 Ma) whereas intermediate-sulphidation veins cut Middle Jurassic or older andesite (host to 169 Ma molybdenite). Both underlie the Suárez pull-apart basin, a Late Jurassic clastic-volcanic depocenter linked to the regional Las Peñas fault zone. The exceptional preservation of the epithermal deposit is due to deposition of conglomerate on top of the still-active epithermal paleosurface. Alteration (silicification ± marcasite without gold) continued after the initial burial by conglomerate but ceased before the eruption of Late Jurassic andesitic lava (ca. 157-154 Ma) at the top of the Suárez basin sequence.

1 Introduction

Epithermal precious and base-metal deposits form by hydrothermal processes at shallow crustal levels (<1.5 km), typically at convergent plate margins. Active geothermal sites are recognized as the modern analogs for epithermal precious and base-metal deposits (White 1981; Henley and Ellis 1983). The common association of epithermal deposits with coeval Tertiary or younger volcanic rocks, and the relative paucity of pre-Tertiary examples, may reflect their susceptibility to post-deposition erosion. Despite their siliceous character, this is particularly true for epithermal paleosurfaces (Sillitoe 2015), based on the relatively rare preservation of sinter in the geologic record.

The Fruta del Norte Au-Ag vein-stockwork deposit (FDN) is hosted within the Zarza roof pendant of the Zamora batholith in southeast Ecuador about 10 km west of the Peruvian border. The epithermal deposit is noteworthy for its discovery beneath >100 m of mainly unaltered, barren cover; the rich gold endowment (resources of 9.8 million ounces of gold (Au) in ore grading ca. 9.59 g/t Au), the combination of low- and intermediate-sulphidation veins; and the exceptional preservation of epithermal textures including an extensive sinter horizon above the deposit (Leary et al. 2016).

We describe the geological circumstances that contributed to the deposit's discovery, and the remarkable preservation of the FDN deposit and epithermal paleosurface. As our observations and data are limited to drill core up to ca. mid-2009, we acknowledge that information produced since then may supersede some of the conclusions presented here.

2 Regional setting

The Zamora batholith consists of mainly Jurassic, medium-to coarse-grained monzonite, tonalite and granodiorite plutons and associated volcanic rocks in the Cordillera del Cóndor of southern Ecuador (Litherland et al. 1994). The Zamora batholith and volcanic arc rocks were constructed between two marine transgressions on the stable, northwest margin of the Amazon craton (Litherland et al. 1994). Middle Jurassic volcanism (Romeuf et al. 1995) followed limestone deposition and broadly accompanied the change from marine to clastic deposition in the upper part of the Late Triassic-Middle Jurassic Santiago Formation (Baby et al. 2004). Misahualli volcanism and porphyry magmatism post-dated plutonism and accompanied deposition of the subaerial Middle to Upper Jurassic Chapiza Formation. Early Cretaceous shallow marine quartz sandstone of the Hollín Formation was deposited after erosion of the arc and exposure of its plutonic roots (Litherland et al. 1994). Tectonism during the Andean orogeny exposed the arc relicts beneath the partially eroded Cretaceous and younger cover. Age relationships in roof pendants in the Zamora batholith have been crucial to interpreting the stratigraphic position of Zamora arc volcanic rocks and their metallogeny (Litherland et al. 1994; Chiaradia et al. 2009; Drobe et al. 2013; Leary et al. 2016).

3 Local setting

The roughly 10 x 50 km, north-trending Zarza roof pendant consists of mainly andesitic volcanic rocks and porphyries that are intruded by phases of the Zamora batholith. The FDN deposit is situated at the northeastern extremity of the pendant between strands of the Las Peñas fault zone, a regional transpressive fault that structurally controls other gold-silver prospects in the pendant to the south. Volcanic host rocks of FDN are assigned to the Piuntza unit of the Santiago Formation (Leary et al. 2016).
The northern 10 km of the Zarza roof pendant, including the FDN deposit, are overlain unconformably by sediments filling the Suárez pull-apart basin, a volcano-sedimentary sequence spatially and temporally related to the Las Peñas fault zone (Leary et al. 2016). This regionally extensive, transpressive fault zone bounds the Suárez basin to the east, and cuts both the pendant and batholith. Down-to-the-west motion on the steep West fault splay thickens the basin to the west and juxtaposes the deposit against unaltered conglomerate. The Suárez basin consists of lower fluviatile conglomerate with interbedded dacitic ignimbrite. The mixed upper siltstone-sandstone-conglomerate beds are in part lateral, facies-equivalent to basin margin conglomerate. Unaltered andesite caps the basin in the west, reaching >500 m in thickness west of the West fault at the southern end of the FDN deposit. Piuntza volcanic and porphyry clasts predominate in conglomerate although clasts derived from the Zamora batholith are also present. The conglomerate base is therefore interpreted as an intra-arc unconformity. Sediments filling the Suárez basin are therefore assigned to the subaerial Chapiza Formation, and the uppermost andesite is correlated with the Misahualli unit of the upper Chapiza Formation (Leary et al. 2016).

4 The deposit

The FDN vein-stockwork deposit is up to 300 m wide, extends over 300 m vertically and is at least 1.3 km long (Fig. 1). There are two principal types of colloform-crustiform veins. Veins in the northern ca. 500 m of the deposit are composed mainly of quartz, chalcedony, calcite and marcasite, and are manganese and base metal poor. These occur in the hanging wall of a large feldspar quartz porphyry, distinctive from the typical feldspar hornblende porphyry typical of Piuntza andesite. Veins to the south are dominated by quartz and manganoan carbonates, with abundant base metal sulphides. They are hosted by Piuntza andesite and feldspar hornblende porphyry. Colloform, crustiform, botryoidal, cockade, drussy, finely laminated chalcedonic, and saccharoidal bands, plus replacement and recrystallization (micropumose, flamboyant) textures (Sander and Black 1988; Dong et al. 1995) are prevalent in both vein types. The northern and southern veins are typical of low- and intermediate- sulphidation epithermal deposits, respectively (Sillitoe and Hedenquist 2003). Adularia is a common but minor gangue mineral in both vein types. Bladed calcite occurs in both vein types and ranges from preserved calcite with open spaces to blades completely replaced by quartz with quartz infill. These features imply boiling of the mineralizing fluid (Simmons and Browne 2000). In the absence of cross-cutting relationships, especially where the vein types are proximal at the southern end of the feldspar quartz porphyry, the two vein styles are considered broadly contemporaneous.

Each vein type is abruptly transitional upward, and westward toward the West fault, to a third ore type marked by intense chalcedony silification and disseminated marcasite (± pyrite) veinlets. The upper silicic zone is locally sulphide deficient, the result of a short-lived supergene oxidation event prior to deposition of basal Suárez basin conglomerate (Leary et al. 2016). The upper sulphidic silicic zone is subtly to strongly enriched in As, Sb and Hg relative to the intermediate- and low-sulphidation vein zones. The relationship of veins to the silicic zone and the vertical distribution of trace metals in the hydrothermal system support the Buchanan (1981) model for epithermal precious and base metal vein systems.

The deposit is notable for the widespread occurrence of fine to coarse visible gold, which gives rise to bonanza grades. Visible gold is associated variably with quartz, chalcedony, carbonate (mainly manganoan), and marcasite vein gangue. Semi-porous masses of visible gold are common, including examples of fractal dendrites (cf. Saunders 2012, Fig. 3 with Fig. 11E in Leary et al. 2016). High grades with and without visible gold also accompany vein intervals with masses of crustiform marcasite.

Figure 1. Simplified plan of the geology of Fruta del Norte showing relationship of sinter horizon to the orebody.

The upper silicic ore zone is up to 100 m thick above both vein zones, thickening to the west but abruptly disappearing across the West fault. It thins to the east across the Central and lesser, unnamed faults. The protolith is
4.1 Hydrothermal alteration

Two alteration styles are distinguished in FDN drill core: the latter is visually identified as illite.

pyrite/marcasite. The widespread pale-green clay mineral in assemblages, and later epithermal quartz/chalcedony-clay-
early porphyry copper-related propylitic and potassic deposits, hydrothermal eruption breccias, and volcanogenic
genicodistles with plant fossils (Leary et al. 2016). This distinctive sinter horizon is traceable for >1 km along the
strike of the deposit, in bands at different depths separated by the West and Central faults (Fig. 1). The sinter horizon
has many similarities with the Taupo Volcanic Zone sinter, including high temperature vent facies (Lynne 2012). The
horizon is texturally gradational with underlying silicic ore and appears to constitute the upper part of the upper
tuffaceous unit. Sinter is overlain abruptly by conglomerate wherein clasts of laminated sinter are uncommon (Leary et
al. 2016). The FDN orebody lies in unusual proximity to overlying sinter compared with most epithermal vein
deposits with preserved sinter (Sillitoe 2015).

4.1 Hydrothermal alteration

Two alteration styles are distinguished in FDN drill core: early porphyry copper-related propylitic and potassic
assemblages, and later epithermal quartz/chalcedony-clay-pyrite/marcasite. The widespread pale-green clay mineral in
the latter is visually identified as illite.

Andesite and porphyries hosting FDN veins display strong quartz-illite-pyrite alteration. The appearance of
calcite in the alteration assemblage typically marks the eastern (and lower) ore boundary. Probable pheotomagmatic breccias cut some porphyry intrusions, mainly below the orebody. These breccias may be overprinted by quartz-illite-pyrite alteration but seldom have economic gold concentrations. The upper silicic zone generally lacks illite. The lowermost ca. 20 m of the conglomerate is silicified, typically with disseminated marcasite, where it overlies sinter or the silicic ore zone. Silicification with marcasite also occurs locally above the West fault, commonly at ignimbrite/conglomerate contacts. Uncommon kaolinite is seen on fractures in silicified conglomerate. Where overlain by silicified conglomerate, the sinter horizon is also silicified. Late-stage drusy barite occurs in silicified sinter and underlying silicic ore, and uncommon cinnabar and metacinnabar impregnations occur in silicified sinter (Leary et al. 2016). The silicified conglomerate and sinter have only subeconmic gold concentrations. Above its base, unaltered conglomerate has the red-brown colour typical of terrestrial sediments, with one critical exception: a steeply inclined silicified zone that connects the underlying deposit to a silicified rib exposed >100 m vertically above the deposit. Drill testing beneath this localized surface expression of epithermal silicification containing anomalous As and Sb values led to the discovery of FDN beneath the Suárez basin (Leary et al. 2016).

The vein minerals and quartz-illite-pyrite alteration indicate near-neutral pH hydrothermal fluids, typical of low- and intermediate-sulphidation deposits (Sillitoe and Hedenquist 2003; Simmons et al. 2005). Changes in vein mineralogy laterally within the deposit differ from coexisting low- and intermediate-sulphidation assemblages at different vertical positions in Mexican vein deposits (Camprubi and Albinson 2007). While the vein types may require two discrete mineralizing fluids, perhaps due to source intrusions at different depths (Leary et al. 2016), the lateral change in vein mineralogy appears to correspond to the change in predominant host rocks (volcanic andesite in the south vs. feldspar quartz porphyry in the north). Both vein types and silicic ore are suspected to have formed from fluids that ascended via the West and Central faults. The upward ore change from vein dominated to the silicic replacement zone is attributed to cooling of the ascendant fluid on approach to the paleosurface sinter. The progressive burial of an active epithermal paleosurface beneath the Suárez basin fill likely caused telescoping of the deposit, the atypical proximity of ore to sinter and possibly the high grades due to repeated hydrothermal sealing and brecciation. Burial of the epithermal paleosurface may have contributed to the suppression and eventual extinction of the epithermal system, with gold mineralization in the conglomerate being inhibited by rheologic and chemical factors (Leary et al. 2016). Burial during hydrothermal activity clearly prevented erosion of the epithermal paleosurface and underlying mineralization.

5 Geochronology

Porphyry copper-style (center-line pyrite-quartz) veinlets are present below the FDN orebody and propylitic
alteration (epidote, chlorite, calcite) is overprinted locally by epithermal veinlets with silica-illite-pyrite alteration.
Molybdenite from a quartz veinlet in Piuntza andesite about 700 m south of the orebody was precisely dated by the Re-
Os method at 169 ± 1 Ma (Stewart, Stein and Roa, in prep.). The proximity of porphyry copper alteration and
mineralization to the conglomerate base (<200 m) indicates substantial erosion of the Piuntza unit before deposition in the Suárez basin. The veinlets and alteration are considered as part of a weakly developed porphyry copper system that is roughly 10-15 m.y. older than Late Jurassic (ca. 158-153 Ma) porphyry copper deposits north of FDN (Gendall et al. 2000; Chiaradia et al. 2009; Drobe et al. 2013).

A maximum age for the FDN deposit is provided by a Late Jurassic U-Pb zircon age of 160 ± 0.2 Ma for the feldspar quartz porphyry that hosts the low-sulphidation veins (Leary et al. 2016; Stewart, Stein and Roa, in prep.). The absence of dikes in the Suarez basin sequence, despite the close proximity of the porphyry to basal conglomerate (<50 m), implies that feldspar quartz porphyry intrusion and solidification predates conglomerate deposition. Hydrothermal activity ceased before eruption of the Late Jurassic andesite in the basin above the deposit (157-153 Ma; 40Ar/39Ar amphibole plateau ages; Leary et al. 2016; Stewart, Stein and Roa, in prep.).

Our use of Re-Os to date FDN marcasite is the first known application of this chronometer to this hydrothermal mineral (Stewart, Stein and Roa, in prep.). Late-stage
minerals in silicified conglomerate is less precisely dated between 160 and 157 Ma. We suggest the deposit formed during the cooling history of the feldspar quartz porphyry, which must temporally precede and overlap with initial Late Jurassic conglomerate deposition.

Vein adularia yields anomalously young Late Cretaceous $^{40}\text{Ar}/^{39}\text{Ar}$ ages (ca. 79–67 Ma) comparable with ages of 68 ± 11 Ma for plagioclase in the Late Jurassic Suárez basin andesite (with hornblende dated at ca. 154 Ma) and 71.0 ± 2.2 Ma for hornblende in a post-tectonic mafic dike in the Las Penasas fault zone (Stewart, Stein and Roa, in prep.). A strength of the Re-Os chronometer, relative to Ar-based chronometers is the retention of primary ages. The Re-Os chronometer is chemically sensitive whereas Ar-based chronology is thermally sensitive (Stein, 2014).

6 Discussion and conclusions

The deposition of Suárez basin conglomerate on top of the hydrothermal paleosurface was critical to the high degree of preservation of the FDN epithermal Au-Ag orebody. Conglomerate directly overlying the sinter horizon is silicified as is the sinter itself. This observation requires burial of the epithermal paleosurface while the hydrothermal system was still active. Rapid burial, therefore, prevented significant erosion of the hydrothermal system responsible for the FDN epithermal deposit, including the typically friable paleosurface features. Sinter and uncommon epithermal vein clasts in basal conglomerate directly above sinter cannot have been eroded from the underlying deposit and must be derived from other epithermal sites in the conglomerate source region.

The Fruta del Norte epithermal event occurred in the Late Jurassic following a porphyry copper episode at ca. 169 Ma and intrusion of feldspar quartz porphyry at ca. 160 Ma. The absence of dikes or epithermal veins cutting the basal conglomerate suggests that Suárez basin sedimentation began after 160 Ma. Proximity of porphyry copper mineralization to the base of the conglomerate requires substantial pre-conglomerate erosion in order to have brought mineralization formed at +1 km depths closer to the paleosurface. The lack of alteration in the andesite at the top of the Suárez basin sequence shows that hydrothermal activity had ceased before 157-154 Ma.

Late Cretaceous plagioclase in Late Jurassic andesite requires a thermal event sufficient to reset Ar/Ar ages in feldspar. Post-tectonic mafic dikes were emplaced in the Las Penasas fault zone at ca. 71 Ma. Although volumetrically minor, the Late Cretaceous magmatism is inferred to have disrupted Ar systematics in vein adularia at FDN and may represent the earliest stage of magmatism in the Andean orogeny.

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Fingerprinting gold mineralization using sXRF at the world-class Dome Mine, Timmins, Ontario

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Abstract. The Dome Mine in Timmins, Ontario has produced over 16 million ounces of gold to date. This world-class gold endowment is the result of a multi-stage mineralization history in which the earliest stage of economic gold mineralization is a set of massive ankerite veins (>2300m strike). These veins are part of an early carbonatization event which played an integral role in the mineralization history of the Dome Mine. Gold in the ankerite veins is intimately associated with pyrite mineralization, and three stages of pyrite growth are observed with distinct geochemical fingerprints characterized by synchrotron x-ray fluorescence (sXRF) mapping. The ankerite forming fluids were auriferous and enriched in metals and metalloids (Cu, As, Ni, Zn) with respect to the main stage quartz vein hosted. A second early (Pre-Timiskaming) stage of mineralization was gold poor, enriched in Ni, and may be related to quartz-fuchsite veining. Refractory gold is associated with all three mineralization events, but the largest gold endowment to the ankerite veins is free gold during the third event; main stage quartz veining.

1 Introduction

The Timmins gold camp, in the Western portion of Canada’s Abitibi Greenstone Belt (AGB) is host to some of the world’s most prolific gold deposits. It sits on the Northern margin of the Porcupine Destor Deformation Zone, a crustal scale deformation zone which stretches over 300km E-W across the AGB (Fig.1) (Bateman et al. and references therein; Bleeker, 2015). The Dome Mine is located on the Southern limb of the Porcupine Syncline and has been mined underground and as an open pit. It has produced over 16 Moz of gold since 1910, and this world-class gold endowment is the result of a complex multi-stage mineralization history (Proudlove et al. 1989; Gray et al. 2001). The earliest stage of economic mineralization at the Dome is a 2,690-2,679 Ma (Ayer et al, 2005) set of massive ankerite veins which stretch over 2,300 m and 1,500 m down dip underground, and have contributed ~20% of the ore at the Dome mine. The depositional context, fluid source, and gold content of the ankerite veins has been historically contentious and their role in the history of the deposit is not well understood (Fryer et al. 1979; Kerrich and Fryer, 1979; Proudlove et al. 1989; Pressacco, 1999; Gray and Hutchinson, 2001; Dubé and Gosselin, 2007; Bateman et al. 2008). As the earliest phase of vein formation at the Dome mine, the ankerite veins are overprinted by subsequent quartz-tourmaline and quartz vein hosted mineralization events, recording the entire mineralization history of the deposit. Gold in the ankerite veins is intimately associated with pyrite mineralization, and occurs as inclusions and fracture fill, as well as refractory gold. Given the refractory nature of pyrite, characterizing its trace element content is a powerful tool for fingerprinting the geochemical signature of different mineralization events (e.g. Large et al. 2009; Gregory et al. 2017). The plethora of minor and trace elements found in pyrites, as well as the inherent difficulty in characterizing trace elements in gold make synchrotron X-ray fluorescence (sXRF) a very effective technique for exploring the relationship between gold, trace elements,
2 Approach and methodology

This study takes a unique mine to micron approach combining underground mapping and traditional geochemical analysis with high-resolution in situ trace element analysis. 40 ankerite vein samples from underground (Fig. 2) at the Dome mine and from their surface expression; the Curts vein were collected as well as an additional 19 samples of key lithologies and vein types in the mine sequence. Mineralogy, petrography and bulk rock geochemistry has been determined and was complemented by a suite of 99 bulk rock geochemical analysis of the host rock Vipond Formation metavolcanics. Carbon and oxygen stable isotope analysis of carbonate separates from ankerite vein samples was undertaken at the Laboratory for Stable Isotope Studies at Western University. sXRF mapping was undertaken at the Argonne National Lab, the Advanced Photon Source, the Cornell High Energy Synchrotron Source, and the Canadian Light Source. Maps were collected at 13.1 keV with spatial resolutions ranging from 1-20um. This was complemented by d-SIMS (dynamic secondary ion mass spectrometry) analysis at Surface Science Western.

3 Results

3.1 Bulk rock geochemistry and stable isotopes

Across their over >2300m strike length, there are no trends in trace or major element geochemistry of the ankerite veins observed. There are clear positively correlated relationships observed between the mobility of trace metals such as Ni, Cr, V, Co, Ti, Zr, and REE with enrichments in Al2O3 and K2O (Fig. 2).

The Vipond formation volcanics are high Fe-tholeiites and evolve up stratigraphy with respect to Zr, Al2O3 and TiO2 contents (Fig. 3). As well as being more Fe and Ti rich, the V10 and V8 flows (which sit higher in the stratigraphy) are enriched in REE and P2O5 and depleted in Al2O3, SiO2, and transition metals with respect to the V6 and V99 flows.

![Figure 3. Scatter plot showing the positive relationship between K2O, Al2O3, and Ni (split into quartiles) in the ankerite veins.](image)

Carbonate separate extracted from ankerite vein samples has δ13C and δ18O values range from -2.2 to 0.97‰ δ13C-PDB and 10.8–14.9‰ δ18O-SMOW. No correlations are observed between isotopic values and bulk rock geochemistry. There is little evidence for post depositional influence on the ankerite δ13C-PDB and δ18O-SMOW values based Mn/Sr, Fe/Sr, Mg/Ca and Sr/Ca values (Swain et al. 2015). A spatial trend of increasing δ18O values is observed down dip of the veins and away from the DFDZ to the far west and east regions of the deposit, likely related to fluid temperature.
3.2 *In situ* trace element geochemistry

Three generations of pyrite growth were identified in the Dome ankerite veins, each with a distinct geochemical signature (Fig 4-7). The most commonly observed pyrite morphology is ragged, sieve textured, inclusion rich fine, and grained (Fig.4-5). These pyrite grains are associated with primary ankerite vein formation, either in the sulphide rich vein margins or the centre of the vein. They have a core enriched in metals and have the highest Au and As content of the three grain types (Fig. 6).

![Figure 4](image4.png)
**Figure 4.** sXRF map of a sieve textured pyrite with an As enriched core with inclusions of Au, sphalerite and chalcopyrite.

![Figure 5](image5.png)
**Figure 5.** sXRF map of a pyrite grain with a core enriched in Cu, As, and Zn overgrown by a Ni rich stage of pyrite.

![Figure 6](image6.png)
**Figure 6.** Plot of As and Au contents of three types of pyrites determined by d-SIMS. Increasing Au contents of pyrites correlates with As content where fine grained pyrites have the highest Au contents.

![Figure 7](image7.png)
**Figure 7.** sXRF map of a pyrite grain which lacks rim/core structures and haloes, but with Au at the grain margins and in fractures.

d-SIMS depth profiles indicate that the gold in this early stage of pyrite growth is lattice bound refractory gold. This As enriched inclusion rich core is commonly overgrown by a Ni rich secondary generation of pyrite growth (Fig. 5). Grains which display this intermediate stage of pyrite growth have lower Au and As content than their finer grained predecessor (Fig. 6 P2).

The most spectacular gold showings are associated with overprinting quartz veining either as free gold or associated with coarse grain pyrites which are depleted in trace metals and gold (Fig. 6-8). Gold is found at grain margins and in fractures and refractory gold is in the form of nano-particles (not lattice bound).

![Figure 8](image8.png)
**Figure 8.** sXRF map of a pyrite grain with multiple growth haloes enriched in metals both as inclusions (Cu) and laminations (As, Ni). Gold occurs along fractures and on grain boundaries.

4 Discussion and conclusions

Ankerite vein formation is restricted to the narrow corridor of the Vipond Formation Fe-tholeiites due to permeability barriers, rheological weakness along flow contacts and early shear structures, as well as the high iron content of the Vipond flows. The nuggety nature of gold grades...
across the ankerite veins is the result of variability in the degree of overprinting by quartz-tourmaline and quartz veining events, making vectoring towards ore inherently difficult. However, fingerprinting the gold content and trace element geochemistry of different mineralization events at a high spatial resolution, with low detection limits directly from the mine to micron scale provides a new framework for investigating mineralizing fluid and depositional mechanisms. This represents a paradigm shift in the application of high resolution analysis for exploration as it provides mineralogical contextual information on key trace element associations with minimal sample preparation.

The ankerite vein forming fluid was enriched in As, Cu, Zn and Au as evidenced by the geochemistry of syn-ankerite pyrite growth. This may be related to interaction with local lenses of massive sulphide in the volcanic pile. Oxygen stable isotope values indicate that the ankerite forming fluid was a metamorphic fluid which likely used the Dome fault deformation zone, a splay off the PDDZ as a fluid conduit. This resulted in the intense carbonitization of the surrounding ultramafic and quartz-feldspar porphyry in the PDDZ locally referred to as “carb rock”. This early carbonate alteration of the Hersey Lake Formation komatite facilitated a rheological and geochemical regime favouring auriferous vein formation during subsequent fluid events. This is observed in the formation of the quartz-fuchsite vein, the highest producing single structure at the Dome mine (Moritz and Crocket, 1991).

The distal portions of the secondary Pre-Timiskaming vein event which formed the quartz-fuchsite vein also overprinted the Dome ankerite veins and resulted in a secondary phase of pyrite growth which was gold poor. This second fluid event was enriched in Ni and associated with tourmaline, sericitization, and enrichments in of REE, V, Cr, Co, and TiO₂. There are also local Ag-tellurides and galena observed which may be related to this mineralization event (Harris, 2013). The bulk of the gold endowment in the Dome ankerite veins is from the final stage of gold mineralization at the mine; main stage quartz veining. This main stage gold event is observed across the mine and was pyrite and trace metal poor with respect the ankerite forming event. Gold precipitated as free gold, along quartz vein margins as well on pyrite grain boundaries, and along fractures of earlier syn-ankerite or syn-quartz-tourmaline veining pyrites.

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Geology and structural controls of the Garrison gold deposits, southern Abitibi greenstone belt, eastern Ontario, Canada

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Abstract. The Garrison property is located along the east-trending, >300-km-long Porcupine Destor deformation zone (PDdz) in the Archean southern Abitibi greenstone belt. Four lithologically and structurally distinct gold deposits define the Garrison mineralizing system. The Jonpol and 903 deposits are defined by albitized, quartz-carbonate veins, pyrite-rich, syenite intrusions that occur along the PDdz and a splay of it, the Munro deformation zone that represents the NW margin of a sinistral jog in the PDdz. The Buffonta deposit occurs along a NNW-trending fault zone that parallels the western margin of the 2678±2 Ma Garrison granodiorite stock. Hosted in the youngest sedimentary succession on the property, the Garrcon deposit is represented by free gold in a fault-fracture-fill interlinked quartz-vein system. Despite unique gold paragenesis and ore grades, three of the four deposits show a common linkage to a local sinistral transtensional jog within the PDdz. This jog controlled the emplacement, deformation, and mineralization of the intrusive rocks potentially related to the Garrison stock. After sinistral motion led to disseminated gold deposition in three locations, the regional shortening direction changed to a northerly orientation causing westerly-directed extension. The north-trending quartz vein system formed in this structural regime.

1 Introduction

The Garrison property includes four gold deposits with distinct lithological and structural features at the deposit scale, but a similar tectonic setting at the district scale. The property represents an ideal area to investigate the various structural controls responsible for the local differences between the four deposits, within a more regional structural framework. This study is focused on those regional and local structural controls, as well as the timing of gold events, to establish a comprehensive structural-metallogenic evolution for the area. Understanding local variations within a larger setting may help us predict the location of other potential ore deposits in adjacent regions. The Abitibi greenstone belt represents one of the most prolific fragments of Archean crust on Earth. Several long-lived hydrothermal systems were responsible for the accumulation of numerous mineral deposits, particularly volcanogenic massive sulfide and orogenic gold deposits (Robert et al. 2005). Approximately 80 m.y. (~2750 Ma - ~2670 Ma) of submarine volcanism, followed by clastic sedimentation, plutonism, and multiple phases of crustal shortening comprise the dynamic evolution of the region. Six volcanic successions include an un-named >2750 Ma assemblage, and the 2750-2735 Ma Pacaud, 2730-2724 Ma Deloro, 2723-2720 Ma Stoughton-Roquemaure, 2719-2711 Ma Kidd-Munro, 2710-2704 Ma Tisdale, and 2704-2696 Ma Blake River assemblages (Ayer et al. 2005). The compositions of these successions vary from komatiitic-tholeiitic to calc-alkaline volcanic rocks. The 2690-2685 Ma Porcupine unconformity overlies the volcanic successions, and the 2676-2670 Ma Timiskaming assemblage unconformably overlies all successions (Ayer et al. 2005). The Porcupine and Timiskaming assemblages are primarily composed of clastic sedimentary rocks, representing the transition from a subaqueous to a subaerial depositional environment. The Porcupine assemblage is defined by fine-grained clastic rocks, which are mainly turbidite sequences with minor occurrences of felsic volcanic rocks, conglomerates, and iron formation (Ayer et al. 2005). The Timiskaming assemblage consists of coarse-grained clastic rocks, polymictic conglomerate, and sandstone (Ayer et al. 2005). The Timiskaming assemblage is localized along two major >300 km curvilinear east-trending crustal-scale shear zones: the Porcupine Destor deformation zone (PDdz) and the Larder Lake-Cadillac deformation zone (LLCdZ). The vast majority of the gold deposits is located along proximal splays of the PDdz and LLCdz, also called lower-order structures (Groves et al. 1998; Goldfarb et al. 2005; Dubé and Gosselin 2007). Several granitic plutons were emplaced at various times and at various depths along the PDdz and LLCdz (Feng and Kerrich 1990).
2 Geology of the Garrison property

2.1 Rock units and field relationships

The Garrison property, located 100 km east of Timmins, Ontario, is a 6×5 km area with limited exposures. It lies along the PDdz between two major gold deposits: the Black Fox deposit (Primero Mining) to the west and the Holt-Holloway deposit (Kirkland Lake Gold) to the east (Fig. 1).

Figure 1. Location of the Garrison property along the extensive PDdz. Modified from Poulsen et al. (2000).

Exploration in the Garrison region dates back to 1935. The first detailed geological maps of the area were produced by Satterly (1949). Berger (2002) compiled the available information into a more regional geological map for the area from Matheson, Ontario to the Quebec-Ontario border.

Three main rock units occur on the Garrison property: (1) a mafic volcanic succession, (2) ultramafic volcanic succession forming part of the Kidd-Munro assemblage, and (3) a younger, clastic sedimentary succession that is interpreted to be part of the Timiskaming assemblage (Berger 2002). The subvertical, ENE-trending rock units were intruded by dikes of various compositions and orientations, and were deformed by high strain events and altered by gold-bearing hydrothermal fluids. The ore fluids resulted in widespread albitionization, particularly near gold occurrences. The original stratigraphic relationships between these units have been disrupted by regional folding and thrusting, and the contacts are only observed in drill core where they are characterized by sheared fabrics. The mafic succession present along the northern and southern boundaries of the property represents the unmineralized footwall (Fig. 2A). It is characterized by both massive and pillowed basalt, showing a SSE younging direction. Minor localized high strain zones exist surrounding the deformed pillow margins, and ENE-trending Z-folds with subvertical hinge lines occur locally. The ultramafic volcanic unit shows high strain, recrystallization and carbonate alteration along the Munro deformation zone (Mdz), which exists along the NW margin of a sinistral dilational jog in the PDdz (Fig. 2B). Locally preserved primary volcanic textures, including cumulate and spinifex textures, occur in undeformed domains. Massive, weakly deformed quartz-feldspar porphyritic bodies occur exclusively along shear zones in the volcanic successions. The clastic rocks of the Timiskaming assemblage are characterized by a fine-grained and pervasive albite-quartz-carbonate-sericite-pyrite alteration assemblage cut by several barren lamprophyre dikes altered along its margins when cut by gold-bearing quartz veins. Primary depositional features, such as graded bedding (Bouma sequence), are only noticed in low strain zones in drill core. Although the overall Abitibi belt, especially marginal to the PDdz and LLCdz, was affected by multiple generations of regional thrusts and folds (Wilkinson et al. 1999; Bateman et al. 2008; Bleeker 2015), the sedimentary succession at the Garrison property does not show folds at the outcrop scale. An interlinked quartz vein system is the most remarkable feature in this unit. The southern boundary of the property, south of the PDdz, is formed by the ~5×4 km 2678±2 Ma Garrison granodiorite stock (Corfu et al. 1992). The Garrison stock is estimated to have been emplaced at 3-4 km depth, based on a geobarometry study by (Feng and Kerrich 1990). It is a late tectonic stock emplaced simultaneously with several granitic plutons marginal to the PDdz.

2.2 Structural geology and gold deposits

The sinistral dilational jog in the PDdz (Fig. 2B) crosses local, NNW-trending shear zones at variable angles. Field mapping, drill core logging, and microstructural studies revealed a constant sinistral, NNW-side-up motion along the Mdz. Locally pervasive foliation, shear banding, refolded quartz-carbonate veins, easterly-trending folds, and several undifferentiated intrusive rocks along the shear zone system define the structural history along the Mdz. The PDdz does not outcrop on the Garrison property, but is visible at depth in drill core. Kinematic analysis on selected oriented drill core also supports a consistent sinistral sense of shear on this regional fault system.

Four gold deposits have been recognized to date on the Garrison property. The low-grade Garrcon deposit, hosted by sedimentary rocks of the Timiskaming assemblage, is defined by a northerly trending, fault-fracture fill quartz-vein system that dips ~60° to the east, cutting across bedding planes and locally following them.
The ~1-cm-wide quartz veins carry free gold and associated minor pyrite, and are surround by pervasive albite alteration envelops. Post-mineralization northerly-trending vertical fault surfaces with randomly oriented slickenlines at the Garrcon deposit minimally offset the gold-bearing quartz veins. The Jonpol deposit lies along the Mdz. The deposit is hosted in deformed ultramafic volcanic rocks of the Kidd-Munro assemblage (Berger 2002). Mineralization at the Jonpol deposit is represented by albitized, quartz-carbonate veins, pyrite-rich dikes of unknown composition, that cut this succession. Less than 1 km to the south of the Jonpol deposit, sulfidized porphyritic syenite dikes define the 903 deposit that occurs immediately to the north of the Garrison stock. The 903 deposit lies marginal to a lithological contact exploited by the DPdz. The Buffonta deposit is represented by NNW-striking shear zones hosted in mafic and ultramafic volcanic rocks, occurring less than 200 m west of the Garrison stock. The deposit comprises quartz veins within the sheared system. Figure 2A shows the relationships between these four deposits. A potential pervasive sodic event is interpreted as the most dominant product of the hydrothermal alteration associated with the gold event on the property. A high albite volume in thin sections of altered rocks from all of the deposits analyzed on a scanning electron microscope show that it is the primary plagioclase in dikes and in the sedimentary sequence that have been mainly albitized.

Figure 2. a Schematic block diagram showing the main features and relationships between rock units, as well as the locality of the gold deposits within the Garrison property. b Structural model for the Garrison property.
3 Structural-metallogenic model

Based on the structural and ore characterization of the four deposits, a structural-ore model for the Garrison property is proposed (Fig. 2B). A local sinistral transtensional jog within the east-trending sinistral PDdz facilitated the emplacement, deformation, and mineralization of intrusives rocks that are possibly related to the Garrison stock. The shortening direction changed to a northerly orientation after sinistral motion, causing westerly-directed extension and deposition of the north-trending gold-bearing quartz veins at the Garrcon deposit. The emplacement of the Garrison stock immediately to the SSE of the dilational jog in the PDdz suggests a direct link between them. However, it is not clear whether the jog triggered the stock or vice versa. Although it is unlikely that the Garrison stock contributed a magmatic-hydrothermal fluid to the gold event, it may have provided a physical competency contrast that controlled the development of structures forming conduits for the ore fluids. For example, the mineralized syenite dikes at the 903 deposit could represent an alkalic flow derived from the Garrison stock, which was later preferentially mineralized along local high strain zones. The location of the Garrison stock and possibly pre-existing discontinuities may have controlled the location of the Buffonta deposit.

4 Implications for a modern exploration approach

Recently, low-grade orogenic gold deposits, particularly past uneconomic remnants of previously mined extremely high-grade known deposits, have become new bulk-tonnage exploration targets, because (1) a significant shift in economics substantially increased the price of gold, and (2) more than 100 years of gold exploration in the Abitibi greenstone belt has depleted the major near-surface (<400m) obvious targets. The fact that, at the Garrison property, four lithologically and structurally distinct deposits are linked to the highly favorable PDdz indicates that property-scale detailed structural studies are essential in order to predict potential lower grade ore locations related to known higher-grade vein-type deposits to the east and west. This approach of structural evaluation of lower-grade gold occurrences that were previously considered uneconomic encourages the reexamination of other gold properties across the Abitibi belt that were overlooked in the past.

5 Conclusion

In summary, the Garrison property comprises four gold deposits that are lithologically and structurally distinct at the deposit scale, but, at the property scale, are all related to the same structural setting dominated by the DPdz, Mdz, and possibly by the emplacement of the Garrison stock. The deposits show various ore grades, ore paragenesis stages, and local structural controls that are connected at property scale.

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The making of Archean orogenic gold deposits: tracing sulfur sources in the Agnew gold camp

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Abstract. In the world-class Agnew Gold Camp (Yilgarn Craton, Western Australia) structural and paragenetic relationships, combined with compilation of geochronological data, indicate that mineralisation has developed during a two-stage process that involved contrasting fluid sources. The initial event is related to the onset of folding and presents the characteristics compatible with magmatic intrusion related mineralisation. The second event is, in contrast, typical to Archean orogenic-like gold mineralisation, and has developed at a late stage of the formation of the Lawlers anticline. Recent measurements of $\delta^{34}$S and $\Delta^{33}$S from spatially constrained samples from three of the deposits from the Agnew Gold Camp constrain the fluid sources involved in the formation of the Agnew Gold Camp. Our results show that each of the deposit is associated with contrasted $\Delta^{33}$S values highlighting the role for both magmatic and metamorphic reservoirs in the making of orogenic gold deposits.

1 Introduction

In the Yilgarn Craton of Western Australia, field-based structural reviews and geochronological datasets obtained on Precambrian orogenic gold provinces point toward multiple periods of mineralisation developing continuously during a period ranging from c. 2670 to 2630 Ma (Thébaud et al. 2015). The key question remains as to what is the metal and/or fluid source? Proposed fluid sources include proximal source models, in which ore fluids are derived from mid- to upper-crustal granitoids (e.g. Doublier et al. 2014), and distal models, in which gold-bearing fluids were derived from deep metamorphic (e.g. Phillips and Powell 2010) or, distal magmatic/mantle fluids (Salier et al. 2005). Whereas orogenic lode gold deposit fluid inclusions studies favour a single ore fluid source, isotopic and noble gas data suggest a diversity of potential fluid compositions (Goldfarb and Groves 2015).

Accordingly, isotopic investigation focused on sulfur, one of the critical elements commonly associated with gold mineralisation, in order to fingerprint its potential source reservoir/s (Alt et al. 1993). However, because $\delta^{34}$S isotopic variation is sensitive to chemical processes, the measured orogenic ore-fluid compositions may reflect the influence of fluid–rock interactions along fluid pathways and ore-depositional processes at the deposit site rather than being indicative of its source (e.g. Ridley and Diamond 2000); Hodkiewicz et al. 2009). Recent development in the acquisition of mass independent fractionation of sulfur (MIF-S) offers an isotopic signature unique to a single reservoir, the Archean sedimentary record (Farquhar et al. 2000) that is chemically conservative and importantly not affected by the dynamic chemical processes. Recently, MIF-S has been identified in Archean orogenic gold deposits (e.g. Agangi et al. 2017) demonstrating that some orogenic gold deposits source a portion of their sulfur from Archean sediments. Here, we further this observation by presenting a camp scale multiple sulfur isotope study from sulfides in equilibrium with gold mineralisation in three distinct deposits in the Agnew Gold Camp: the Waroonga, Turret and Songvang deposits. We combine deposit scale structural observations and constraints on mineralisation ages and multiple sulfur isotope data to lend insight into the diversity of fluids reservoirs at play in the formation of a world-class orogenic gold camp.

2 The Agnew gold camp

The Agnew gold camp sits in the southwest corner of the Agnew–Wiluna belt in the Eastern Goldfields Superterrane (Fig 1), and consists of a moderately tightly folded greenstone belt. Supracrustal rocks comprise a basal interlayered greenstone pile that consists of fine-grained tholeiitic basalt, high-Mg basalt, ultramafic rock, gabbro and gabbro-pyroxenite peridotite sills, and minor interbedded sedimentary layers deposited between ~2720 Ma and ~2690 Ma (Platt et al. 1978). The upper greenstone sequence is the Jones Creek sequence and comprises polymictic conglomerate and quartzo-feldspathic sandstones (e.g. Platt et al. 1978). Coarse beds from the Jones Creek sequence near the New Holland–Genesis deposit (Fig 1) host detrital zircons that provided a maximum depositional age for the sandstone of 2664 ±5 Ma, with an inherited zircon population ages of 2.70-2.69 Ga and 2.82-2.81 Ga (SHRIMP U–Pb on zircon (Dunphy et al. 2003). Tonalite to monzogranites stocks intrude the hinge of the Lawlers antiform through successive pulses and dated at 2690±6 Ma, 2665±4 Ma and 2622±6 Ma respectively (SHRIMP U–Pb on zircon, Champion unpublished 2003 and Thébaud et al. 2013). On the western limb of the Lawlers Antiform, the NNE-trending Emu Shear zone hosts or is close to the majority of existing high-grade Au deposits (Aoukar and Whelan 1990). These include from north to south, the New Holland-Genesis and Waroonga deposits (7.5Moz), the Turret (0.01Moz), the Redeemer (0.75 Moz), the Crusader (0.5 Moz), and the Songvang (0.2 Moz) deposits. These deposits exhibit mineralogical variability including: magnetite-rich quartz and sulfide poor Au mineralisation at Crusader, Au-Ag rich system with Bt-F-Act-Cep in
Combining structural geology together with targeted geochronology, Thébaud et al. (2013) demonstrated that mineralisation developed over a two stage process coeval with the formation of the Lawlers Antiform during regional E-W contraction. The initial event was dated at c. 2662 Ma in the Songvang deposit and presents the affinities with magmatic intrusion-related mineralisation (Thébaud et al., 2013). The second mineralisation event was dated in both Redeemer and Turret to be c. 2625 Ma, which is coeval with typical Archean orogenic-like gold mineralisation, and has developed at a late stage of the Lawlers Antiform formation (Thébaud et al., 2013). The model proposed that mineralisation developed during a polyphased and protracted process involving contrasting fluid sources. In the absence of direct fluid tracers it remained, however, difficult to ascertain the involvement of a magmatic source.

3 Methods

Characterisation of <50 µm sulfides by Energy-dispersive X-ray spectroscopy, and identification of fractures, inclusions and zoning by backscatter electron (BSE) at the CMCA, University of Western Australia (UWA). Multiple sulfur isotopic ratios were determined using a CAMECA IMS1280 large-geometry ion microprobe located at CMCA-UWA. A 3.7–4.6 nA focused Cs+ primary beam interacted with the sample at 20 keV. The beam, in Gaussian mode, bombarded the sample surface to create a 15 µm analytical pit. Isotopes $^{32}$S, $^{33}$S and $^{34}$S were simultaneously detected by three Faraday Cups using amplifiers with $10^5 \Omega$ (L2), $10^6 \Omega$ (L1), and $10^7 \Omega$ (FC2 or H1) resistors. Data were collected over 123 s of acquisition time in 20 integration cycles. Measurements were interspersed with Sierra pyrite ($\delta^{34}$S = +2.17‰, $\Delta^{33}$S = −0.02‰) to correct for drift and monitor internal sample repeatability. As well, analyses of matrix-matched reference material were used to calibrate isotope ratios following procedures in LaFlamme et al. (2016). Measurement error on $\delta^{34}$S is equal to about ~0.4‰ and on $\Delta^{33}$S is ~0.25‰.

4 Deposit investigations

4.1 The Songvang deposit

The Songvang deposit is the southernmost deposit of the Agnew Gold Camp, and is located at the contact between a granitic to tonalitic pluton and the basaltic supracrustal cover (Fig. 1). Gold endowment is structurally controlled by two shear zones localised on, and partially crosscutting, the margins of the tonalitic intrusion. The western shear zone dips steeply east, and the eastern shear zone dips 30–40° to the west. The main ore shoot is located at the intersection between the two splays plunging shallowly to the south. Sub-horizontal stretching lineations and associated cryptic kinematic indicators on the eastern shear zone indicate dextral shearing compatible with ENE-WSW shortening. The gold related alteration assemblage displays a strong preferential orientation suggesting that mineralisation developed early to syn-shearing. Gold mineral assemblage is associated with enrichment in Ag, Cu, W, As, Sn and Bi (Fisher et al. 2011). The ore-related mineral assemblage consists of Bt + Qtz + Chl + Act + Cb + Ttn + Fl + Py and Ccp as sulfide phases. U-Pb dating of hydrothermal Ttn returned an age of 2662±7 Ma (Thébaud et al. 2013).

Multiple sulfur isotope analyses were targeted on Py since Ccp grains were too small to be analysed (Fig. 2). Nine analyses performed on nine pyrite grains yield $\Delta^{33}$S values that range from -0.01‰ to +0.14‰ with a mean of 0.03 and yield $\delta^{34}$S values that range from +0.99‰ to +1.54‰.
4.2 The Waroonga deposit

The Waroonga deposit lies to the west of the old Agnew town-site. Mineralised rocks at Waroonga occurs as several ore shoots located at or near the contact between the Scotty Creek Sediments and the Mine Conglomerate Sequence that dip ~60° to the WNW. Structural examination of the lodes points towards a two stages mineralisation process. Early quartz lodes formed at the intersection of the sandstone-conglomerate stratigraphic contact and north trending discrete sinistral-normal shear zones creating the northerly ore shoot plunge (~50°N). This stage of mineralisation is characterised by variably deformed laminated quartz veins and breccia with a link to NW-SE shortening. Late flat tension veins locally forming en-eclenon vein-set overprints the early quartz lodes. Shallow dipping easterly and westerly conjugated mineralised vein-sets imply reverse-dextral sense of shearing within a local ENE-WSW shortening event at the time of mineralisation. Both mineralisation stages at Waroonga are characterised by Qtz + Cal + Act + Bt with Asp >> Ccp + Gn as sulfide phases and associated with enrichment in Ag, As, W, Sn and Bi. This alteration assemblage similarity suggests that both mineralisation stages were intimately related. The obliteration of all early fabrics by the alteration mineral assemblage suggests that mineralisation developed syn- to late-deformation. The timing of mineralisation for the Waroonga deposit is best estimated from that obtained on the Redeemer deposit, which presents structural similarity to the Waroonga system and returned a model age of 2636 ± 8 Ma (Re-Os Molybdenite Colgan writ. comm. 2002).

Sixty-seven Apy multiple sulfur isotope analyses were acquired from Warronga mineralised breccia yielding $\Delta^{34}S$ values that range from 0.08 ‰ to 0.55 ‰ with a weighted mean of 0.32 ‰ and yield $\delta^{34}S$ values that range from -5.71 ‰ to +1.47 ‰.

4.3 The Turret deposit

The Turret deposit lies to the east of the old Agnew town-site in the Lawlers Antiform hinge region. Mineralisation at the Turret deposit is hosted within the Agnew Ultramafic unit. The mine lithostatigraphy can be subdivided into the hanging wall olivine cumulate, a footwall thin flow komatiite and a basal tholeiitic basalt unit (Voute and Thébaud 2015). The Turret ore body occurs as discontinuous lodes distributed over a strike length of 450 m. The geometry of primary gold mineralisation at Turret is controlled by a north-striking, east dipping shear zone forming at least two pencil-shaped lodes plunging about 35° to the north. In the Turret pit, the shear zone consists of a 10 to 15 m-wide, westerly dipping, N-striking high strain zone that juxtaposes the olivine cumulate unit and the komatite thin flow unit. Kinematic indicators such as S/C fabrics and asymmetrical boudins indicate reverse-sinistral oblique-slip movement. Two distinct alteration assemblages are recorded in the Turret deposit (Voute and Thébaud 2015). Early barren alteration consists of carbonate and talc with chalcopyrite and pyrrhotite as the sulfide phases. The second alteration stage is confined to a Cb ± Tlc ± Chl ± Ap shear hosted breccia. The breccia is monomictic containing fragmented carbonate clasts set in chalcopyrite-rich cement. Ore minerals are in decreasing order of abundance: Ccp + Po + Pn + Ba + Mo + parkerite + melonite + hedleyite + native bismuth + copper-gold alloys and gold (Voute and Thébaud 2015). Re-Os dating of Mo in association with gold from the Turret deposit returned a model age of 2622 ± 12 Ma (Thébaud et al. 2015).

In situ multiple sulfur isotope analyses were targeted on Ccp and Pn from the early alteration stage as well as on of Ccp, Pn and Po belonging to the later gold mineralisation assemblage. Early alteration Ccp (n=18) and Po (n=12) yield $\Delta^{34}S$ values ranging from -0.02 ‰ to +0.30 ‰ with weighted mean value of 0.11 ‰. Ccp yields $\delta^{34}S$ values that range from +0.39 ‰ to +1.62 ‰ whereas Po displays $\delta^{34}S$ values ranging from +0.89 ‰ to +1.91 ‰. Analyses performed on gold related sulfide assemblage were acquired on Ccp and Pn sulfide phases. Proximal Ccp (n=94) displays $\delta^{34}S$ ranging from -0.42 ‰ to +1.93 ‰ and $\Delta^{34}S$ value of +0.46 ‰ to +0.75 ‰ with a mean of 0.56 ‰ whereas Pn (n=10) exhibits $\delta^{34}S$ ranging from -0.12 ‰ to +1.72 ‰ and $\Delta^{34}S$ value of +0.46 ‰ to +0.60‰ with a mean of 0.55.
5 Discussion

Sulfur isotope analyses of three of the deposits forming the Agnew Gold Camp yield contrasting δ³⁴S values. δ³³S variations across the deposits are consistent with that of Archaean orogenic gold deposits and may illustrate processes specific to the deposition site and therefore difficult to attribute to a specific source (Palin and Xu 2000; Hodkiewicz et al. 2008). MIF-S signature, in contrast, exhibits internally consistent MIF-S signatures specific to each of the deposits investigated. Songyang Au mineralisation assemblage dated at 2662±7 Ma exhibits restricted δ³³S values with a mean value calculated at 0.03 ± 0.12 ‰ (2σ). Together with the atypical metal inventory associated with this deposit, the MIF-S values obtained on Songyang mineral assemblage suggest a sulfur source that has not undergone mass independent fractionation pointing toward a mantle derived sulfur source (Farquhar and Wing, 2003).

Samples from the Waroonga deposit interpreted to have formed at 2636±8 Ma return consistently positive Δ³³S signature ranging from 0.08 ‰ to 0.55 ‰. Such positive Δ³³S values imply that the sulfur source interacted with the Archaean atmosphere, causing the mass-independent fractionation processes (e.g. Farquhar et al. 2000) and therefore suggest that sulfur in the Waroonga deposit was at least partially derived from a sedimentary reservoir. Finally, the Turret deposit associated with overprinting alteration stages shows a rather more complex Δ³³S distribution. Ccp and Po associated with the early alteration stage preserving a weighted mean value Δ³³S = 0.11 ± 0.2 ‰ (2σ). With Δ³³S values close to 0 ‰, the early alteration in the Turret deposit associated with Cb, Ccp and Po mineralisation present affinity with a sulfur reservoir that has not undergone mass independent fractionation and therefore akin to a mantle derived source rather than solely crustal derived. Stage 2 of Turret alteration record is associated with gold mineralisation dated within error to Redeemer / Waroonga mineralisation at 2622 ± 12 Ma. In situ multiple sulfur isotope analysis returned positive Δ³³S values with a weighted mean at 0.55 ± 0.06 ‰ (2σ) suggesting that sulfur in the Turret deposit was partially derived from a sedimentary reservoir.

6 Conclusion

In situ multiple sulfur isotope analyses conducted on three distinct gold deposits from the Agnew Gold Camp confirm that the protracted and polyphased mineralisation process that took place over ~40 m.y. is associated with contrasted Δ³³S signatures pointing toward contrasted fluid and or metal sources. In the case of the Songyang deposit, MIF-S values are compatible with a magmatic sulfur reservoir whereas deposits such as the Waroonga and Turret deposit exhibit positive Δ³³S signature implying a sedimentary contribution to the sulfur budget. The latter results greatly contrast with the initial interpretation proposed for the Turret deposit and suggest a magmatic affinity. It is however notable that although a nil Δ³³S value must highlight a mantle derived source reservoir; positive Δ³³S values could be acquired through fluid-rock interaction processes as deeply sourced fluids percolate through the crust.

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The Silver Bullet: Ag isotope systematics in native gold from the central Victorian goldfields, Australia

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Abstract. In recent years, there has been an increased interest in Ag isotope variations in natural systems. Considering gold is mono-isotopic, but is closely associated with silver, a particular field of interest is the Ag isotopic composition of gold and its relation to ore-forming processes and source regions. In this study, a suite of native gold samples from numerous orogenic gold deposits located in central Victoria, Australia, have been measured for Ag isotopic composition using MC-ICP-MS. Despite being from a single geologic terrane with consistent deposit type, age, and host rock composition, the data reported here exhibit a significant spread in $^{107}\text{Ag}/^{109}\text{Ag}$ ratios ranging from -6.6 to +8.3 $\varepsilon^{107}\text{Ag}$ (relative to the Ag standard NIST SRM 978a). It thus appears that an inherited isotopic signature from a single metal source is not responsible for the difference in $^{107}\text{Ag}/^{109}\text{Ag}$ ratios, and values do not correlate with age or host rock composition. Instead, it is suggested that the Ag isotopic composition of mineral systems are primarily related to physico-chemical processes during ore formation and nuclear volume fluctuations due to s-electron addition/removal during REDOX reactions involving $\text{Ag}^+ \leftrightarrow \text{Ag}^0$ along transport pathways and at sites of ore accumulation.

1 Introduction

Silver is a common trace element in most terrestrial and extra-terrestrial materials and occurs in ppb levels or higher (Woodland et al. 2005). Silver is composed of two naturally occurring isotopes, $^{107}\text{Ag}$ and $^{109}\text{Ag}$, with relative abundances of 48.2% and 51.8%, respectively. Variations in the isotopic composition of silver were first recorded in the 1960’s in an iron meteorite and were scarcely studied in the years following (Murthy 1960). However, in the last decade the development of more sophisticated analytical techniques, such as multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS), has sparked a renewed interest in studying Ag isotopic systematics. An assessment of whether Ag isotopes can be used as a geochemical tracer for mineral exploration and ore forming processes is particularly fascinating.

Gold itself is mono-isotopic and therefore lacks any direct isotopic method for study. However, in nature, gold is found in close association with silver. Therefore, Ag isotopes can provide a valuable tool for studying native gold directly. Researcher have applied Ag isotope signatures to ore minerals from a limited number of deposits world-wide to aid in describing geological processes related to ore deposition and source regions (Hauri et al. 2000; Woodland et al. 2005; Chugaev and Chernyshev 2012; Tessalina et al. 2015). Variations in Ag isotopic composition from these studies are thought to be related to (i) stable isotope fractionation at relatively low temperatures during the physico-chemical processes of ore formation; (ii) natural variations in Ag isotope signatures inherited from protoliths or metal sources; and (iii) nuclear volume effects due to s-electron addition during the reduction of $\text{Ag}^+$ into $\text{Ag}^0$ during the precipitation of silver and gold species. However, the results of Ag isotopic ratios for geological materials remains somewhat enigmatic. Here, we report on a suite of native gold samples from various orogenic gold deposits located in central Victoria, Australia, that have been measured for Ag isotopic composition using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).

2 Geological setting

Eastern Australia is composed of a series of geologic terranes, known as the Tasmanides, that were accreted to the Pacific margin of Gondwana during the Paleozoic (VandenBerg et al. 2000; Willman et al. 2010; Phillips et al. 2012). The terranes that make up the Tasman Fold Belt System include the Delamerian, Lachlan, and New England Orogens. The Lachlan Orogen itself is divided into western, central, and eastern sub-provinces, where the western sub-province is host to most all of the orogenic gold-style mineralisation in Victoria (Phillips et al. 2012). The deposits in the Victorian goldfields are hosted by ~8-12 km of variably carbonaceous turbidites that sit above a ~20 km thick package of mafic volcanic rocks and are clustered along regional north-south trending structures (Fig.1) (Willman et al. 2010; Cayley et al. 2011). On a deposit scale, ore bodies are associated with local structures (i.e., upright chevron folds and reverse fault zones), which act as traps for mineralising fluids. Most of the gold deposition pre-dates intrusive emplacement, with the possible exception of the poorly age-constrained Sb-Au mineralisation at certain localities (e.g., the Fosterville and Costerfield deposits) (Phillips et al. 2012). Gold occurs in two main styles: 1) free gold within quartz veins (e.g. Bendigo), and 2) refractory gold locked into fine-grained disseminated pyrite and arsenopyrite crystals throughout the wall rock proximal to veining (e.g. Fosterville).
3 Methodology and results

Samples used in this study are natural gold ores from various deposits located in Victoria, Australia. Seventeen of which were donated by Museum Victoria and one of which was donated by Newmarket Gold. Lapidary preparation consisted of sectioning specimens with a steel scalpel and took place at Monash University. Sample dissolution and ion exchange chemistry were conducted at the Curt-Engelhorn-Zentrum Archäometrie (CEZ) located in Mannheim, Germany. A detailed summary of these procedures can be found in Brauns et al. (in prep). Ag isotopic analyses were carried out on a ThermoFinnigan Neptune Plus MC-ICP-MS at the CEZ. $^{107}\text{Ag}/^{109}\text{Ag}$ ratios were corrected for instrumental mass bias by normalizing to $^{108}\text{Pd}/^{105}\text{Pd}$ = 1.18899. The mass bias-corrected $^{107}\text{Ag}/^{109}\text{Ag}$ in unknowns were normalized to the average of the $^{107}\text{Ag}/^{109}\text{Ag}$ in bracketing runs of NIST SRM 978a. Typical in-run precisions were <20 ppm (2σ) while external precision for Ag standards run as unknowns was ±20 ppm (2σ).

Table 1 displays the results of $^{107}\text{Ag}/^{109}\text{Ag}$ measurements of native gold samples as their corresponding $\epsilon^{107}\text{Ag}$ values calculated relative to the SRM 978a standard. Additionally, Au and Ag concentrations are displayed for each analysis. Ag contents in these samples vary widely from 0.43 to 13.35 wt% with Pd/Ag ratios being effectively zero for all specimens and Cu content between 9 to 400 ppm. $^{107}\text{Ag}/^{109}\text{Ag}$ ratios range from -6.6 to +8.3 $\epsilon^{107}\text{Ag}$ for the entire sample suite (14.9 $\epsilon$ units). Variations in terrestrial objects from previous studies are from –9.4 to +5.3 $\epsilon^{107}\text{Ag}$, which including our new data, increases the total range of terrestrial samples to 17.7 $\epsilon$ units. The data reported here, although from a single geologic terrane, deposit type, age, and host rock composition, exhibit the largest spread in $\epsilon^{107}\text{Ag}$ values recorded to date in an ore deposit study (Fig. 2).

Table 1. The Ag isotopic and elemental composition of natural gold ore from Victoria, Australia.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Location</th>
<th>Ag %</th>
<th>Au %</th>
<th>$\epsilon^{107}\text{Ag}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5071</td>
<td>Bendigo</td>
<td>7.93</td>
<td>92.07</td>
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<td>92.28</td>
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<td>96.2</td>
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<td>95.45</td>
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<td>-6.6</td>
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</table>

Figure 1. Simplified geological map of central Victoria modified from Phillips et al. (2012). Infilled circles show the sample locations of specimens discussed in this study.
4 Discussion

It has been suggested that a probable reason for Ag isotopic variation in ore minerals is due to isotopic geochemical heterogeneity of Ag sources (Hauri et al. 2000; Chugaev and Chernyshev 2012; Tessalina et al. 2015). In this concept, sources with different $^{107}\text{Ag}/^{109}\text{Ag}$ ratios could contribute metal to hydrothermal solutions, which then mineralize ore bodies, instilling Ag isotopic signatures reflecting the source of the ore. This hypothesis is supported by the investigation of Ag isotope systematics of potential source rocks (Hauri et al. 2000; Woodland et al. 2005; Schonbachler et al. 2007; Schonbachler et al. 2010), where significant $^{107}\text{Ag}/^{109}\text{Ag}$ variations were revealed. This idea was taken further by Tessalina et al. (2015) who defined ranges of $\varepsilon^{107}\text{Ag}$ values for different deposits types with metals of known origins, describing potential signatures of inherited isotopic variability (Fig. 2).

If Ag isotopic variations are due to isotope geochemical heterogeneity of sources, we would expect to see a correlation in the $\varepsilon^{107}\text{Ag}$ of gold in deposits that are genetically equivalent. However, this doesn’t appear to be the case for results presented here. Considering the large spread in $\varepsilon^{107}\text{Ag}$ values (-6.6 to +8.3 $\varepsilon^{107}\text{Ag}$), it is not likely that these values represent a single, or even multiple metal sources. Difficulties are presented by gold samples from the Walhalla and Fosterville deposits, which have significantly lower $\varepsilon^{107}\text{Ag}$ values (-6.6 and -4.7 respectively) than the Bulk Silicate Earth (BSE) range; the BSE value of -2.2 is derived from unaltered mantle-derived igneous rocks (Schonbachler et al. 2010), thus it is expected that the Cambrian basaltic basement below Victoria would have this value. Similarly, the Costerfield gold sample has a $\varepsilon^{107}\text{Ag}$ value (+8.3) significantly higher than the “crustal origin” range (supposedly an analogue for the Ordovician turbidites in Victoria) described by Tessalina et al. (2015) (Fig. 2). Given the large Ag isotope heterogeneity between otherwise similar deposits, a better explanation may be provided by physico-chemical fractionation of Ag isotopes during extraction from the source, transport and ore formation.

Heavy isotope fractionation is not always dominated by mass-dependant mechanisms because differences in zero-point vibrational energies that drive these reactions are small for heavy elements (e.g., mass difference for $^1\text{H}/^2\text{H}$ or $^{12}\text{C}/^{13}\text{C}$ is much larger than that for $^{107}\text{Ag}/^{109}\text{Ag}$). However, tremendous fractionalations of 18-20 $\varepsilon$ and 30-50 $\varepsilon$ have been observed for the heavy elements Tl and Hg in natural seafloor systems (Rehkamper et al. 2004; Smith et al. 2005). These large variations have been attributed to a mechanism referred to as the nuclear-volume effect, a result of the relative contraction of s-orbitals in charged nuclei (Schauble 2007). In this mechanism, heavy isotope enrichment occurs in phases formed by oxidised species relative to those formed by reduced species. Therefore, s-electron occupational changes between the two Ag species (i.e., $\text{Ag}^0$ [Kr]$4d^{10}5s^1$ $\rightarrow$ $\text{Ag}^+$ [Kr]$4d^{10}5s^0$) will lead to $\text{Ag}^{109}$ enrichment in the most oxidized phase (e.g., $\text{Ag}^{2+}$ occurring in pyrite). This is significant during the formation of hydrothermal ore deposits as Ag is likely dissolved in the $\text{Ag}^+$ state during transport in fluids (Migdisov and William-Jones 2013). Deposition of Ag occurs by crystallization of $\text{Ag}^+$ in sulphides and sulfosalts, or as $\text{Ag}^0$ in native metal alloys such as gold. Reduction of $\text{Ag}^+$ to $\text{Ag}^0$ is significant during ore genesis as there should be a relative enrichment in the $^{109}\text{Ag}$ isotope in the fluid relative to $\text{Ag}^0$-bearing phases such as native gold. Furthermore, there should be a fractionation between coegenetic phases where one contains $\text{Ag}^+$ and the other $\text{Ag}^0$.

This nuclear volume effect may be responsible for the wide spread of $\varepsilon^{107}\text{Ag}$ data between the genetically similar deposits in Victoria, as well as intra-deposit variations such as those seen in the Bendigo, Ballarat, and Maryborough samples (Table 1) (Fig. 3). In the case of Bendigo and Ballarat samples, the isotopic values only vary by a modest amount, 1.5 and 1.55 $\varepsilon$ units, respectively. This result fits well within the 2-4 $\varepsilon$ unit range for total equilibrium fractionation observed for ruthenium, which has a close range of atomic masses (Schauble 2007). Unfortunately, the lack of textural context limits the amount of speculation that can be made about these data. However, in the case of the Maryborough samples, there is a distinct difference in not only the $\varepsilon^{107}\text{Ag}$ values of each specimen, but also the mineralogy associated with the gold. Sample M18738 contains native gold in quartz with no other Ag-bearing phases associated with it and has a $\varepsilon^{107}\text{Ag} = -1.3$. Conversely, sample M42560 contains native gold on malachite, with associated pyrite hosted within quartz.

Figure 2. Frequency distribution histogram of Ag isotopic compositions in terrestrial materials from this study (blue) as well as Hauri et al. (2000); Woodland et al. (2005); Schonbachler (2007); Schonbachler et al. (2010); and Chugaev and Chernyshev (2012). Bulk silicate Earth (BSE) is defined by Schonbachler et al. (2010) and crustal origin is defined by Tessalina et al. (2015). Epsilon units are relative to the NIST SRM 978a Ag isotope standard.
Considering the discussion above, and that silver acts as both a chalcophile and aurophile element, it would be reasonable to conclude that Ag would substitute into pyrite and chalcopyrite (later weathered to malachite) as oxidized Ag$^+$ and that Ag$^0$ would partition into the native gold. In this way, there would be a fractionation that enriched both chalcopyrite and pyrite in $^{107}$Ag while leaving the associated gold relatively depleted in $^{109}$Ag. This reasoning could explain why sample M42560 is substantially enriched in $^{107}$Ag compared to its counterpart M18738, which had no other Ag-bearing phases to preferentially sequester $^{109}$Ag. Furthermore, a similar variation of 5.9 $\epsilon$ has been observed in other Ag-Au deposits (Chugaev and Chernyshen 2012), suggesting that nuclear volume effects during REDOX may be the main driver behind Ag-isotopic fractionation.

Figure 3. $\epsilon^{107}$Ag values and corresponding locations for Victorian gold samples and standards discussed in this study. Ag isotopic compositions of gold samples relative to NIST 978a.

5 Conclusion

The suite of native gold samples from various deposits located in Victoria, Australia, have a range of $^{107}$Ag/$^{109}$Ag ratios from -4.7 to +8.3 $\epsilon^{107}$Ag. This spread in data does not correlate with the age or host rock composition of the deposits, and likely does not simply reflect a metal source. Although the latter may have contributed a proportion of the variation, this signature may be overwhelmed by transport- and deposition-related fractionation. It is suggested that Ag isotopic composition of mineral systems are related to primarily (i) physico-chemical processes related to ore formation (e.g., phase separation, boiling, etc.); (ii) nuclear volume fluctuations due to s-electron addition/removal during REDOX reactions involving Ag$^+$ $\leftrightarrow$ Ag$^0$ along transport pathways and at the sites of ore accumulation; (iii) a small component of mass-dependant fractionation that may be unrecognisable due to the stronger effects of (i) and (ii); and (iv) possible Ag isotopic variability inherited from metal source and/or host rocks. It is likely that all of these factors played a role and that Ag isotopic heterogeneity exists on the large scale and is altered on the deposit scale by ore-forming processes. An increase in the Ag isotope global database is needed to aid in the interpretation of $^{107}$Ag/$^{109}$Ag ratios. Furthermore, experimental investigations into the effects of temperature, REDOX, and ligand and mineral speciation on the fractionation of Ag isotopes is warranted. A better understanding of Ag isotopic fractionation in natural systems can provide groundwork for applications including cosmochemistry, meteoritics, economic geology, archaeometry, and environmental studies.

References


Factors in the localization of super-large gold deposits in northeastern Russia

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Abstract. The Russian Northeast super-large gold deposits (Nezhdanenskoye and Natalka) are located within the southern flank of the post-accretionary East Yakutian metallogenic belt (EYMB) near its intersection with the Okhotsk-Chukotka volcanogenic belt along the Pacific Rim. For the first time, the EYMB internal structure is evaluated in conjunction with the deep synclinal depressions and rifts of the Laptev Sea on the Arctic ocean shelf, which allows the identification of three structural-metallogenic zones within EYMB. Both of the super-large deposits follow the strike of their respective EYMB zone. Recently recognized magmatism and hydrothermal activity along the Gakkel Ridge spreading zone allows for support of the concept of a “Through Oceanic-Continental Mineralogenetic System” that includes Gakkel Ridge, shelf structures, and the EYMB. The complex and long-lived formation of the super-large gold deposits in terrigeneous sediments, including mobilization of disseminated gold and other ore-related components from the sedimentary rocks, is shown to occur through the process of metamorphism and possibly with hydrothermal solutions also being derived from deep magmatic sources. Another giant deposit is predicted on the southern flank of the third structural - metallogenic zone near its intersection with the Okhotsk-Chukotka belt.

1 Tectonic framework of the East Yakutia-Magadan Province

Super-large (>15 Moz) gold deposits in northeastern Russia, comprising Nezhdaninskoye and Natalkinskoye, are located in the area of the intersection of the East-Yakutian Metallogenic Belt (EYMB) with the Okhotsk-Chukotka Volcanogenic Belt (OChVB) along the Pacific Rim (Fig.1).

The polymetallic (Au, Sn, Pb, Zn, Sb, Ag, W, Mo) East Yakutian metallogenic belt of Aptian to Late Cretaceous age formed after the accretion of terranes and the Kolyma Omolon superterrane (microcontinent) to the Siberian continent in the Late Jurassic-Early Cretaceous (Parfenov et al. 1999, 2001, 2010; Nokleberg et al. 2005). Association of the EYMB with major structures of the neighboring Laptev Sea shelf, as well as the approaching Gakkel mid-ocean ridge, was not considered important by previous workers.

The deep structure of the Laptev Sea has been examined with respect to its oil and gas potential (Malyshev et al. 2010), including the deep basins of the West Laptev...
regional syncline with terrigenous deposits up to 15 km in thickness (Drachev et al. 2003) that can be traced towards the continent (Fig. 1). The syncline is separated from the Eastern Laptev anticline by the large-scale Lazarev fault a normal fault system with 5-7 km of vertical displacement. According to our interpretation, the extension of this fault system onto the continent separates two sectors of the EYMB characterized by different styles of mineralization. Data on the widespread magmatism and hydrothermal activity in the spreading zone of Gakkel Ridge (Michael et al. 2003) have allowed it to considered as a potential source of massive sulfide occurrences and to be attributed to the globally common oceanic-continental mineralogenetic systems that may here include the shelf structures and EYMB (Andreev, 2008, Antonov, 2012).

Previously, numerous but insufficiently documented metallogenic zones were distinguished within the EYMB. Examination of the internal structure of the EYMB together with the shelf structure has allowed us to identify three structural - metallogenic zones within the EYMB (Fig. 1). These include the western (I), middle (II), and eastern (III) zones. Significant tectonic and metallogenic events occurred in the southern parts of the structural - metallogenic zones of the EYMB near its intersection with the OChVB and this likely resulted in formation of giant gold accumulations accompanied by occurrences of other metals.

2 Gold mineralization of the East Yakutia–Magadan Province

The majority of the region’s gold deposits are best classified as orogenic Au-Ag deposits (Sidorov et al. 2007, 2009; Struzhkov and Konstantinov, 2005), with variable gold/silver ratios localized in volcanic rocks of the OChVB. Predominantly they are small to medium, with only rare large deposits.

Numerous gold deposits in the EYMB are also small and medium in size, and they are typically associated with antimony and mercury enrichments and localized in late Paleozoic-early Mesozoic terrigenous rocks.

Only those deposits close to the intersection of two zones of the EYMB with the OChVB are characterized by super-large concentrations of gold-sulfide mineralization in the perivolcanic area of the OChVB. The super-large Nezhdaninskoye deposit (about 20 Moz Au) and even larger Natalkinskoye deposit (as much as 50 Moz Au) are localized at the intersections of the western zone (zone I on Fig. 1) and middle zone (zone II on Fig. 1) with the OChVB. Both deposits are localized in Permian-Triassic siltstone-sandstone or terrigenous schist and tuff intruded by wide belts of Late Jurassic diorite, spessartite, and lamprophyre dikes.

Ore-controlling structures at these deposits strike NNW or submeridionally, consistent with the strike of the zones of the EYMB. Numerous small deposits and occurrences of other metals, including tin, zinc, lead, and tungsten, formed adjacent to the Nezhdaninskoye and Natalkinskoye deposits.

As opposed to the typical OChVB gold and silver deposits, sulfide content in the ores of these deposits is typically 5-6%, comprising arsenopyrite (3%), pyrite (1%), sphalerite (1%), galena (0.6%), and fahlore (0.3%). The mineralization process was multistage. As established by Gamianin (2000), the Nezhdaninskoye deposit was formed in three stages: 1) hydrothermal-metamorphogenic stage, 2) main productive gold-quartz hydrothermal stage associated with gold-bearing beresites, and 3) silver- polymetallic hydrothermal stage. Metamorphogenic quartz veins with low sulfide content and low-grade gold mineralization formed during the first stage prior to accretion of terranes. Gold-bearing arsenopyrite and veins with pyrite-arsenopyrite-quartz, chalcopyrite-galena- sphalerite and fahlore-sulphoantimonite mineral associations formed during the main secons, post- accretionary stage. Remobilization of earlier assemblages and precipitation of an electrum-pyargyrite-freibergite assemblage took place during the third stage.

At the Nezhdaninskoye deposit, Gamianin (2000) noted the presence of a thick (50-200 m) zone of hydrothermally altered rock along the ore-controlling structure. Metasomatic zoning is described as follows: hydromicaceous metasomatites hydromicaceous-carbonate and hydromicaceous-albite-carbonate zones regional greenschist alteration assemblages. The best and most observable indicator of the alteration zoning is the sulfidization of the inner part of the zone of metasomatites. Two sub-zones are distinguished here, namely an outer pyrite and internal pyrite-arsenopyrite zone, with gradual increase in the abundance of arsenopyrite towards the ore zone. The outer sub-zone thickness is 20-25 m with pyrite volumes of 1-3%; the internal sub-zone has a thickness up to 5 m with increasing sulfide volumes up to 10%. High grades of gold and silver are commonly associated with the metasomatic sulfides (pyrite: 20-80g/t Au, arsenopyrite: 100-500g/t Au). The observed “wave-like” pattern of mineralogical zoning is probably controlled by cyclic activation of the ore-controlling structures. Similar mineral associations (macroscopic zoning) and variability of typomorphic properties of minerals (hidden zoning) is common for each “wave” or distinct assemblage of the zoning. Zoning for ore mineral associations includes from top to bottom replacement of sulphosalt minerals by galena-sphalerite-chalcopyrite and subsequent replacement of the latter by pyrite-arsenopyrite. Hence, sulphoantimonites are present in lower levels of the deposits and are absent in the intermediate or upper levels, indicating the beginning of a new wave of mineralization. In the mineralized veins, there is lesser carbonate in the lower levels of each wave. Zoning wave amplitude is typically 200-400 m. Early sulfides, deposited over practically the entire vertical range of mineralization, are silver, antimony, and gold enriched near the top, lead and zinc enriched in the middle, and cobalt and nickel enriched in the bottom.

The possible time of mineralization for the Natalkinskoye deposit is estimated over a broad range
from 135-130 Ma to 110-100 Ma according to K-Ar dating (Goncharov et al. 2002). Formation of the Natalkinskoye deposit is also considered to be polygenetic with both metamorphic and magmatic processes being important. Carbonaceous terrigenous rocks are considered to be the main source of fluid and metal components based on isotopic study of the ores.

3 Prediction of another super-large gold deposit in the EYMB

Intersection of the eastern structural-metallogenic zone (zone III) of the EYMB with the OChVB is a prospective area for discovery of another super-large gold deposit (Fig. 1). The large (9,000km2) Nevllyaenga ore district (Struzhkov et al. 2005), with Au-Ag occurrences and developed deposits of medium size in volcanic rocks (e.g., Julietta), is located here.

The main part of the district is underlain by terrigenous rocks intruded by Cretaceous granitoids with poorly examined vein occurrences of gold, arsenic-rich minerals, and other sulfides, as well as gold-rich porphyry mineralization, being the most prospective types of mineralization likely to form large and super-large gold deposits.

Exploration work continues in the southern part of the district with some limited drilling (Radchenko et al. 2009). It has already resulted in identification of a gold-polymetallic sulfide-quartz stockwork system at one target (e.g., Vetvisty).

The target is confined to the NW-striking trend of the metallogenic zone. All structural, geophysical, and geochemical attributes of the mineralization conform to this direction. In particular there is a 3 km x 5 km brachyanticline with a NW-oriented axis; a deep, NW- to NNW-striking ore controlling fault with local electric and magnetic field anomalies, with a potassium isocorentrate up to 2.5%; and a complex lithgeochemical anomaly in Ag, Au, and Zn, for 2 km in a NW direction. The gold-polymetallic sulfide-quartz stockwork is exposed in the center of the geochemical anomaly.

The stockwork corresponds to a potential complex (Au-Ag-Zn) and large-scale deposit. It has a possible average gold equivalent grade of 2.0 g/t. Disseminated rare metal enrichments that include Ga, Ge, Te, and Se define much of the economic value of the potential ores, where the actual gold grades within the tested target are themselves only about 0.3 g/t. Even more significantly, estimated gold and silver resources of 2 Moz and 50 Moz, respectfully, indicate a large deposit. Geochemical data point to this being an upper level of a magmatic-hydrothermal system, with important hidden or slightly eroded mineralization at depth.

The Nezhdaninskoye deposit could serve as a model to be targeted within the entire Niavlenenga district. Common exploration factors for such deposits include: (1) Localization in terrigenous sediments intruded by Late Cretaceous granitoid stocks and dike swarms in the crest of the large anticline. (2) Intersection of four systems of discontinuous faults, one subparallel to the NW Eastern Yakutian belt and the other three within the OChVB. Well-developed fault formation is one of the factors typically contributing to formation of super-large deposits, aiding development of exceptionally long an thick orebodies. (3) Spatial proximity of gold and silver- polymetallic mineral occurrences. (4) A multistage process of ore formation, remobilization, and reprecipitation of metals as observed at the Nezhdaninskoye deposit (Gaminin et al. 2000). Multistage mineral formation is also observed in the explored part of the Vetvistyore occurrence. (Radchenko et al. 2009).

A few more targets that are prospective for large mineral deposits are identified near the deep levels of the Vetvisty target within the Niavlenenga district.

Good agreement of geological information with surface geophysical data (magnetic and electric) has been recognized during the assessment of the Vetvisty target. Interpretation of these data allowed for clear localization of zones of sulfide stockworks, as well as of linear veins and vein-veinlet zones with polymetallic sulfides and sulfide-bearing quartz. Application of a modern high precision and rapid airborne survey is recommended due to large size of the prospective region.

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Trace element quantification in gold as a means of distinguishing the genesis of placer gold

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Abstract. Analyses of placer gold has largely been restricted to the major components, Au, Ag, Cu, Hg from electron microprobe analysis (EMPA) due to the relatively high detection limits for other minor elements. LA-ICP-MS has sub-ppm detection limits for most elements in gold, but by comparison with EMPA is both destructive and penetrates the gold to much greater in depth. We have analysed gold grains for a suite of elements to assess which are present in sufficient concentration to form a basis for the discrimination of gold from different localities and different styles of mineralization. High resolution multi-element maps of selected grains, analysed by icpTOF-MS, reveal some elements are controlled by crystal structure, grain boundaries or random events.

1 Introduction

Southern and central British Columbia (BC) are complex terranes which host different styles of gold mineralization. Placer gold is often reported, but the nature of the hypogene source may be unclear. The ability to ascribe a source style on the basis of alloy and mineralogical features of placer gold particles may underpin a new exploration methodology based on gold as an indicator mineral. Gold compositions are traditionally measured using the electron microprobe (EMP), which can easily characterise a population of Au grains in terms of their Ag content. Corresponding data for Cu, Hg and Pd are obtained where their concentrations exceed the limit of detection (< 0.02 wt %, 0.3 wt % and 0.04 wt % respectively). Very often, Cu, Hg and Pd values straddle these detection limits yielding a ‘partial’ data set. Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can provide quantitative analyses of trace elements within gold. We aimed to establish which elements were present in natural gold, their mode of occurrence within gold particles and whether they can be used as discriminants between gold formed in different mineralizing systems.

The northern cordillera has been the focus of traditional prospecting for nearly 200 years. Placer-gold occurrences are widespread and have supported an industry that has underpinned many local economies. In some cases, further prospecting has identified significant in situ mineralization that has also been profitably exploited, but the relationship between placer gold and its source lode is less clear at other localities, either as a consequence of extensive surficial sediments or because complex bedrock geology provides several potential geological settings for source mineralization. Both these factors have constrained Figure 1.

Figure 1. a location of the Cariboo gold district (box; see part b) and sample locations near Kamloops (Afton mine, Tranquille River placer; and Cherry Creek) and in the Princeton area (Copper Mountain mine, Similkameen River placer, Whipsaw Creek placer, and Friday Creek). b detail of sample locations in the Cariboo gold district (Spanish Mountain, Mount Polley). Geology adapted from Mortensen and Chapman (2010).
exploration in BC. The use of gold compositional studies has elevated the potential value of detrital gold from a simple physical marker to an indicator of the potential style of mineralization. For example regional studies in the Yukon and the Fortymile district of the Yukon and Alaska have identified the importance of gold derived from orogenic systems in local placer inventories, even when an intrusion-related source type has been proposed (Wrighton 2013). This approach has also been used in BC to elucidate detailed variation in the mineralogy of detrital gold in the Cariboo gold district and to infer the relative importance of source veins (Chapman and Mortensen, 2016). The alcalic copper-gold porphyries of BC are both potential sources of detrital gold and located within wider auriferous areas. Consequently, the region provides an excellent study area in which to explore the potential of gold compositional studies in the context of exploration in a challenging environment.

2 Methodology

Some 1600 gold grains, mounted in polished blocks, provided populations of grains from the placers derived from different types of source deposits. Individual grains were analysed with a Geolas ablation system that utilises a Compex 193 ArF excimer laser and an Agilent 7500c quadrupole ICP-MS (operated without the reaction cell) with a laser fluence of 6 J/cm² and a repetition rate of 5Hz. At higher energies or repetition rates the gold grains were ablated all the way through too quickly to achieve a sufficiently stable signal and analyses were less reproducible and accurate. As an estimate, it was found that 150 pulses ablated the gold to a depth of around 100μm. All the gold grains were analysed with spot diameters of 25–100 μm, with 50 μm being the most frequent size used, to ensure ablation continued for the full 150 pulses.

The gold grains were analysed for a large number of elements to see which were detectable and to provide an appraisal of which would be useful in distinguishing between different deposits, metallogenic types, and potentially be indicative of processes operating during precipitation. The elements analysed were Al, Si, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Nb, Mo, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, La, W, Pt, Au, Pb, Bi, Th, U, all at 10 ms dwell times. Quantification of the full element suite required 4 standards to provide ratios of different elements to the internal standard element Au. NIST 610 silicate glass, AuRM2 London Bullion Standard, NIST 481 gold silver wies and USGS MASS-1 synthetic sulphide standard enabled all the elements to be determined as weight ratios relative to Au and the actual concentrations in ppm to be calculated based on 100% normalization.

The standard single-spot LA-ICP-MS analysis does not capture any elemental heterogeneity within gold grains. Multi-element mapping with LA-ICP-MS can shed more light on the nature of the grain formation, but the method is very time consuming with standard LA-ICP-MS technology and does not show all the heterogeneities present. Here we have carried out high-speed multi-element mapping of detrital gold by combining the TOFWERK icpTOF (time of flight) mass spectrometer and Analyte G2 193 nm excimer laser with a recently developed aerosol rapid introduction system (ARIS) from Teledyne CETAC Technologies. All isotopes (in the sample shown approximately 20 elements were determined above the limit of detection) present in a 500 μm gold grain were mapped with 5 μm resolution in less than 15 minutes, therefore 11,000 multi-element spot analyses. The combination of the icpTOF and fast laser ablation systems enables rapid mapping of all elements in gold grains, exposing elemental heterogeneities that are not captured with single-spot analysis. The simultaneous analysis reveals the elemental associations at a single spot which is not possible with a quadrupole-MS system.

3 LA ICP-MS quantification

In Figure 2, bivariate plots of the major elements in the gold are shown for all the grains analysed so far, differentiated on the basis of the deposit type from which the gold originated. The alkali porphyry deposits have, in general, the highest concentrations of elements other than the Au and Ag that dominate the gold-grain composition as a binary mixture. The alkali porphyry deposits plot below a binary mixing line due to the high concentrations of Hg, up to 10%, in these grains. There are reasonably strong negative correlations of Hg with Au and Ag, over a large range in Hg concentrations, which is indicative of Hg replacing both Au and Ag in the porphyry gold grains. The dataset available that relates to epithermal deposits is relatively restricted when compared to the other two types. Nevertheless, the initial indication is that, for these types of deposit, there may be distinction based on the higher Ag and the low Cu and Hg concentrations. The number of gold grains from orogenic deposits analysed is relatively large and some clearly defined trends have emerged. The majority of gold grains are binary Au and Ag mixtures, with these elements making up well over 99% of the composition, a result that is well known from previous alloy studies using EMP. In general, other elements are present at lesser concentrations than the alkalic porphyry deposits but greater than the single epithermal deposit studied here. There is a good positive correlation of Ag and Sb, and good negative correlations of Ag with Cu and Hg. These trends have not been previously observed in EMP datasets because of the higher detection limits. It is encouraging, at this level of data interpretation, that different sources of gold grains do seem to have observable differences when looking at the dataset as a whole. The observed correlations from measurement of trace elements at low concentrations show that these are not just random analyses, but may be related to processes during gold deposition.
In Figure 3, three individual deposits (Spanish Creek, Black Dome and Similkameen) have been chosen as examples of gold derived from orogenic, low-sulphidation epithermal and alkaline porphyry systems, respectively. Although some differences in alloy compositions can be identified in the EMP data (and corresponding inclusion assemblages), a number of further differences can be observed in the suite of minor elements whose concentrations have been measured using LA-ICP-MS. Gold from the Similkameen placer (alkaline porphyry related) shows the most complex elemental signatures and with trace elements at the highest concentrations. Gold from the Black Dome deposit contains fewer elements and at lower levels, whereas the signature of gold from Spanish Mountain (orogenic) falls midway between the other two. Three elements are worthy of particular attention: Hg, Cu and Pd. Concentrations of Hg in gold alloy from the alkaline porphyry system are around ten times higher than in the gold from Spanish Mountain, which in turn exhibits Hg concentrations ten times those of the gold from Black Dome. The detection limit for Hg by EMP is around 0.3%, so the use of LA-ICP-MS allows measurement and interpretation of Hg in the alloy at far lower levels. Copper concentrations were generally highest in gold from the alkaline porphyry system, although most grains from this sample suite and the Spanish Mountain suite returned quite similar values for Pd; however, some individual grains from the Similkameen River exhibited far higher Pd values. Palladium was absent in the gold from Black Dome, where Cu concentrations were also very low.

4 Elemental distribution in gold

Several gold grains were analysed using LA-icpTOF-MS which enables all detectable isotopes to be measured from a single laser ablation spot simultaneously. Element distribution maps (figure 4) show that in some parts of the
grains the concentrations are homogeneous while there are areas that are quite heterogeneous. Small inclusions, such as Te, can be associated with other elements that may be present at the same spot as the analysis is simultaneous for all elements. Some elements show migration away from the grain boundaries while others show enrichment, but why this is so is unclear at present. However, TOF-based MS is clearly the future in element mapping.

5 Conclusions

The differences between alloy signatures in gold from different deposit types previously identified by (electron microprobe) EMP analysis are evident in the LA-ICP-MS data, but the quantitative analysis of Cu, Hg and Pd at trace levels permits additional interrogation of these datasets. Most importantly, the use of LA-ICP-MS has identified the potential for other elements (e.g., Sb) to be used as discriminators and the ability to spot trends in element ratios where analyses were close to the detection limit by EMP. It is evident that for analyses to be relevant populations of grains must be analysed to fully appreciate the elemental concentration distribution at each location. Regardless of the preliminary nature of the data, it appears there are reproducible compositional similarities between populations of gold derived from the same source, and that differences exist between signatures of gold from different source types. As yet, there are insufficient data to establish whether such differences are generic or a consequence of specific environments of mineralization.

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References


Deciphering sulfide recrystallization and Au remobilization through 2D chemical mapping and microstructural analysis, Detour Lake mine, Superior Province

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Abstract. The Detour Lake deposit is a Neoarchean orogenic gold deposit located in the northwestern Abitibi district within the Superior Province, Canada. The mine is situated along the high-strain, sub-vertical brittle-ductile Sunday Lake Deformation Zone, which parallels the east-west trending Abitibi greenstone belt. The deposit possesses a lower amphibolite facies metamorphic assemblage of actinolite-biotite-plagioclase-almandine, differing from other classic ore deposits in the dominantly greenschist facies subprovince. Ore zones at Detour Lake are co-spatial with sulphidized mafic volcanic host rocks and ductily deformed, auriferous quartz veins. The close spatial relationship between gold and pyrite-pyrrhotite is also repeated at the micro-scale. Herein we combine electron backscatter diffraction (EBSD) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) trace element mapping to evaluate the influence of pyrite crystallization and deformation on the distribution of precious and base metals within common microstructures. The EBSD results reveal grain misorientations of up to 45°, development of low-angle grain boundaries, and late fracturing. The LA-ICP-MS maps show enrichment of gold and other trace elements at pyrite grain boundaries, low-angle grain boundaries, and late brittle fractures. Our results point to syn- to post-peak metamorphic gold remobilization at the microscale, occurring during pyrite recrystallization and trapped within deformation-induced substructures.

1 Introduction

Pyrite is an important and ubiquitous gold-bearing sulfide phase in greenschist to amphibolite facies metallic ore deposits. Despite its common occurrence, the behavior of pyrite in deformed rocks under such conditions remains poorly understood. Pyrite is conventionally considered a competent and rigid mineral under greenschist to lower amphibolite metamorphic conditions, and experimental studies have demonstrated the onset of plastic pyrite deformation occurs at temperatures above 450°C (Cox et al. 1981; Graf et al. 1981; Levade 1982; Levade et al. 1982). Notably, Barrie et al. (2011) documented plastic deformation of pyrite at temperatures as low as 260°C. These and other studies have described that plastic deformation within pyrite crystals occurs primarily as slip on \{100\} and more rarely \{110\} systems with rotation about <100> and more rarely <110> axes (Boyle et al. 1998, Barrie et al. 2008). Due to peak metamorphic conditions at the Detour Lake deposit, which reached maximum conditions of 550°C and 3.3 kbar (Oliver et al. 2011), we suggest that pyrite within and at the margins of syn-metamorphic and ductility deformed auriferous quartz veins may record a range of brittle to ductile deformation mechanisms; therefore, possibly supporting a syn- to post- peak metamorphic- and deformation-driven gold upgrading model. We predict gold and other trace elements are remobilized through deformation-induced diffusion pathways. Herein we discuss our results of a coupled EBSD mapping and LA-ICP-MS trace element mapping strategy to investigate the pyrite deformation mechanism and to assess the influence of deformation and metamorphism on the distribution of gold and other trace elements in pyrite.

2 Geological setting

The Detour Lake deposit is located in the northwestern region of the well-known Abitibi district of the Archean Superior Province. The regional geology of the Detour Lake area is interpreted as an east-west trending synform, with the Caopatina sedimentary assemblage (ca. 2700 Ma) forming the core, and the older volcanic sequences of the Detour Lake Formation (ca. 2725 Ma) exposed along its northern and southern limbs (Oliver et al. 2011). The northern limb is further deformed into a sub-vertical, brittle-ductile, regional-scale zone known locally as the Sunday Lake Deformation Zone (SLDZ). The Detour Lake Formation is a Fe-rich tholeiitic volcanic sequence, which forms the hanging wall of the SLDZ. This assemblage is further sub-categorized into the Upper Detour Lake Formation, a thick sequence dominated by tholeiitic basalts, and the Lower Detour Lake Formation, a sequence dominated by ultramafic flows. The rocks in the region, unlike the rocks in the Abitibi greenstone belt, have undergone lower amphibolite facies metamorphism based on the actinolite-biotite-plagioclase-almandine metamorphic mineral assemblage (Oliver et al. 2011).

The Detour Lake area has undergone four major
Deformation events, recognized by Oliver et al. (2011): $D_3$ the regional unconformity juxtaposing the volcanic unit of the Detour Lake Formation and the sediments of the Caopatina assemblage; $D_3$ the formation of shallow west-plunging folds with sub-vertical, east-west trending axial planes slightly overturned to the south and a penetrative foliation, $S_2$ (main deposit fabric); $D_4$ the formation of open north-northwest shallow dipping folds and an associated crenulation structure; and $D_4$ the formation of a series of southeast fault splay of the main SLDZ.

The gold grade of the overall mineral resource at Detour Lake is unusually low averaging 0.99g/t; however, high-grade domains do occur within the main ore zone, which are often associated with sulphidized (pyrite- pyrrhotite) mafic volcanic rocks and auriferous quartz veins. We have identified nine vein types based on vein mineralogy and relative timing relationships: six of which are interpreted to be pre- to syn-$D_2$, and three interpreted to have formed post-$D_2$. The pre- to syn-$D_2$ vein types include: pillow veins ($V_1$), "ghost" veins ($V_2$), laminated- sulphidized ($Py$, $Po$, $\pm Cpy$, $\pm Gn$) $Qz$ veins ($V_3$), folded $Qz$- Cal veins ($V_4$), folded-sulphidized ($Py$, $Po$, $\pm Cpy$, $\pm Gn$) $Qz$-Cal-Chl veins ($V_5$), and Cal veinlets ($V_6$). The post-$D_2$ veins consist of planar Cal veinlets ($V_7$), carbonate breccia veins ($V_8$), and $Qz$-Cal breccia veins ($V_9$). The most important vein set for our study is the pre- to syn-$D_2$ folded-sulphidized $Qz$-Cal-Chl vein set ($V_3$) as they contain coarse, visible gold and are the most common veins within the main ore zone at the deposit.

3 Sampling and petrography

In an attempt to better understand the internal crystal plasticity of pyrite and its behavior under relatively high temperature and high strain conditions, we sampled pyrite within the deformed and sulphidized pre- to syn-$D_2$ veins ($V_3$). These veins are mostly composed of quartz and calcite with some chlorite, biotite and sulfides ($Py$, $Po$, $Cpy$) and usually have a biotite, and more rarely sericite- calcite-bearing, alteration halo. Typical shear vein structures such as foliated wall rock selvages and dilational jogs between en-echelon isolated veinlets are preserved. Evidence for ductile deformation consists of folding and pinch and swell structures. The pre- to syn-$D_2$ veins are transposed parallel to the $S_2$ fabric and isoclinaly folded with axial planes that parallel the dominant deposit fabric ($S_2$). $V_5$ veins are associated with high-grade ore zones and locally contain visible gold, which is associated with pyrite and pyrrhotite within high-grade veins. Gold also occurs as clusters of precious-metal inclusions (Au-Bi-Te). Therefore, the pyrite-bearing samples for our study were collected from this vein set. Reflected and transmitted light microscopy was used to identify deformation structures within the pyrite. Structures include late brittle fractures, precipitation of pyrite in pressure shadows of boudinaged quartz veins, pinch and swell structures, and grain-grain contacts. Pyrite samples were subsequently analyzed via orientation contrast (OC) imaging, EBSD mapping and LA-ICP-MS trace element mapping.

4 Deformation of pyrite

In an attempt to confirm the presence of plastic strain in pyrite, OC images of the deformation structures identified with petrography have been taken using a Forescatter Electron detector. For quantification of the internal crystal plastic deformation, EBSD data are presented as deviation angle maps, grain boundary maps, misorientation profiles, and pole figures representing the crystallographic orientation of the $<100>$ axes (Fig. 1).

All crystallographic data were collected at the University of Vienna, Department for Lithospheric Research, using an FEI Quanta 3D FEG instrument equipped with an EDAX Pegasus Apex 4 system. Thin sections for OC imaging and EBSD mapping were chemo-mechanically polished with Köstrosol 3530 and afterwards carbon coated to establish electric conductivity. Samples were tilted to 70°. Analytical conditions were set to a probe current of 4nA, an acceleration voltage of 15kV with a working distance of ~14 mm. A spot size of 1 was used for OC imaging and a step size of 0.8-1.5, depending on intensity of plastic deformation and grain size, was used for EBSD mapping. All data were processed using the OIM Data Collection and Analysis software.

Grayscale variations in the OC images reveal plastic strain in the form of linear, chessboard, and more complex heterogeneous misorientation patterns. In most cases, late brittle fractures cut across the previously described patterns indicating brittle deformation post-dates the main period of ductile deformation (Fig. 1A). The EBSD mapping complements our observations revealing local misorientation linear patterns that can be described by continuous rotation around one of the $<100>$ axes; higher strain areas reveal more complex misorientation patterns described by continuous rotation about two or more of the $<100>$ axes; and development of low-angle grain boundaries with late fractures, possibly indicative of dislocation creep and strain hardening (Fig. 1B, C, D). Late fracturing is an important micro-structural setting for gold and clusters of precious-metal mineral inclusions (Te-Bi minerals). Minor recrystallization can also be observed along phase boundaries between pyrite and more competent amphibole crystals and at micro-cracks within the pyrite crystals. The evidence of strain localization at micro-fractures is indicative of synductile brittle fracturing.
5 Pyrite chemical mapping

To assess the influence of brittle and plastic deformation in pyrite on the retention and the release of trace elements, we have conducted 2D LA-ICP-MS trace element mapping on three samples that were previously examined under EBSD. We selected four mapping areas representative of the range of microstructures in our samples, including continuous linear misorientation, low angle grain boundaries, and brittle fracturing (syn- to post-D2).

The LA-ICP-MS trace element mapping was performed at the Geological Survey of Canada using an Agilent Technologies 7700x ICP-MS coupled to a Teledyne Photon Machine Analyte G2 excimer laser ablation system ($\lambda$=193 nm). Element mapping was completed following the approach of Lawley et al. (2015). Edge to edge spot-mapping with a 10 µm spot size was used to produce ~1 mm$^2$ maps.

The LA-ICP-MS trace element maps document primary, syn-metamorphic oscillatory zoning of some chalcophile and siderophile elements during syn-metamorphic crystallization of pyrite porphyroblasts. These primary pyrite features are cut by late metal-rich fractures suggesting that remobilization of gold occurred with trace element enrichment of other chalcophile and siderophile elements (Cu, Pb, Zn, Ag, Bi, Te). Metal enrichment post-dates the main period of syn-metamorphic pyrite crystallization. Pyrite grain boundaries and low-angle grain boundaries are also precious and base metal-rich (Fig. 1E), suggesting that late gold remobilization also occurred during pyrite recrystallization.

6 Working model and conclusions

Results from EBSD analyses indicate that pyrite, under high strain, deforms ductily forming substrates that may act as traps for gold. Our results support a syn- to post-peak metamorphic and deformation-driven gold upgrading model. We document that late-D2 brittle fractures are important micro-structural settings for concentrating gold. This micro-scale gold paragenesis reflects the importance of syn-D2 structures for controlling the geometry of gold ore zones at the deposit scale.

We propose a model where gold is trapped into the deformation induced micro-structures through one of two possible intragrain diffusion mechanisms: 1) high diffusivity pathway (PIPE) diffusion; 2) dislocation-impurity pair (DIP) diffusion (Vukmanovic et al. 2014). In both cases, gold is introduced pre- to syn-D2, possibly incorporated as nanoparticles or solid solution within early sulfides. The free gold from syn-D2 vein forming fluids and the gold within the sulfides are then remobilized during high-strain ductile deformation. Dislocation glide and dislocation creep mechanisms followed by PIPE and/or DIP diffusion then trap gold within micro-structures.

At this stage, we have four major conclusions: 1) pyrite deforms ductily under lower amphibolite facies conditions; 2) pyrite plastic deformation is present as linear, chessboard and more complex heterogeneous misorientation patterns, described by rotation about at least one of the $<100>$ axes; 3) deformational substructures in pyrite act as traps for gold and other trace elements; and 4) gold at Detour Lake was locally remobilized into late, brittle fractures that post-date syn-metamorphic pyrite crystallization. The significance of the metamorphic gold-upgrading model to the overall endowment of the Detour Lake deposit is the focus of ongoing study.

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References


Figure 1. a OC image of a deformed Py vein with Act inclusions in a Qz-Ab-Bt-Act-Mag-Po matrix showing a heterogeneous misorientation pattern cut by late brittle fractures. b Pole figure of <100> axes for "grain 1" (equal-angle lower hemisphere projection) showing rotation about at least one of the <100> axes. c Orientation deviation angle map of Py showing a heterogeneous misorientation pattern with a maximum misorientation of 30°. d Grain boundary map of Py revealing low-angle grain boundary development in high strain areas. E. 2D LA-ICP-MS trace element maps of Py vein revealing Au, Ag, Bi, and Te enrichment at grain and low-angle grain boundaries and in late fractures.
Structural architecture and metamorphism of the Borden Lake greenstone belt, Kapuskasing Structural Zone, Abitibi–Wawa Terrane

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Abstract. A mapping program by the Ontario geological Survey in the summer 2016 has updated our knowledge on the Borden Lake greenstone belt (BLGB) and the high-pressure granulite facies Kapuskasing Structural Zone (KSZ) in the Abitibi-Wawa Terrane. A major gold deposit discovery at the north edge of Borden Lake by Probe Mines Limited in 2012 has revived the interest of both the exploration industry and the academic world in in the KSZ. The structural framework and tectonic evolution of both the KSZ and the BRGB are outlined in this communication. The BLGB is in tectonic contact with the underlying KSZ. The BLGB expands to the east over 70 km along what is probably a major transcurrent shear zone possibly being the westward extension of the Porcupine-Destor deformation zone. Both entities were involved in multiple tectonic events, starting at 2665 Ma by widespread partial melting in the KSZ and by coeval burial of the BLGB. Nevertheless, the youngest dextral transcurrent tectonic event is the only event they have in common. Placed in its tectonic framework, the Borden gold deposit is thought to have been formed between 2665 and 2640 Ma.

1 Introduction

The Borden Lake greenstone belt in the Abitibi-Wawa Terrane hosts the Borden gold deposit (Murahwi et al. 2012; Dzick 2014). In contrast to gold deposits found in similar settings farther east in the Abitibi Subprovince along the Porcupine-Destor or the Larder-Cadillac deformation zones, the supracrustal rocks hosting the Borden gold deposit were metamorphosed at higher metamorphic grades reaching middle amphibolite conditions. Another major difference is that the relative substratum of the BLGB is composed of high-pressure diatexites and mafic granulites of the Kapuskasing Structural Zone (KSZ) instead of the tonalitic and granitic batholiths seen in the Abitibi. Although the Borden gold deposit is mostly hosted by a garnet-biotite gneiss unit parallel to the regional stratigraphy, the deposit lacks of a clear lithological control because alteration and mineralisation also affect the surrounding units (Murahwi et al. 2012; Dzick 2014).

On the other hand, the Borden gold deposit displays strong similarities with gold deposits in the Abitibi Subprovince such as being structurally controlled and spatially associated with Timiskaming-type conglomerates and quartz-carbonate alteration (Dzick 2014; Bateman et al. 2008). Yet, the structural architecture and tectonic evolution of the BLGB are poorly constrained, thereby impairing our ability to make comparison with better described gold deposits. The results presented here provide a regional tectonic framework for the Borden gold deposit which allows it to be compared with those seen in the Abitibi Subprovince.

2 Structural geology and relationship with metamorphism

Prior mapping by Percival (1981) and Moser (1993) recognized the asymmetric sinistral boudin shape of the BLGB. At first approximation, the BLGB can be described as a synform sitting on top of the diatexites and intrusive rocks of the KSZ (Moser 1993). In addition, the tectonic nature of the contact between the BLGB and the KSZ was discussed by Bursnall et al. (1994). Examination of airborne magnetic anomalies from geophysical survey data (Ontario Geological Survey 2002a, 2002b) and field work confirmed this overall map-scale geometry and also the kinematics of the faulted contact between the BLGB and KSZ (Figure 1). This structural pattern results from a complex and polyphase tectonic history that will be detailed in the sections below. Because of the early structural events of the BLGB and the KSZ are distinct, they will be described separately.

2.1 Kapuskasing Structural Zone (D1-KSZ early deformation event)

Within the map area (Figure 1), the diatexites are composed of tonalitic leucosomes and mafic granulate melanosomes.

The early deformation event is better defined along Highway 101 in the northeastern corner of Borden Township (Figure 1). The diatexites are consistently and strongly deformed. The main deformation stage is characterized by a flat-lying to shallowly northeast-dipping foliation that is well expressed in the tonalitic leucosomes. This dominant foliation wraps around melanosome boudins and pods, which typically possess an internal foliation commonly folded and disconnected from the outer flat-lying foliation. Thus, the internal foliation described in the melanosomes can be interpreted as a relict S1-KSZ foliation reworked by the external S2-KSZ foliation. The S2-KSZ foliation bears a composite stretching and mineral lineation (defined as a L2-KSZ lineation) oriented roughly east and plunging shallowly to the east. On sections parallel to the L2-KSZ lineation and perpendicular to the S2-KSZ foliation, shear criteria, such as asymmetric...
boudins and shear bands, gave a consistent top-to-the west-southwest shear sense. On sections perpendicular to the foliation and the lineation, intrafolial folds with their axes parallel to the lineation are present. Despite the strong S₂ foliation, the tonalitic leucosomes texturally show little to no plastic ductile deformation, which strongly suggests that the deformation responsible for the S₂ KSZ foliation likely occurred above their solidus. Moreover, the monzogranitic melts, derived from the partial melting of the tonalite, display identical textural relationships to those described for the tonalite. Monzogranitic melts migrating along shear bands were commonly observed, suggesting that the D₂ KSZ deformation also was occurring during this second partial melting event. Although under-represented within the map area, this domain is likely of regional extent within the KSZ. On the other hand, the sense of shearing documented in this study (i.e. top-to-the southwest) has not been reported before and has not been documented in the overlying BLGB.

2.2 Borden Lake Greenstone Belt (D₁ BLGB early deformation event)

The BLGB also underwent a polyphase structural history, which is, for the early event, different to that described for the KSZ.

Evidence of the first deformational event (D₁ BLGB) was observed mainly on the north flank near the contact with the KSZ migmatites. The D₁ BLGB event is particularly well preserved in the mafic volcanic and interlayered felsic volcanic rocks and is characterized by a penetrative S₁ foliation, generally parallel to the original bedding S₀, such as pillows and compositional layering. This S₁ BLGB foliation orientation varies according to its position in the BLGB and follows the shape of the BLGB (i.e. east-trending in the central part of the belt, northwest trending in the southwestern part and northeast trending on the southeastern part). The S₁ BLGB foliation usually dips moderately to steeply to the north. Nonetheless, because of subsequent folding events, dips to the south are frequent. The S₁ BLGB foliation is always associated with composite stretching and mineral L₁ BLGB lineations. The L₁ BLGB lineations usually plunge steeply (>45°) to the northeast.
where the $S_{1 \text{BLGB}}$ foliation dips to the north; alternately, where the $S_{1 \text{BLGB}}$ foliation dips to the south, the lineation plunges to the southeast. In the appropriate sections (parallel to the lineation and perpendicular to the foliation), shear criteria, such as recrystallization tails around garnet porphyroblasts, asymmetric synkinematic hornblende porphyroblasts and asymmetric boudinage, were observed and gave a consistent apparent north-side-up shearing with a sinistral horizontal component. Such down-dip stretching lineations were also sporadically found in the amphibolites on the southeastern corner of the BLGB. However, because of less favourable exposure, kinematics in this part of the belt were assessed only from oriented samples. Only a few samples on the southern flank were identified as coeval with the $D_{1 \text{BLGB}}$ event. Nevertheless, they gave consistent top-to-the southeast shear sense.

Because of the strong overprint of deformation subsequent to the $D_{1 \text{BLGB}}$ event and the paucity of good observations on the southern flank of the BLGB, the tectonic significance of the $D_{1 \text{BLGB}}$ event can be interpreted in different ways. However, our observations favour a scenario in which the BLGB was overthrust upon the KSZ with a top-to-the southeast displacement during the $D_{1 \text{BLGB}}$ event.

### 2.3 Regional late dextral strike-slip event

Early events (i.e. $D_{1 \text{BLGB}}$ and $D_{1-2 \text{KSZ}}$) were reworked by a subsequent belt-scale dextral strike-slip event. Although the dextral strike-slip event is present in the surrounding migmatite of the KSZ, it is more developed in the BLGB. Within the BLGB, the $S_{1 \text{BLGB}}$ fabrics were overprinted by such intensity that most of the foliations observed in the field are better defined as a composite $S_{1-2}$ foliation. The $L_{2 \text{BLGB}}$ composite stretching and mineral lineation associated with the $S_{2 \text{BLGB}}$ foliation plunge shallowly to the east-northeast and is particularly well developed in the Timiskaming-type metaglomerates. Dextral shear sense indicators were observed within metaglomerates and the late synkinematic granodiorites. An interesting feature of this $D_{2 \text{BLGB}}$ event is that the ellipsoids of deformation alternate, in places as small as on the scale of a metre, between domains of prolate and oblate shapes. This pattern was better observed in the metaglomerates and the porphyritic granodiorites, which constitute good markers of the deformation. This $D_{2 \text{BLGB}}$ event is also well developed in the fault-bounded unit hosting the Borden gold deposit (Figure 1) and it is possible that it played a significant role in the gold mineralisation (Dzick 2014).

Both the KSZ and the BLGB were also affected by a major folding event. Consistent dextral shearung throughout the belt suggests that this folding event might have been coeval with or occurred prior to the aforementioned dextral shearing. Within the KSZ, this folding event is characterised by west- to northwest-trending, upright to southwest-directed $F_3$ folds. In the BLGB, the fold axes follow the boundary of the belt in a similar way to the one described for the $S_{1}$ foliation trajectories. On the other hand, axes of smaller scale parasitic folds plunge consistently to the east-southeast.

### 3 Metamorphism and metamorphosed alteration

In contrast to the KSZ, which shows fairly homogeneous metamorphic conditions ranging from granulite to upper amphibolite, the BLGB in the map area is characterized by a lower grade metamorphism in which partial melting is rare and restricted to the southeastern flank of the greenstone belt. In this southeastern flank, partial melting affected mainly the metasedimentary rocks and was only observed in the more pelitic compositions where stromatic metatexites are well developed. Moreover, at the outcrop scale, well-defined leucosomes are absent from the garnet-bearing quartzofeldspathic layers interbedded with the pelitic layers, suggesting a lower partial melting ratio and/or a lack of melt segregation. In this area, garnet-bearing amphibolites derived from mafic volcanic rocks are also devoid of visible partial melting, although the garnet seems to have crystallized homogeneously throughout the amphibolites during the $D_{1 \text{BLGB}}$ event. Thermobarometry, using the average PT mode of THERMOCALC, was performed on 3 garnet-bearing amphibolites of the BLGB and yielded temperatures between 500 to 600 °C for pressures ranging from 5 to 6 kbar. These values confirm that rock units of the BLGB never reached the P-T conditions required for partial melting and thereby are interpreted as reflecting the maximum P-T conditions experienced by the BLGB. An interesting feature is that all the investigated garnets did not display any chemical zoning which is surprising considering that chemical zoning during garnet growth by Rayleigh fractionation is a rather common feature in rocks metamorphosed under these P-T conditions. Garnet is also stable in the metaglomerates affected by the dextral $D_{2 \text{BLGB}}$ event, albeit in much lower quantity. Thus, metamorphic conditions during the $D_{2 \text{BLGB}}$ event seem to have taken place under amphibolite facies conditions.

The BLGB hosts remarkable examples of metamorphosed alteration. For instance, garnet abundance in the mafic metavolcanic rocks and their interlayered felsic counterparts is clearly chemically controlled and can reach modes up to 40% in altered compositions. It is a recurrent pattern seen throughout the BLGB but it is more conspicuous on the northern flank of the BLGB. The dominant type of altered layers (or alternatively pods or clots), parallel to the general fabric (bedding and foliation), is composed typically of calc-silicates containing clinopyroxene (augite, diopside), epidote, scapolite (meionite) and carbonates along with garnet and reflects likely the metamorphism of former carbonate alteration. This carbonate alteration along with garnet-biotite and garnet-grunerite “veins” derived respectively from sericite (or potassium feldspar) and chlorite alteration is recurrently associated with Cu mineralisation. Occurrences of malachite and disseminated chalcopyrite and pyrrhotite were observed in breciated felsic flows interlayered with
the mafic metavolcanic rocks. This alteration was interpreted as being synvolcanic and very likely differs from the one coeval with the Borden gold deposit which affected locally the upper units including the metaconglomerates. Although metamorphosed and similar in composition to the earlier event, the alteration associated with the Borden gold deposit is characterised by an abundance of silica (either veins or massive silicification) and a potassic component, both in siliciclastic rock and feldspar porphyries (Murahwi et al 2012; Dzick 2014). This second alteration also affected the underlying mafic metavolcanic rocks where it tends to crosscut the general fabric.

4 Discussion

The \( D_1^{BLGB} \) event occurred under middle amphibolite facies conditions and is clearly a distinct event from the early top-to-the southwest shearing within the KSZ. The mode of burial of the BLGB remains unconstrained by direct structural analysis and thermodynamical modelling. Burial could either happen at the footwall of a major thrust or be the result of sagduction or be a conjunction of sagduction and strike-slip shearing (Lin et al. 2013). Early thrusting (and/or reverse faulting) prior major strike-slip shearing was also inferred by some authors (Snyder et al. 2008) to explain the structural pattern of the supracrustal rocks in the area of Timmins along the Porcupine-Destor fault zone. On the other hand, early sinistral strike-slip shearing described both in the Porcupine-Destor and Larder-Cadillac fault zones is missing in the Borden Lake area. It is unclear, for the moment, if this event was truly absent, overprinted or not documented because of the poor exposure. Only the overall asymmetric sinistral boudin shape of the BLGB gives some credence to the presence of this event. A remarkable feature is that the Borden gold deposit is located at centre of the BLGB in a shear-zone-bounded megaboudin strongly affected by the late dextral transcurrent shearing (Figure 1). However, it is still unclear if this structure played a genetic role in the formation of the deposit. The Timiskaming-type conglomerates in the BLGB were moderately affected by carbonate alteration (now metamorphosed) similar to those observed in gold deposits in the Abitibi Subprovince. Moreover, quartz-feldspar porphyries intruding these conglomerates were affected by potassic alteration compatible with gold mineralisation as well (Duguet and Szumylo 2016; Murahwi et al 2012). If these alteration types are associated with the Borden deposit, it is likely that the gold mineralisation occurred during or sometime after 2667 Ma (maximum age of deposition of the Timiskaming-type conglomerates; 2664±6 Ma: Percival et al. 1981; 2667±2 Ma: Krogh 1993) and possibly before 2640-2630 Ma (age of the youngest pegmatite dikes; Krogh 1993).

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References


Palaeozoic orogenic gold in New Zealand: the Globe-Progress shear zone viewed through pyrite trace element geochemistry

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Abstract. Micro-analytical techniques were carried out on gold-bearing pyrite from 12 polished thin sections sampled from diamond drill core from the shear zone of the Globe-Progress mine, near Reefton, New Zealand. These samples were selected with the aim of identifying the major, minor, and trace element compositions, which can help to constrain the stages of ore formation, the source of the metals, and the role of hydrothermal fluids. We observed geochemical differences between the type 1 pyrite porphyroblasts that formed during syn-metamorphic, greenschist facies and type 2, 3 and 4 pyrites that were formed by subsequent hydrothermal events.

1 Introduction

The Reefton Goldfield is located within the Westland District on the South Coast of New Zealand (Fig. 1). The orogenic gold deposits in this area are hosted in turbidite sequences of alternating greywacke and argillite beds that are included in the Greenland Group of the Buller Terrane. These turbidites were deposited during Cambrian to Ordovician time and folded and metamorphosed starting in the Silurian. Mineralisation is thought to have occurred during stages of shear zone formation and greenschist metamorphism between 438-395 Ma (Goldfarb et al. 1995). OceanaGold’s Globe-Progress mine is located 5 km SSE of Reefton Township. In the 1980s new gold resources were identified in two styles of mineralisation. One style is associated with quartz-vein remnants and another with disseminated sulphides within the metasedimentary hosted rocks and fault breccias surrounding and adjacent to remnant quartz veins within the Globe-Progress shear zone (Christie and Brathwaite 2003; Christie et al. 2006; Madambi and Moore 2013).

Within the Reefton Goldfield, several stages of gold deposition have been identified from the sulphide mineral textures and morphology, and relationships with host rock lithology, veining, alteration and structures (MacKenzie et al. 2014). However, very little work has been done to characterise the disseminated and vein sulphides that host a significant part of the gold budget in the deposits of the goldfield. This paper presents the results of an ongoing study examining the morphology, textures and composition of the gold-bearing sulphide minerals within the shear zone at the Globe-Progress mine. Micro-analytical techniques including electron probe microanalyses (EPMA) and particle induced X-Ray emission (PIXE) (Trompetter et al. 2005) were used to carry out investigations on gold-bearing sulphides, from 12 polished thin sections sampled from drill core intervals with high bulk Au assay results. These samples were targeted with the aim of identifying the major, minor, and trace element compositions, which may help to constrain the stages of ore formation, the source of the metals, and the role of hydrothermal fluids.

2 Pyrite morphologies and textures

There are a range of morphologies and textures in the disseminated and veinlet pyrites from the Globe-Progress shear zone. Textures include grain-boundary fractures, cataclastic deformation, and open- and infilled-fractures that are ubiquitous and often obscure the crystal habit of the pyrite grains. Pyrite has been classified into four types based on primary discriminants of grain size and shape, followed by As contents and zoning patterns (Fig. 2). Type 1 occurs as relatively large (100 to 300 µm), well-rounded grains disseminated throughout the groundmass of the greywacke and argillite (Fig. 2a). This pyrite is relatively rare and is surrounded by a quartz fringe. Type 1 pyrite is interpreted to be equivalent to the syn-metamorphic pyrite described by MacKenzie et al. (2014) in their regional study of the Reefton Goldfield. Type 2 pyrite is similarly large, anhedral to euhedral, but lacks the surrounding quartz fringe present in Type 1 (Fig. 2b). Type 3 pyrite is smaller (30-40 µm), euhedral, and more closely associated with quartz veining and quartz-rich breccia zones. Some grains are pristine, however more commonly they are cataclastically deformed with overgrowths of arsenopyrite (Fig. 2c). Type 4 pyrite is similarly small and anhedral. This pyrite is very common and is seen in vein quartz and within areas of stibnite infill (Fig. 2d). Pyrite types 2, 3 and 4 are interpreted to have formed during hydrothermal events.
3 Trace element geochemistry

3.1 Arsenic zoning in pyrite

Chemical zoning is most pronounced for As in all of the pyrite types (Fig. 3). Type 1 and 2 pyrites have As-rich rims and depleted cores. There is also a slight oscillatory nature to the As zoning (Figs 3a, b), which indicates multiple growth generations under changing conditions. Type 3 pyrites show concentric As zonation around earlier formed grains and are depleted in the outermost rims. Type 4 pyrite is similar to Type 2, both having As enrichment in the rim relative to the core. It should also be noted that Type 1 pyrite has significantly higher As concentrations overall, ranging from 2.3 to 3.6%, compared to Type 2, 3 and 4 pyrites whose As concentrations range from 0.01 to 2.3%. This pattern of concentrations suggest the fluids responsible for the formation of the hydrothermal pyrite either had lower As contents or, alternatively, under changing temperature regimes As was being taken up by the precipitation of other sulphides such as arsenopyrite (Morey et al. 2008) and stibnite.

3.2 Gold in pyrite

Visible gold in the form of micro-inclusions or fracture infilling was not observed petrographically nor in any of the pyrite grain maps. The lack of visible gold implies that remobilisation of gold was not a determining factor in the formation of the ore, but rather gold was carried in the metamorphic and hydrothermal fluids that flowed through the sediments and precipitated the pyrite. Gold was however detected using both EPMA and PIXE spot analyses and it is observed as disseminations in the pyrite in the 2D elemental maps from both techniques. This indicates that the gold is present as invisible gold and is bound within the crystal lattice of the pyrite. It was incorporated via solid solution during syn-metamorphism and/or subsequent hydrothermal alteration events. In the Type 1 pyrite, the Au content in the core of one grain is 293 ppm whereas no Au was detected in the As-rich rim. In pyrite Types 2, 3 and 4, Au in the cores range from 46 ppm to 0.11% and in the rim of one grain Au is 311 ppm. A
positive correlation between Au and As in pyrite has been reported in the literature in numerous studies on orogenic gold deposits (Morey et al. 2007; Morey et al. 2008). The pyrites within the Globe-Progress shear zone also show a broad, positive trend between Au and As, though the data set is too small at this stage to discern more detailed relationships between Au and As with respect to the different types of pyrite.

3.3 Other trace elements detected in pyrite

We observed geochemical differences between the Type 1 pyrite porphyroblasts that formed during syn-metamorphic, greenschist facies and Type 2, 3 and 4 pyrites that were formed by hydrothermal events. For instance, the pyrite porphyroblasts have lower Pb, Co, Ga, V and Au contents compared to the pyrites that formed during the hydrothermal events. Scandium was not detected in the Type 1 pyrites, but it was detected at elevated concentrations ranging from 0.2 to 3.4% in the hydrothermal pyrites. In contrast, Ni and Zn are elevated in the Type 1 pyrites compared to Types 2, 3 and 4 pyrites and may reflect relict compositions of syn-depositional conditions (Large et al. 2007; Large et al. 2014).

Interestingly, hydrothermal pyrite is also elevated in elements such as Bi, Cu and Sb, which have been used at other Paleozoic orogenic deposits as indications of magmatic affiliations (Arne et al. 1998).
4 Conclusions

This preliminary work on pyrite from the Globe-Progress gold deposit provides some interesting insights into the complexity of the ore deposit formation. Elemental mapping and spot analyses using two complementary microanalytical techniques distinguish at least two main types of pyrite, one syn-metamorphic and the other hydrothermal in origin. Furthermore, the hydrothermal pyrite can be further subdivided into three types based on variations in size, shape, texture, As zoning patterns and trace element abundances. Elevations in elements related to magmatic sources stands in stark contrast to a purely metamorphic origin for gold in the Reefton Goldfields.

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The new Vindelgransele gold ore domain, northern Sweden; preliminary results from the Fäbodtjärn lode gold deposit

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Abstract. The Fäbodtjärn lode gold deposit is located in the Vindelgransele area, in the Skellefte District, in northern Sweden. The mineralization consists of a quartz vein system hosted in a sequence of turbiditic greywackes and pelitic sedimentary rocks, situated 20–30 meters above the contact with a granodiorite sill. The aim of the study is to better understand the genesis and controls on ore at Fäbodtjärn and improve exploration guides for the area. Gold deposits have been known in the Skellefte District for over a century. However, there is an ongoing debate whether some of these deposits are intrusion-related or orogenic gold. Several gold deposits in the Vindelgransele area are spatially associated with intrusive rocks. There might thus be a genetic link between the Fäbodtjärn deposit and the intrusion, or the intrusive rocks have simply acted as structural traps during compressional stress conditions.

1 Introduction

Fäbodtjärn (previously known as Fäbodliden C) is a lode gold deposit located in the Vindelgransele area, in the Västerbotten county, in northern Sweden. This area constitutes the westernmost part of the well-known Skellefte District, but also borders the Gold Line District and is host to numerous gold occurrences on either side of the Vindel river (Fig. 1). The area has for many years been regarded as a potentially ore-rich province (Markkula et al. 1985). However, some of the prospects are relatively low in both grade and tonnage (Table 1). They were thus considered not economically viable and did not lead to any major efforts prior to the state-financed gold exploration project carried out by the Swedish Geological Company from 1984 to 1991 (Lindroos et al. 1992). The amount of outcrops in the area is limited due to an extensive till overburden. At that time, two trenches were thus excavated over Fäbodtjärn revealing metamorphosed sedimentary rocks and a granodiorite. Gold mineralization was also found within the metasedimentary rocks (Markkula et al. 1985). Since then, drilling of the prospect has been done by multiple companies over the years. Analytical results from the core drilling program conducted by the present owner, Botnia Exploration, which included 30 holes for a total length of 5585 meters, strengthen the expectations for the Vindelgransele area as a future gold mining district.

Fäbodtjärn currently presents an indicated mineral resource of 111,000 metric t, at 8.5 g/t Au (Botnia Exploration 2015). The gold deposits in the Vindelgransele area have in the past seen only very limited scientific research (i.e. the Middagsberget deposit, Öhlander and Markkula 1994), so a contribution on Fäbodtjärn will add to our understanding of the gold metallogenesis in this prospective area. In the Vindelgransele area, several intrusions spatially associated with several gold prospects are of interest when discussing the genetic aspects of ore formation. Fäbodtjärn displays several characteristics typical of orogenic gold deposits (quartz veining, low base metals content, metal association, structural control), but the role of the multiple intrusive rocks needs to be investigated further to properly classify the deposit. This contribution describes the geology of the deposit and discusses the possible link between gold and intrusive rocks. Results from this study may have direct impact on the ongoing mineral exploration in the area.

Table 1. Au grade and tonnage of the gold occurrences in the Vindelgransele area (modified after Bark and Weihed 2003).

<table>
<thead>
<tr>
<th>Occurrences</th>
<th>Tonnage (t)</th>
<th>Au grade (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fäbodliden A</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>Fäbodliden B</td>
<td>No data</td>
<td>No data</td>
</tr>
<tr>
<td>Fäbodtjärn</td>
<td>111 000</td>
<td>8.5</td>
</tr>
<tr>
<td>Middagsberget</td>
<td>300</td>
<td>3</td>
</tr>
<tr>
<td>Vargbäcken</td>
<td>No data</td>
<td>No data</td>
</tr>
</tbody>
</table>

2 Regional geological setting

The Skellefte District is a Palaeoproterozoic volcanosedimentary belt. The district is located in the northern Swedish part of the Svecokfenian domain. It has been one of the most important mining districts in Europe for the last century, hosting over 80 volcanogenic massive sulphide and numerous gold deposits (Rickard 1986; Weihed et al. 1992; Allen et al. 1996).

In a general sense, Kathol and Weihed (2005) describe the district as an area of 120 by 30 km, bordered to the south and east by marine, mainly epiclastic, supracrustal rocks, the Bothnian Group, and to the north and west by areas consisting mainly of marine and subaerial volcanic arc assemblages, the Arvidsjaur Group. The stratigraphy of the district is complex and laterally variable (Weihed et al. 1992; Allen et al. 1996; Weihed et al. 2005). It has been divided into a sequence dominated by subaqueous felsic
volcanic rocks, the Skellefte Group, which is interfingered with a coeval sequence dominated by mixed turbiditic greywackes and coarse clastic sedimentary rocks, the Vargfors Group (Weihed et al. 1992; Allen et al. 1996; Bergman Weihed 2001; Weihed et al. 2005; Mercier-Langevin et al. 2013). The supracrustal rocks have been intruded by voluminous plutonic rocks; calc-alkaline I-type granitoids and associated mafic rocks of the Jörn GI suite, intrusive rocks of the Perthite Monzonite suite and granites of the Skellefte, Härnö and Revsund suite (Weihed et al. 1992; Allen et al. 1996; Billström and Weihed 1996; Bergman Weihed 2001; Weihed et al. 2005). Both supracrustal and intrusive rocks have been affected by major deformation events and have been subjected to regional metamorphism in greenschist to lower amphibolite facies. The metamorphic grade increases towards the Bothnian Basin (Rickard 1986; Weihed et al. 1992; Bergman Weihed 2001).

Figure 1. Geological map of the Vindelgransele area (modified after Bergström and Sträng 1999) with location of the 5 known gold prospects of the area. V – Vindelgransele village.
3 Methods

Six drill cores that transect the mineralized body were logged in detail and 20 samples were collected for chemical and petrographical studies, using both optical and scanning electron microscopy, with energy-dispersive spectrometry (SEM-EDS), at Luleå University of Technology, Sweden. The aim was to investigate the dominating hydrothermal alteration styles and the gold mineral associations.

4 Fäbodtjärn geological setting

A strongly sheared metasedimentary sequence dominated by both turbiditic greywackes and pelites constitutes the main rock type in the Fäbodtjärn area (Fig. 1). These terrigenous clastic rocks belong to the Vargfors Group, are black to grey in colour and are distinctly banded. The mineralogy dominantly consists of very fine- to fine-grained quartz and biotite. The sequence is in places overlain by a polymict, clast-supported conglomerate or arenite with disturbed contacts. Various amounts of sulphides (<2% pyrrhotite, pyrite and some minor arsenopyrite) occur in the sedimentary sequence, as fine-grained disseminations and veinlets, controlled (aligned) by the foliation. The rocks are in places rich in graphite, mostly occurring on fracture surfaces, and are strongly overprinted by rounded medium-grained porphyroblasts of plagioclase. The sedimentary rocks are irregularly silicified or crosscut by up to 10 cm wide quartz veins, typically parallel to the foliation. The foliated rocks in the area show evidence of folding, forming large anticlines with fold axes dipping steeply to the west (Öhlander and Markkula 1994). The area has been metamorphosed to greenschist facies (Rickard 1986), and small scale shearing and micro faults are common.

A granodiorite forms an elongated sill-like body with a north-western to south-eastern strike and a south-western dip (Fig. 1). This granodiorite appears grey in colour, inequigranular and has an aphaniptic texture. The mineralogy consists of medium- to coarse-grained plagioclase phenocrysts, very fine-grained biotite, quartz and alkali feldspar. The character of the rock shifts from strongly feldspar-porphyritic to more gabbroic with depth. The upper contacts with the sedimentary sequence are generally sharp but locally irregular and quite diffuse (Fig. 2). The contact zone with the sedimentary rocks is characterised by intense alteration (bleached margins). Irregular and multidirectional quartz- and carbonate veins, commonly 2 to 10 cm wide, crosscut the granodiorite. Various amounts of arsenopyrite are seen as very fine- to medium- grained disseminations or as coarse-grained crystals related to strongly altered quartz veins. Other sulphide minerals include very fine-grained pyrite, pyrrhotite and chalcopyrite.

Some dolerite dykes locally occur into the sedimentary sequence. These mafic rocks are black to green in colour. The dykes are barren, massive, 20 to 60 cm wide and fine-grained with sharp contacts.

5 Fäbodtjärn gold mineralization

The gold mineralization at Fäbodtjärn appears in a nearly north-south-striking quartz vein, but also in the granodiorite (Fig. 2). The main vein is located in sedimentary rocks, commonly in close association with mafic dykes, about 20–30 meters above the contact with a granodioritic sill. The vein is massive with a width varying from 0.5 to 3 meters. The mineralogy of the vein consists of equigranular, medium-grained quartz. Sulphides occur as fracture infillings of very fine- to fine-grained chalcopyrite, pyrrhotite, sphalerite, galena, pyrite and some arsenopyrite. The gold grain size in the vein ranges from coarse-grained (+300 µm) to very fine-grained (ca. 3 µm). However, most of the grains (65%, n=60) are smaller than 30 µm in size and typically occur as free grains in the quartz vein or sometimes as fracture fillings in arsenopyrite. Apart from the gold-arsenopyrite mineral association, gold is also associated with pyrite, pyrrhotite, chalcopyrite, galena and sphalerite. The upper and lower contacts of the vein are sharp and concordant with the foliation of the sedimentary sequence. Several ore shoots with high gold grade (2.0 m at 20.3 g/t Au, 0.7 m at 9.1 g/t Au, 1.6 m at 14.9 g/t Au, 2.1 m at 9.7 g/t Au) have been followed over 200 meters along the strike and over an estimated 300 meters in the dip direction. The extent of the ore zone is still open both down-dip and along strike to the north (Botnia Exploration 2013).
6 Genetic considerations

Both the Skellefte District and the Gold Line District host several gold deposits and prospects that have, in the sense of Groves et al. (1998), been classified as orogenic gold (Björkdal, Weihed et al. 2003; Fäboliden, Bark and Weihed 2007; Svartliden, Schlöglova et al. 2013). However, there is an ongoing debate whether the Björkdal gold deposit in the eastern part of the Skellefte District is in fact an intrusion-related gold deposit as it is spatially closely associated with intrusive rocks (Broman et al. 1994; Billström et al. 2009). The Åkerberg lode gold deposit, situated ca. 15 km north of Björkdal, is also suggested to be intrusion-related (Billström et al. 2012). Fäbodtjärn displays several characteristics typical of orogenic gold deposits. However, the gold deposits in the Vindelgransele area are also spatially associated with intrusions (Fig. 1). In agreement with the genetic discussion on the Björkdal and Åkerberg gold deposits, it is important to address the genetic significance of these intrusive rocks. There might be a genetic link between the gold deposits and the intrusions, or it might simply be that the intrusive rocks in the area are more competent, compared to the surrounding metasedimentary rocks, and have acted as rigid bodies during deformation and thereby facilitated the gold-bearing fluids (structural traps). In the area, the intrusive rocks are clearly folded and at least three major deformation zones are identified (Fig. 1). This structural complexity needs to be further investigated, to deduce the structural control on the intrusive rocks and the gold deposits.

Acknowledgements

We are indebted to Botnia Exploration for granting access to the Fäbodtjärn deposit. The study would not have been possible without their support. The project is funded by the European Union, through the Swedish Agency for Economic and Regional Growth and the Norrbotten County Council, as research project no. 20200552.

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Geologic and geochemical study of the Laird Lake property and associated gold mineralization, Red Lake greenstone belt, Ontario

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Abstract. The Laird Lake area encompasses the regional unconformity between the Balmer (2.99-2.96 Ga) and Confederation (2.75-2.73 Ga) assemblages on the southwestern end of the Red Lake greenstone belt, NW Ontario. Geochemical and mapping techniques have identified gold occurrences in the vicinity of the major break, which have features in common with larger lode gold deposits throughout the Red Lake gold camp. The stratigraphic layering in the Confederation, along with an increase in deformation at the break, suggest an erosional unconformity later activated during D2. The geochemical data indicates that part of the Balmer assemblage underwent crustal contamination implying eruption of this unit onto an older sialic crust. The Confederation assemblage comprises tholeiitic mafic, and calc-alkalic intermediate to felsic metavolcanic rocks, which display FI, FII, and FIIIb rhyolite trends. U-Pb geochronology of Confederation and intrusive units yielded age dates of 2741±19 Ma (quartz-feldspar porphyritic crystal tuff) and 2737.68±0.79 Ma (diorite). The geochemistry and age of the tuff correlates within error to the Heyson sequence of the Confederation whereas the diorite is likely a synvolcanic intrusion. Gold mineralization is often found associated with a mineral banded texture, accompanied by arsenopyrite and pyrrhotite, which draws strong similarities with the nearby Madsen gold Mine.

1 Introduction

The Red Lake greenstone belt (RLGB) is one of world’s best endowed gold districts and like many other gold-rich regions, the individual deposits are closely associated with regional unconformities (Fig. 1; Robert et al. 2005). The unconformity in Red Lake separates the Mesoarchean and Neoarchean assemblages and is locally defined by the presence of clastic sedimentary rocks of the Huston assemblage (Sanborn-Barrie et al. 2001; 2004). Only 10 km east of the study area is the past-producing Madsen Mine, which lies on the north side of the angular unconformity between the Balmer and Confederation assemblages. The ore is locally defined by the Austin and McVeigh ore zone, which displays a characteristic mineral banding (Dubé 2000).

The Laird Lake area consists of the Balmer assemblage to the north, which is separated from the Confederation assemblage to the south by a major unconformity. Multiple gold occurrences on the Laird Lake property generally occur within 200 m of the regional unconformity and could represent the continuation of a similar gold system as seen at the Madsen Mine. This study examined the gold mineralization and its association with the primary volcanic assemblages and first order structures. The project has characterized the nature and tectonic setting of the volcanic rocks and assessed the likelihood of significant gold mineralization by using a combination of mapping, petrology, geochemistry and isotopes.
the Balmer and Confederation assemblages have been reported (Atkinson 1994). The Balmer assemblage is characterized by submarine pillowd tholeiitic basalts, komatiites, basaltic komatiites, minor felsic metavolcanic rocks, iron formation and fine-grained elastic rocks, whereas the Confederation assemblage is defined by two major units: 1) the McNeely sequence, composed of calc-alkaline intermediate breciated tuff and felsic metavolcanic rocks; and 2) the Heyson sequence, composed of tholeiitic to calc-alkaline metavolcanic felsic rocks, tholeiitic mafic rocks and quartz-feldspar crystalline tuffs, and basaltic andesites (Sanborn-Barrie et al. 2001).

2.1 Gold mineralization in the RLGB

The largest gold endowments in the RLGB are hosted within the Mesoproterozoic Balmer assemblage and are commonly proximal to the regional angular unconformity with the Neoarchean Confederation assemblage. The Red Lake Gold Mines account for roughly 81% of the gold production in the RLGB and is located on the greenschist-amphibolite isograd, whereas the Madsen Mine only accounts for roughly 9% of gold production and is hosted in amphibolite-grade rocks (Lichtblau et al. 2016; Dubé et al. 2004). A total of 75.16 t of gold and 12.99 t of silver were extracted from Madsen from 1938 to 1976, with ore grades averaging 10 g/t Au (Durocher 1983). Gold mineralizing events at the Red Lake Gold Mines are estimated to have occurred between 2723 and 2712 Ma, whereas mineralization at the Madsen Mine is estimated to be between 2744±1 Ma (age over overlying Confederation assemblage) and 2699±4 Ma (age of crosscutting post-ore dike; Dubé et al. 2000; Corfu and Andrews 1987). A second stage of mineralization throughout the belt, smaller than the first, or remobilization of gold is thought to have occurred later than 2702 Ma (Dubé et al. 2004).

3 Results

3.1 Mapping

The Laird Lake property lies within a slier of the RLGB between the Killala–Baird batholith (2704 Ma) and the Medicine Stone batholith (pre- to syntectonic). Detailed mapping of the Laird Lake property in 2015 and 2016 has shown that the Balmer and Confederation assemblages display outcrop-scale textural differences that can be used to subdivide them. The Balmer assemblage typically consists of fine-grained, aphyric, locally pillowsed mafic metavolcanic rocks, ultramafic metavolcanic rocks with flow-breccia textures and local spinnex-bearing clasts, and banded-iron formations. In contrast, the Confederation assemblage consists of phenocrystic (feldspar) or poikiloblastic (amphibole) mafic metavolcanic rocks intercalated with intermediate to felsic metavolcanic rocks that include flows, lapilli tuffs, crystal tuffs and tuffs.

The Laird Lake property shows a dominant east-trending foliation defined by weak to strong mineral alignments and mineral banding, which most likely represent structures associated with D2 deformation. At the Laird Lake property, the unconformity is defined by a prominent mineral banding texture on the Balmer assemblage side of the unconformity, which is most commonly in contact with moderately foliated felsic to intermediate metavolcanic rocks of the Confederation assemblage and a lack of metasedimentary rocks. Late pyroxene-rich mafic dikes and xenolithic diorites are commonly associated with the unconformity. The mineral banding observed within the Balmer assemblage is defined by alternating bands that are biotite-rich, amphibole-rich, diopside-rich, and clinzoisite + muscovite-rich with local biotite-rich bands containing up to 15% garnets.

Gold mineralization at the Laird Lake property is strongly associated with the unconformity. Typically, pyrite ± arsenopyrite ± pyrrhotite, and rarely chalcopyrite, are associated with elevated gold values. Most gold showings are hosted in the Balmer assemblage, either in mafic metavolcanic rocks or, rarely, in banded iron formation and smoky quartz veins. The Lee Lake Au showing was discovered during the 2016 field season and hosts the mineral banding texture. The biotite-rich bands are typically associated with higher concentrations of fine-grained arsenopyrite (7-10%) and pyrrhotite (3-5%) with elevated gold values. Bounty Gold Corp. received assay values up to 17 g/t Au over 20 cm and 5.4 g/t Au in hand samples, after their initial sampling of the area during the summer of 2016 (LeBlanc 2016). The Confederation assemblage hosts weakly mineralized gold zones, which are typically hosted in quartz veins or in a pyrite-rich quartz-feldspar porphyritic crystal tuff.

3.2 Geochemistry

Whole-rock geochemical data for 100 samples were used to subdivide the tectonic assemblages. The Laird Lake trace element data (Fig. 2) shows a clear distinction between the Balmer and Confederation assemblages. The mafic metavolcanic rocks of the Balmer assemblage are tholeiitic and display two trends on a primitive mantle-normalized REE diagram (Fig. 2A): trend 1 has a relatively flat REE pattern compared to trend 2, which has enriched to depleted LREE and higher Th/Nb values. The ultramafic metavolcanic rocks of the Balmer assemblage typically have depleted LREE with strong negative Nb anomalies. The Confederation assemblage intermediate to felsic metavolcanic rocks are calc-alkaline whereas the mafic metavolcanic rocks are tholeiitic. On a primitive mantle-normalized diagram (Fig. 2B), the rocks are LREE enriched, with flat to sloping HREE, and large Nb and Ti negative anomalies.
Figure 2. Primitive mantle-normalized trace element profiles for the metavolcanic rocks, a Balmer assemblage. b Confederation assemblage. Normalization factors from Sun and McDonough (1989).

3.1 U-Pb Geochronology

Sample LL-16BG427A01 was collected from a strongly deformed medium-to-fine-grained dioritic intrusion within the Confederation assemblage roughly 500 m from the unconformity. The diorite yielded a weighted age of 2737.68 ± 0.79 Ma with all four zircons analysed plotting on concordia (Fig. 3). Sample LL-16BG068A01 was collected from a deformed fine-grained quartz-feldspar porphyritic crystal-tuff of the Confederation assemblage less than 20 m from the unconformity. A total of five zircons were analysed with very scattered results. Three of the grains analysed display a tight and concordant age (±3 Ma), yet all ages are different: 2841 Ma, 2875 Ma and 2911 Ma. A fourth zircon is about 10% discordant, probably the result of Pb loss. The fifth zircon grain had low Pb and U concentrations and lead to an imprecise but concordant age of 2741±19 Ma. This age correlates within error of the Confederation assemblage 2750-2730 Ma which has been identified elsewhere in the RLGB. The three oldest ages have been interpreted as xenocrystic zircons.

4 Discussion

The tholeiitic Balmer assemblage and calc-alkalic to tholeiitic Confederation assemblage in the Laird Lake area represent very contrasting tectonic settings. The geochemistry of the Balmer assemblage is consistent with a plume-origin having erupted onto an older sialic crust in a deep ocean environment, given the presence of komatiites, tholeiitic basalts, and rare sedimentary rocks. The negative Nb anomaly observed in the mafic trend 2 (Fig. 3A) has been attributed to crustal contamination, yet no older basement rocks have been found. The Confederation assemblage shows evidence for multiple sources of magmatism. The calc-alkalic quartz-feldspar porphyritic crystal tuffs show trends similar to Lesher’s (1986) FII and FIIIb-rhyolites, whereas the rest of the intermediate to felsic volcanic rocks are more typical of FI-rhyolites. The intercalated nature of the calc-alkalic and tholeiitic rocks would require a dynamic environment where all three geochemical signatures could form simultaneously. Geochemical trends and field observations suggest that the Confederation rocks are part of the Heyson sequence which has been previously interpreted to have formed as the result of intra-arc rifting on the continental margin (Sanborn-Barrie et al. 2001) due to the presence of tholeiites and isotopically juvenile signatures. However, this model does not take into account the various sources of calc-alkalic volcanism. A model involving the combination of arc and back arc volcanism, erupting onto Balmer assemblage crust would account for the geological and geochronological relationships at the Laird Lake area.

The regional unconformity that transects the Laird Lake area represents an erosional unconformity, which was activated during $D_2$ deformation. The stratigraphy in the overlying Confederation assemblage is parallel to sub-parallel to the unconformity, but an increase in fabric intensity towards the unconformity suggests structural activity along the break. The U-Pb zircon age dates of 2737.68 ± 0.79 Ma (diorite) and 2741±19 Ma (quartz-feldspar porphyritic crystal tuff) falls within error of the Confederation assemblage elsewhere in the belt (2750-2730 Ma) and only the volcanic unit overlaps in age with the Heyson sequence (<2744-2739 Ma). The age of the
oldest xenocrystic zircon with the quartz-feldspar porphyritic crystal tuff corresponds to the youngest zircon dated in the Slate Bay assemblage, which is entirely composed of elastic metasedimentary rocks containing mostly Balmer- and Ball-age detrital zircons. The two younger xenocrystic zircons do not correlate to any specific intervals of volcanism for units in the RLGB but are close in age to the Bruce Channel and Trout Bay assemblages. Inherited zircons would suggest the assimilation of older crust, however, since none of the xenocrystic zircons dated fall within periods of volcanism in the RLGB, it is possible that the Confederation assemblage erupted through older crust that has yet to be found.

The mineral banding found within the Balmer assemblage in the vicinity of the unconformity is likely the result of deformation and metamorphic processes that enriched the rocks in K2O, As, Sb, Ba, and W, and stripped them of Na2O. The drastic competency contrasts between the Balmer and Confederation assemblages would have allowed the unconformity to act as a zone of weakness and fluid pathways for the Au mineralization. The mineral banding containing the Au mineralization is parallel to D2 foliations and therefore the alteration and mineralization are pre- to syn-D2 or could have been remobilized during D2. At the Madsen gold Mine, the ore is located within zones that contain the same mineral banding as observed at the Laird Lake area but show much stronger elemental enrichments (K2O, As, Sb, Ba, and W) and depletions (Na2O). It is very likely that the Laird Lake area and Madsen Mine underwent similar gold enrichment processes as they share multiple features including first order structures, degree of metamorphism, macroscopic textures, and style of mineralization.

5 Conclusions

The Laird Lake area contains the Balmer and Confederation assemblages, separated by an erosional unconformity later activated by D2 which is directly associated with elevated Au mineralization. The mineralization within the mineral banding at the Laird Lake property and ore at the Madsen Mine share many features and could represent an extension of the same gold system along the regional unconformity. The Balmer and Confederation assemblages were formed in very different tectonic settings, but share the fact that they both were erupted through older crust, as demonstrated with the geochemistry and U-Pb geochronology.

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References

The Paleocene Sinongduo intermediate–sulfidation epithermal Pb–Zn–Ag deposit in the Linzizong volcanic succession, southern Tibet of China: exploration potential based upon Si–H–O stable isotope data

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Abstract. The volcanic belt of the Paleogene Linzizong Volcanic Succession (LVS; ~69–41 Ma) extends for >1000 km along the Lhasa terrane and contains volcanic rocks related to Tethyan subduction beneath the Lhasa terrane. We have identified intermediate–sulfidation (IS) epithermal Pb–Zn–Ag mineralization at Sinongduo hosted by rocks of the Dianzhong Formation (61.9 ± 0.4 Ma) of the LVS. Metallic minerals include sphalerite and galena, with minor chalcopyrite and argentite; alteration minerals include illite, chalcedony, sericite, montmorillonite, and jasper, with minor calcite, rhodochrosite and siderite. These assemblages resemble those of typical IS epithermal deposits. Extremely fine siliceous bands that developed from a paleo-hydrothermal vent were recently found in the Sinongduo exploration area. These siliceous bands contain low values of δ³⁰Si NBS–28 (-1.2‰ to -0.4‰) and δ¹⁸O V–SMOW (+2.2‰ to +3.6‰), with δ¹⁰DV–SMOW values for quartz veins cutting the mineralization ranging from -171‰ to -143‰, thus indicating silica of a paleo-hot spring. Therefore, exploration potential exists for associated low–sulfidation epithermal Au–Ag orebodies at Sinongduo.

1 Regional geology and geology of the Sinongduo deposit

The Linzizong Volcanic Succession (LVS; ~69–44 Ma) and the coeval dioritic to granitic batholiths represent a magmatic response to the India–Asia collision (Ding et al. 2003, 2005; Mo et al. 2008; Zhu et al. 2015)(Fig. 1). Zircon U–Pb and Ar–Ar geochronology studies subdivided the Linzizong volcanic succession into the Dianzhong, Nianbo and Pana Formations, forming at 69–61 Ma, 61–54 Ma, 54–44 Ma, respectively (Zhu et al. 2015). In the eastern part of the central Lhasa terrane, a “northern Gangdese Pb–Zn–Fe–Mo–W polymetallic belt” was suggested to have formed at ca. 69–51 Ma (Zheng et al. 2015). The ore belt can be subdivided by the Nyenchen Tanglha Mountains into eastern Cu–Pb–Zn–Ag (Lawu, Hahaigang, Mengya–a, Dongzhongla, Dongzhongsongduo, Yaguila, Sharang, and Tangbula deposits) and a western Pb–Zn–Ag (Narusongduo, Sinongduo, Qiagong, and Lazong deposits) sub-belts. The Sinongduo deposit is situated in the western sub-belt (Zheng et al. 2015). The Pb–Zn–Ag orebodies at the Sinongduo deposit are hosted by rhyolite porphyry and pyroclastic rocks (~61.9±0.4 Ma) of the LSV. The metallic minerals at Sinongduo include sphalerite, galena, pyrite, chalcopyrite, argentite, pearceite and siderite. Sphalerite and galena are the major ore minerals, and occur as massive, brecciated (Fig. 2a), or vein ores in the felsic volcanic rocks. Most galena grains are affected by late-stage deformation and show plastic deformation with crumple structure. Chalcopyrite occurs as exsolution lamellae in sphalerite. Isolated Ag-bearing minerals (e.g., argentite and pearceite) occur in Fe–Mn– carbonates as crevasse silver or between Fe-Mn–carbonates and early stage sulfides as intergranular silver. Silver-bearing minerals (argentite and pearceite) also locally coexist with sphalerite (Fig. 2b). Gold is highly enriched in pyrite from the rhyolite porphyry beneath the silica cap. Quartz–chalcedony–jasper, siderite–rhodochrosite, barite–fluorite, and ililite–sericite are the main alteration assemblages at Sinongduo. Two silica caps were identified and comprise mainly chalcedony and jasper, with minor quartz. Carbonate minerals are mainly siderite and rhodochrosite (Fig. 2c), with minor calcite (Fig. 2d). Due to weathering, the medium- to fine-grained massive Fe-Mn carbonates are yellowish–brown in hand specimen. The carbonate minerals are oolitic, rhombic or vein-like in shape, and some were silicified by later–stage metasomatic fluids.

2 Si–H–O isotopic data indicating a paleo–hot spring

A suite of banded siliceous sediments in the LVS was discovered at Sinongduo and most of the sediments were brecciated by hydrothermal cryptoexplosion or intruded
Figure 2. Sinongduo mining area a drill core of Pb-Zn-Ag cryptoexplosive breccia ore body. b argentite and galena. c siderite, rhodochrosite, sericite in the cryptoexplosive breccia- type orebody. d calcite, e vent of paleo-hot spring in LVS, exhibited as a rock mass in rhyolite porphyry. f hand specimen of band silicate. Abbreviations: Arn-argentite; Cal-calcite; Gn-galena; Py-pyrite; Rds-rhodochrosite; Sd-siderite; Ser-sericite; Sph-sphalerite.

by rhyolite porphyry (Fig 2e, f). We collected ten samples of the brecciated banded siliceous sediment (TD008–1, –2, –3; TD009–1, –2, –3, –4, –5, –6, –7), among which three pure banded silicate samples were selected, using a binocular microscope, for geochemical analysis. In addition, four quartz vein samples cutting the ore (BZK0201–142; BZK0201–189A; BZK0201–189B; BZK0202–133) were collected.

The $\delta^{30}$Si values of the quartz separates (−1.2‰ to −0.4‰) and whole-rock silicate bands (−0.1‰ to +0.3‰) from the TD008 and TD 009 groups are very different. $\delta^{30}$Si values of typical silicate rocks are > −1‰, whereas those of hydrothermal precipitates show relatively lower values. The $\delta^{30}$Si data suggest that the silicate bands were likely hydrothermal precipitates related to volcanic hot springs. The $\delta^{30}$Si values of whole rock silicate bands (−171‰−143‰) are distinctly lower than magmatic water (−40‰−80‰) (Taylor 1974 but similar to meteoric hot springs of the Tibetan Plateau (−130‰−220‰) (Zheng 1982).

3 LA–MC–ICP–MS zircon U–Pb dating

Zircons from the tuff (TD006–1) show igneous oscillatory-zoning in (CL) images (Fig. 3c) and have Th/U ratios of 0.47 to 1.26, indicative of a magmatic origin. The zircon grains are euhedral, long or stubby prismatic, and are 100–200 μm long, 70–100 μm wide, and aspect ratios 1.0 ~ 2.0. A total of 23 zircons (including two inherited zircons) were analyzed, among which 16 zircons yielded a concordant $^{206}$Pb/$^{238}$U age of 61.9 ± 0.4Ma (Fig. 3a). This constrains the tuff to the Dianzhong Formation (ca. 69 – 61 Ma) of the LVS (Huang et al. 2013).

Figure 3. a Concordant U-Pb; b weighted age diagrams for the zircons from the tuff (TD006-1). c CL images of the selected zircons from the sample of tuff (TD006–1).

4 Discussion

4.1 Intermediate–sulfidation epithermal mineralization

The zircon concordant $^{206}$Pb/$^{238}$U age of wall–rock at Sinongduo is 61.9 ± 0.4 Ma (Fig. 5a), and thus is belongs to the Dianzhong Formation (Zhu et al. 2015). The andesitic Dianzhong Formation was formed by the subduction of Tethyan oceanic crust and shows geochemical characteristics of high–K calc–alkaline magmatism (Mo et al. 2008; Zhu et al. 2015). The definition of intermediate–sulfidation (IS) for epithermal mineralization was mainly based on deposits in the Great Basin, USA (Hedenquist et al. 2000). The area hosts high K calc–alkaline magmatic rocks that formed in a continental–margin arc related to subduction of oceanic crust beneath western North America (John 2001). Therefore, the LVS and its coeval intrusive plutons in southern Tibet have potential to form intermediate–sulfidation deposits.

The metallic minerals at Sinongduo comprise mainly sphalerite and galena, and minor chalcopyrite and argentite, similar to typical IS epithermal deposits such as Cheshmeh Hafez in Iran (Mehrabi and Siani 2012), Sahinli/Tespih Dere in Turkey (Yilmaz et al. 2010), and Patricia in northern Chile (e.g., Chinchilla et al. 2016). Alteration mineral assemblages of typical IS epithermal deposits include quartz + carbonate + rhodonite + sericite ± adularia ± barite ± anhydrite ± hematite ± chlorite (e.g., Einaudi et al. 2003; Sillitoe and Hedenquist 2003). This is similar to those at Sinongduo, which includes quartz + carbonate + rhodonite + sericite + barite + hematite + illite + chlorite, and chalcedony + montmorillonite + jasper.
### 4.2 Prospectivity for LS Au–Ag deposits at Sinongduo

The ore-forming intrusions of the northern Gangdese Pb–Zn–Ag–Fe–Mo–W polymetallic belt are mainly granite, quartz porphyry, and granite porphyry, emplaced during 65–55 Ma (Gao et al. 2011; Zheng et al. 2015). Meanwhile, in the western part of this polymetallic belt, coeval volcanism (~62 Ma) formed the Narusongduo and Sinongduo IS epithermal deposits. The porphyry Cu–Mo deposits, skarn Pb–Zn deposits, and IS epithermal Pb–Zn–Ag deposits that formed during the main India–Asia collision period might be classified into a porphyry Cu (Mo)–epithermal Au (Ag) metallogenic system (Fig. 4). The porphyry (e.g., Sharang, Yaguila) and skarn (e.g., Lazong, Hahaigang, Mengya-a, Dongzhongla, Dongzhongsingduo, Tangbula) deposits that are located in the eastern part of the polymetallic belt may represent the deepest (>1 km) ore-forming types, whereas the IS epithermal deposits (e.g., Narusongduo, Sinongduo) epithermal deposits formed at a deeper location of 0.5~1 km. Paleo-hot spring sediments have now been confirmed in the Sinongduo mining area by our Si–H–O isotopic data, which indicates exploration potential for low sulfidation epithermal Au–Ag orebodies according to the model that suggested by Hedenquist et al. (2000) (Fig. 4).

![Figure 4. Schematic metallogenic model for the Sinongduo epithermal deposit in the Linzizong Volcanic Succession (modified after Hedenquist et al. 2000; John 2001).](image)

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### References


A new occurrence of argento-pentlandite and gold from the Ait Dawd Cu-Au ore deposit (Erdouz area, western High Atlas, Morocco)

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Abstract. The Ait Dawd Cu-Au vein deposit is located in the northern part of the Erdouz Pb-Zn-Ag district, on the northern range of the western High Atlas, Morocco, about 8 km SW of the Mo-Cu-W Azegour skarn deposit. The deposit is hosted within the Cambro-Ordovician series of the Erdouz folded formations. These formations are during the Hercynian orogeny and the schistosity is striking NNE to NE and dipping 20° to 70°E. The major faults cutting this area are parallels to the NE-SW trending direction of the Erdouz fault. Based on combination of petrographic observations, SEM, and EPMA investigations, the primary mineral assemblages are composed of chalcopyrite, pyrite, arsenopyrite, galena and sphalerite, tetrahedrite, freibergite, native gold and native bismuth. Cobaltite-gersdorffite and argentite-pentlandite are associated or enclosed within chalcopyrite. Native Gold is free in a quartz gangue or argento-pentlandite are associated or enclosed within chalcopyrite. The secondary minerals are composed of malachite, azurite, covellite, anglesite and iron oxides. The gangue minerals are quartz, calcite, dolomite, ankerite and chlorite. The main hydrothermal alterations studied are silicification, chloritization, sericitization and carbonatization This paper presents the main results of new detailed mineralogical features of the Ait Dawd Cu-Au vein deposit.

1 Introduction

Known for their molybdenum, copper, zinc, lead and (silver- gold) productions, the western High Atlas mines represent a mineralized district with various styles of mineralization including skarns (Permingeat 1957; Zerhourni 1988; El Khalile et al. 2014; Berrada et al. 2015), carbonate- replacements (Alansari et al. 2009; Ilmen et al. 2014, 2016) and vein-type ores (Badra 1993; Bouabdellah et al. 2009; Ilmen et al. 2015).

Mineralogical studies of the ore-bearing assemblages have revealed a great variety of minor elements, notably Bi, Te, Se, Au, Ag, Co, Ni, As, Sb, Mo and W. The significance of these elements and minerals and the role of the Azegour granite in their formations and in the formation of the various ores as a whole has been a matter of discussion (Alansari et al. 2009; Ilmen et al. 2015, 2016).

This contribution represents the first documented research on the Ait Dawn Cu-Au deposit and reveals for the first time new reported minerals within the western High Atlas ore deposits. It is part of a large scale metallogenic study initiated in 2009 by Alansari et al. (2009) at the Tighardine Zn-Pb-Cu carbonate-replacement deposit, Ilmen et al. (2014, 2016) at the Amensif Pb-Zn-Cu-(Ag-Au) carbonate-replacement deposit, Ilmen et al. (2015) at the Talat n’Imjjad auriferous shear zone. The aim of this work is to describe the primary mineralogical and chemical characteristics of the Ait Dawd deposit.

2 Geological Setting

The High Atlas mountains, located on the central part of Morocco (Fig. 1), are divided into three parts from east to west: eastern High Atlas, central High Atlas and western High Atlas. The latest is located about 60 km south of the Marrakech and is sub-divided also into three parts. The studied area is located on the ancient massif of western High Atlas, so called “le massif ancien du Haut Atlas” is located on the northern range of the western High Atlas. This area is marked by its geological formations attributed to the Paleozoic ages. These formations are intruded by several plutons which are emplaced during early and late Variscan orogeny (El Amrani 1984; Lagarde et al. 1987; Gasquet et al. 1991). Structurally, the studied area has been deformed during the Variscan orogeny. The mining history of this area is known through several ore deposits which were exploited since the 1920s. The famous ore deposit is the world-class Azegour Mo-W-Cu (Permingeat 1957).

The metallogenic district of Azegour-Erdouz belongs to the northern range of the western High Atlas mountains including base and precious metal mineralization as illustrated at the Azegour Mo-Cu-W skarn deposit (Permingeat 1957; Zerhourni 1988; El Khalile et al. 2014; Berrada et al. 2015), the Assif El Mal Pb-Zn-(Cu-Ag) vein deposit (Bouabdellah et al. 2009), the Erdouz Ag-Zn-Pb vein deposit (Badra 1993), the auriferous shear zone of Talat n’Imjjad (Ilmen et al., 2014a), and the Cu-Pb-Zn-Ag-(Au) carbonate replacement deposit at Amensif (Ilmen et al. 2014, 2016). The regional geology includes Lower to Middle Cambrian and Ordovician volcano-sedimentary formations. According to Pouclet et al. (2008), the volcanic rich-formations were dated at 532 ± 12 and 537 ± 9 Ma. This part of western High Atlas is intruded also by the Al Medinet quartz diorite recently dated at 514 ± 3 Ma (Fekkak 2016) and the Azegour granite dated at 271 ± 3 Ma (Mrini et al. 1992).

Structurally, The Azegour-Erdouz district is delimited by large faults (several km in length) that have been activated since Hercynian times (Fig. 1) (Cornée et al. 1987;
Labiki 1996; Dias et al. 2011; Ilmen et al. 2014, 2015). These large shear zones delineate different blocks in which the remarkably triangular Erdouz bloc is delimited by an ENE-WSW dextral mega-shear zones (Erdouz and Tignarine faults) and a second WNW-ESE sinistral shear zones (Al Medinet fault: Fig.1). Both structures were responsible for producing the strong deformation and structural complexity. The precious and base metal ores described in this contribution are located at the intersections of these faults (Badra 1993; Alansari et al. 2009; Bouabdellah et al. 2009; Ilmen et al. 2015, 2016).

The Ait Dawd deposit is located about 1 km south of the Al Medinet quartz diorite, and 1 km north of the old mine of Erdouz. The deposit is hosted by the Anzig fault which represents the northern limit of the Erdouz block.

Host rocks of mineralizations are part of the Cambro-Ordovician volcano-sedimentary terranes. These terranes are composed of schists, cordierite schists, quartzites, carbonates, tuffs, basalts, dolerites, andesites, trachytes and diorites. These rocks are cut by a swarm of rhyolitic and doleritic dykes which are probably Permian in age (Bensalah et al. 2015).

Figure 1. Geological sketch of the western High Atlas (After Cornée et al. 1987; Dias et al. 2011)

3 Ore mineralization

The Ait Dawd mineralizations occur as veins and disseminated ores. Three principal ore structures are oriented NE-SW and NW-SE.

The mineralizations are mainly composed of chalcopyrite, pyrite, native gold, argento-pentlandite, cobaltite-gersdorffite, arsenopyrite, galena, sphalerite and grey copper. The main mineralogical and geochemical characteristics are given bellow.

3.1 Analytical methods

Thin and polished sections were investigated using ore and optic microscopes at the DLGR Laboratory, Department of Geology (Cadi Ayyad University). The EMPA were carried out at the CAMPARIS Center (Université Pierre et Marie Curie, Paris, France) and the SEM analyses are done at the Reminex Research Center (Managem Group, Marrakech).

3.2 Mineralogy and geochemistry

On the basis of microscope observations and scanning electron microscopy investigations the principal minerals documented at the Ait Dawd are:

Chalcopyrite \((\text{Cu}_{0.92}\text{Fe}_{1.1}\text{S}_{1.98})\): main copper mineral. It occurs as large and coarse gained crystals (up to 1 mm) (Fig. 2). EPMA analyses of chalcopyrite are Cu: 33.93 wt%; Fe: 32.65 wt% and S: 31.50 wt%.

Pyrite \((\text{FeS}_2)\): It occurs as aggregates and cubic crystals up to 0.5 mm across. It is associated with arsenopyrite.

Gold \((\text{Au})\): It is documented here as a native gold as inclusions in the quartz gangue or associated with chalcopyrite (Fig.2f, g).

Argento-Pentlandite \((\text{Ag}_{0.04}\text{(Ni}_{2.03}\text{Fe}_{4.69})\text{S}_{9.23})\): first documentation of this mineral at the western High Atlas. It is present as inclusions within chalcopyrite in close
association with gersdorffite.

Chemical analyses of Argento-pentlandite reveal Ag: 14.26-14.91, Fe: 29.67-33.17, Ni: 15.09-18.82 and S: 36.59-37.48. Using the Mandziuk and Scott (1977) triangular diagram, the plots of these chemical data confirm the silver character of the pentlandite (Figs. 2a; c and 3a).

Cobaltite-Gersdorffite serie ((Co$_{0.44-0.55}$Ni$_{0.22-0.34}$Fe$_{0.21-0.22}$)As$_{0.94-0.97}$S$_{1.02-1.04}$): present as idiomorphic crystals, aggregates and inclusions within chalcopyrite and quartz. It is also associated with argento-pentlandite. Many cobaltite-gersdorffite grains show an enrichment of Sb.

Figure 2. Photomicrographs of the main minerals at the Ait Dawd ore deposit. a Aggregates of gersdorffite (Gr) in close association with chalcopyrite (Ccp) which contains inclusions of argento-pentlandite (Pn). b Rhombic section of arsenopyrite (Asp) within quartz gangue. c Association of argento-pentlandite (Pn) and chalcopyrite (Ccp) with formation of covellite (Cov). d Inclusions of argento-pentlandite (Pn) and sphalerite (Sp) within chalcopyrite (Ccp). e Native bismuth (Bi) as inclusions within chalcopyrite (Ccp). f Native gold (Au) in close association with chalcopyrite (Ccp). g Native gold (Au) free in quartz gangue.

EPMA analyses of cobaltite-gersdorffite are Ni: 10.55-1215 wt%, Co: 15.69-17.42 wt%, Fe: 7.19-7.33 wt%, As: 43.80-44.07 wt% and S: 19.58-19.76 wt% (Figs. 2a, 3b).

Argento-pentlandite and cobaltite-gersdorffite are the main Co and Ni occurrences.

Arsenopyrite (FeAs$_2$): It is associated with pyrite. Arsenopyrite occurs as individual or clustered rhombic and prismatic crystals disseminated in the quartz–carbonate veins (Fig. 2b).

Galena (Pb$_{0.74}$Cu$_{0.22}$Fe$_{0.03}$S$_{0.9}$): It is observed as coarse grained crystals and is characterized by its silver inclusions. Some galena grains are enclosed within chalcopyrite (Fig. 3a). The replacement of galena by anglesite take place in oxidizing conditions and these replacements started from galena rims. Chemical analyses of galena are Pb: 84.27-85.95 and S: 14.05-15.73. SEM and EPMA-EDX analyses indicate that this galena is an argentiferous galena.

Sphalerite (Zn$_{0.75}$Fe$_{0.13}$S$_{1.09}$): is observed as inclusions into chalcopyrite. SEM analyses range from 37.51 to 41.28 wt% for S, from 53.3 to 54.96 wt% for Zn and from 6.92 to 7.97 wt% for Fe.

Native Bismuth: it is enclosed into chalcopyrite as small inclusions (Fig. 2e).

Grey Copper (tetrahedrite and freibergite): These minerals are observed as inclusions into chalcopyrite. SEM investigations reveal that grey copper minerals are composed of tetrahedrite and freibergite.

Gangue minerals: Quartz, dolomite, ankerite and calcite are the main studied gangue minerals. They fill spaces and fractures between the ore minerals.

Figure 3. BSE images of selected minerals. a Inclusions of argento-Pentlandite (Pn), sphalerite (Sp) and galena (Gn) into chalcopyrite (Ccp). b Coarse grained crystals of cobaltite-gersdorffite (Gr) in association with chalcopyrite (Ccp) which contains galena (Gn) inclusions.
4 Discussion

This study documents the first evidence of argento-pentlandite associated with native gold, cobaltite-gersdorffite, arsenopyrite, chalcopyrite, native bismuth, sphalerite and pyrite at the western High Atlas if not in Morocco.

The main hydrothermal alterations documented are silicification, chloritization, sericitization, and carbonatization.

Using the FeAsS–CoAsS–NiAsS system of Klemm (1965), the temperature of the cobaltite-gersdorffite formation ranges between 500° to 600°C.

Argento pentlandite is a stable phase in the Ag-Fe-Ni-S system below 455 °C; it was recognized in nickel ores in various types from Finland (Vuorelainen et al. 1971). The assemblages of cobaltite-gersdorffite, argentoo-pentlandite, native bismuth and native gold are evidence for a contribution of magmatic components to the hydrothermal system known in other ore deposits such as Azegour, Talat n’Imjjad and Amensif (Permingeat 1957; Ilmen et al. 2015, 2016).

5 Conclusion

Based on the petrological and geochemical studies, our study reveals the following conclusions: (i) unusual argentoo-pentlandite, cobaltite/gersdorffite, arsenopyrite, and argentiferous galena included in chalcopyrite were documented in deposits of the western High Atlas. (ii) This mineral assemblage was accompanied by hydrothermal alteration, marked by silicification, chloritization, sericitization and carbonatization. (iii) The presence of Bi, Ag, Co-Ni elements in hydrothermal fluid, suggests a magmatic fluid contribution. (iv) The age and source of this mineralization will be investigated in the following studies.

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Definition of a sampling strategy by statistical analyses of LIBS data in the context of portable gold analyzer

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Abstract. Université Laval, in partnership with the National Research Council Canada (NRC), the National Institute for Scientific Research (NISC) and four mining companies (Agnico Eagle Mines, Canadian Malartic, Hecla Québec and Iamgold) have launched the Laser Induced Breakdown Spectroscopy (LIBS) project for in-situ real-time mining sample analysis. Its main purpose is to compensate for delayed laboratory results which slow down mining activities. This article aims to minimize the amount of sampling points realized on a sample to be deemed representative of the latter. For that, five sampling patterns are proposed. Statistical analysis of the LIBS data were performed by variation of pattern steps. Results of this statistical analysis show that patterns 5 and 1 are those that reduce the number of points of the sample, while remaining representative. Nevertheless, in terms of the type of material, pattern 5 and step 9 are better for core samples, while, pattern 1 and step 8 are better for rock sampling.

1 Introduction

Among the 26 currently active metal mines in the province of Québec, 18 are gold producing. This industry produces around C$1.8 billion of gold annually (Marshall 2015). In every one of these locations, numerous samples of rocks were collected and analyzed daily in laboratories in order to determine the gold content. However, laboratory results are only available within 48 hours of sampling, causing delays in mining activities. In an attempt to solve this issue, LIBS technology was introduced (Noll 2012). The aim of this study is to define the minimum number of LIBS points that needs to be sampled on surface in order to obtain a reliable and accurate measurement of gold content. The main objective is to provide a sampling strategy to be applied in gold mines. For this, a descriptive statistical analysis was applied to the LIBS data obtained on various surface localities. Prior to presenting the results of the statistical analysis, the applicability of LIBS in gold mining will be discussed, followed by the geology where the samples analyzed are collected, and the principle governing LIBS technology. It will be followed by the adopted statistical analysis method, the results obtained, along with discussion and conclusion.

2 Applicability of LIBS in the gold mining industry

Following several industry internships during the summer of 2016, the partnered mines helped define the application scope of LIBS. First, it was realized that LIBS is more important during the production rather than the exploration period. During the production period, determining gold content in a short delay is crucial in making quick decisions regarding extraction and round advancement. In the exploration period, decision making do not need to be instantaneous neither does slow decision making have a real influence on the work progress. Waiting time for laboratory results is not a major issue since it does not lead to slowing down mining activities nor it incurs economics losses.

Second, it was noted the applicability of LIBS at different production stage due to the observations and needs noticed. During the geological surveys, geologists may use LIBS to quickly analyze a scooptram bucket and determine whether it is filled with ore or waste. This seeks to reduce the setting aside of muck due to uncertain classification by the geologist or the miner. It should also reduce operating costs since muck will not be moved twice. However, when the broken rock is already stored, a quickly obtained gold content will allow for immediate decision making in the absence of laboratory results. On definition drill core, it could accelerate the calculation of the gold grade of a mineralized zone. In development areas, it would help decide whether or not to continue the excavation of a mining face. In open pit mines, LIBS would allow for in situ analysis of drilling chips and rocky flanks. This in order to determine whether or not
the drill hole or rock face is mineralized.

3 Geology of deposits

For this project, a partnership was developed with four mining companies which operate six mines (Canadian Malartic, Casa Berardi, Goldex, Lapa, LaRonde Penna and Westwood). These deposits are located in the Abitibi greenstone belt of northwestern Québec (Fig. 1) in the Superior Province of the Canadian Shield (Goutier et al. 2010). The Abitibi greenstone belt is constituted of the assemblage of volcano and sedimentary rocks of mafic to felsic composition, and is crosscut by synvolcanic to post-tectonic intrusions (Goutier et al. 2010). These deposits contain various types of mineralization. Lapa (Simard et al. 2013), Goldex (Genest et al. 2012) and Casa Berardi (Pilote et al. 1990) are vein type deposits, whereas Canadian Malartic is a stockwork-disseminated style deposit that is partly hosted in intrusions porphyry deposit (De Souza et al. 2015) and Laronde is an auriferous volcanogenic massive sulphide (VMS) (Mercier-Langevin et al. 2007). The Westwood deposit (Yergeau et al. 2015), on the other hand, contains auriferous VMS lenses and synvolcanic intrusion-related veins. In light of such diversity, the project results may be representative of most gold deposits present in the province of Québec.

4 LIBS principle

LIBS measuring consists to obtain in real time and in situ the gold grade content. This requires several readings on the same surface for good accuracy. A laser comes in contact with a sample and creates a 600-µm-diameter spot of plasma made of the excited atoms of all chemical elements present that are in plasma. When the atoms deactivate, they emit a radiation which is absorbed by a spectrometer and converted in a spectrum (El Haddad 2013). As there is a known wavelength for every element in the periodic table, the spectrum will help determine which elements are present in the plasma. The selected wavelength for gold is 267.59 nm. Rifai et al. (in press) present all the information on the method for selecting this wavelength and on the field experience of LIBS.

5 Methodology

LIBS data were obtained in the form of a matrix of variable size \( m \times n \), where \( m \) represents the number of rows and \( n \) the number of columns. Each value in the matrix represents the gold content obtained for each measured spot with the LIBS. Mapping of a core sample analyzed with the LIBS technology is presented in figure 2. For this purpose, several patterns have been developed so that the sampled points are perpendicular to the stratification of the samples and/or to the lithology present in the sample. This explains why a mineralized lithology cannot be analyzed.

The proposed patterns are presented in figure 3. Loop pattern can be divided into two sub patterns: row loop and columns loop. In the line loop, entire lines are deleted to evaluate the influence of each line and also to determine the minimum number of lines to have reliable results. Pattern 1 consists of selecting the diagonal points of the data matrix. Pattern 2 is in an inverted z shape. It is formed of diagonal points added to the first and last rows of the matrix. Pattern 3 is simply the inverse of pattern 2. Pattern 4 consists of selecting the points in the form similar of 8 mathematic. Thus, the first and last rows are...
selected to which the matrix diagonal and the inverse of the diagonal are associated. Pattern 5 represents the anti-diagonal of the matrix. Pattern 6, in the form of an x, is a combination of patterns 1 and 5. The last pattern is a checkerboard.

After selecting the points in each pattern, the number of points is minimized by applying steps between 2 and 10. This consists in selecting the points present in a pattern while varying the step between the selected points. For instance, in a 50 × 50 matrix (2500 points), should pattern 1 be applied, or the points on diagonal are selected, analysis would be performed on selected 50 points. Therefore, application of steps equal to 2 consists of selecting one out of two points, thus 25 points remain. On step 3, one point out of three of the 50 points of pattern 1, which makes it possible to obtain 17 points. This has been done until step 10 where only 5 points have been selected. In order to compare the different results, the statistical metrics used are mean, median and the standard deviation.

Descriptive statistic were performed on every step in every pattern. This allows to obtain gold content estimation. One of our objectives is to obtain representative results on the sample. So it was essential to ensure a high level of confidence in the obtained results according to the number of points selected. The confidence interval (CI) was calculated by using the method of large sample and modified Cox method (Olsson 2005). In this article, the CI used is 95%, and it was calculated from LIBS results. Nevertheless, when LIBS results have a percent difference higher than ± 20% with regard to laboratory results, we find the corresponding value of gold content from the margin of error between results rather than the CI.

Figure 3. Proposed patterns - Each small blue square represents the gold grade at this points. The yellow squares represent the selected points which constitute the pattern.

6 Results
Table 1 presents the gold content of samples (ECH) obtained by LIBS and laboratory, the difference between LIBS and laboratory results, the allowed margin of error in gold content (20% laboratory value), the number of points on each sample (n), the pattern which gives the best gold content estimation (Pattern), the number of points used by those patterns (nPattern) and the estimated gold content (µPattern), the lithology, mineralization, material, the deposit and the CI at 95%. In column 20% lab, the red values represent the samples for which LIBS results have a value higher than sensibility and for which it is out of the CI. Green colored cells indicate which samples have higher values than the allowed margin of error albeit still lying inside the CI.

The first results obtained allows to exclude the median among the elements to be used because it is very far from the value of the laboratory due to a large population of points having the value 0. This is why in Table 1 the median is not present and µPattern is the gold content average on the selected points.

The selected pattern and step are those which have the minimum number of points and are still representative of each sample. For 75% of the samples, patterns 1 and 5 are the ones with the gold content estimation within the CI while having the minimal number of points. Although, there is not a single step which comes out, it should be noted that the most successful results are obtained from steps which are greater than 6. In comparing the pattern with the type of mineralization, it was noted that for sulfide, pattern 5 seems to have a better fit. As for quartz veins, no specific pattern comes out. In terms of material type, it was noted that pattern 1 matches well for pieces of rock and pattern 5 is better suited for core samples. As for the steps, although no one step came out of the study for all the samples. However, it was realized that step 8 is the best option for the pieces of rock, while step 9 is the best option for the core samples. As for the mineralization, no step comes out of the lot even though steps 8 and 9 are ideal approaches for quartz veins. Since there were not enough samples in each deposit, comparisons between deposits were not made. Also, LIBS results from pulps and tailings were set aside, as the objective is not to minimize the number of points.
Table 1. Description of samples analyzed by LIBS and statistical analysis results

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<th>ECH</th>
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<th>Deposit</th>
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7 Conclusion

These results tend to show that the application of LIBS in the mining industry for real-time analysis may be possible. However, in order to validate this trend, it is essential to analyze a wide range of mine samples with the LIBS. So, the next step of this study is to collect LIBS data on many samples from different deposits, mineralization and lithology, and reproduce the same type of statistical analyses. Another study using classification or discriminant analysis techniques could allow us to identify correlation between the pattern, step and deposit, mineralization and lithology, and ultimately assign optimal patterns and steps to every sampled units.

Acknowledgements

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Hydrothermal alteration of a shallow-dipping epithermal Au-Ag-Pb-Zn-Cu deposit in Banská Hodruša, Slovakia

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Abstract. The Neogene Banská Hodruša epithermal deposit has a specific geometry of alteration assemblages in response to subhorizontal orientation of the vein system. The hosting low-angle normal shear zone is related to underground cauldron subsidence and/or exhumation of a subvolcanic granodiorite pluton, possibly representing base of a sector collapse of the hosting stratovolcano. Five major alteration assemblages were determined relative to proximity to ore and ore-controlling structures: silicification at the base of the deposit, strong adularia alteration near the main veins, weak adularia alteration in the hanging wall of silicified andesite and close to minor veins, argillisation along roof of the shear zone, and distal propylitic alteration. Early barren silicified breccia was related to a vertically-oriented extension and hydraulic fracturing. Main ore mineralisation is related to focusing of fluids in areas where both low-angle master planes of the shear zone were relatively close together, i.e. where the argillised roof is relatively close to silicified andesite in the base of the shear zone. Ore veins also occur in the argillised roof of the shear zone, controlled by the extensional tectonic regime.

1 Introduction

The intermediate-sulphidation precious and base metal deposit in Banská Hodruša at the Rozália mine has several unique characteristics. The major distinct feature is a complex multi-stage vein system with a subhorizontal orientation, which is related to an underground cauldron subsidence and/or exhumation of a subvolcanic granodiorite pluton, associated with the development of a low-angle normal shear zone, possibly corresponding to the base of a sector collapse in the host stratovolcano. The unusual structural setting of the deposit resulted in a specific alteration pattern, which is presented in this study.

2 Geological setting and characteristics of the deposit

The deposit is hosted by the central zone of a large Middle Miocene andesite stratovolcano (Štiavnica stratovolcano), located in the Central Slovakia Volcanic Field on the inner side of the Carpathian arc. The stratovolcano includes an extensive caldera (some 20 km in diameter), a late stage resurgent horst in the caldera centre and an extensive pre-to syn-caldera subvolcanic intrusive complex emplaced by underground cauldron subsidence mechanism (Konečný et al. 1995). The gold mineralization occurs between the 12\textsuperscript{th} and 18\textsuperscript{th} levels of the Rozália mine (400–650 m below the surface), hosted by pre-caldera andesite, near to the flat roof of a pre-mineralisation subvolcanic granodiorite pluton. The veins are dismembered by a younger set of quartz-diorite porphyry sills and later steeply-dipping mineralized faults of the resurgent horst. The ore deposit consists of two parts, separated by a thick sill of quartz-diorite porphyry, which transfers from the footwall of the vein system in the east to its hanging wall in the west. The western part of the deposit was mined out during the years of 1992–2004. Currently, the eastern part is being mined with the annual production of about ∼30–45 kt of ore with 14 g/t Au, 17 g/t Ag, 0.6% Zn, 0.45% Pb, and 0.15% Cu. This contribution relates to the eastern part of the deposit.

The ore mineralisation originated during several stages (Maťo et al. 1996; Kubač et al. 2016). The oldest stage is related to vertically-oriented extension and hydraulic fracturing along subhorizontal structures above the granodiorite pluton and corresponds to the origin of barren silicified and brecciated andesite (Svetozár vein system) located at the base of the deposit. The second stage is probably related to the origin of the low-angle normal shear zone, where the movement of the downthrown block occurred initially towards south, possibly due to a sector collapse in the volcano. This stage includes the major vein system of the WNW–ESE direction, steeply dipping to S (Karolina vein system), represented by a quartz-carbonate gangue, rich in Mn-minerals (rhodonite, rhodochrosite), sulphides (spalerite, galena, chalcopyrite, pyrite), gold and rare Ag-Au tellurides. The third stage of mineralisation occurs predominantly in tension cracks inside the shear zone with intermediate dip to SE (Krištof vein system). The origin of this stage well corresponds to
the displacement on the low-angle normal shear zone, but with a changed direction of movement of the downthrown block towards SE. The vein system typically contains thin quartz veinlets, containing disseminated gold, while carbonates (calcite) and sulphides are rare. Further evolution of the shear zone is associated with renewed periods of vertical extension, resulting in low-angle drop shear faults (R1 and P types) hosting late shallow-dipping veins (Agnesa vein system). This vein system is located exclusively in the roof of the deposit and it is represented by sulphide-rich veins (sphalerite, galena, chalcopyrite, pyrite) with gold, Au-Ag tellurides and variable amount of quartz, but nearly no carbonates. Late stage minor barren quartz and carbonate veins invade eventually the oldest of the post-mineralization quartz-diorite porphyry sills. Final, much younger hydrothermal activity at the deposit is related to the resurgent horst uplift in the centre of the caldera, resulting in a steeply-dipping system of base metal veins (Rozália, Amália, Bakali), cutting and displacing the earlier veins, but devoid of precious metals.

3 Methodology

Information about the mineral composition of alteration was obtained from quantitative XRD analyses of altered andesite and clay fractions (< 2 μm). Information about the relationship and chemistry of alteration minerals were provided by microscopic and microanalytical studies (EDS, WDS analyses) of polished sections. New digital geological maps of 14th, 15th and 17th level, as well as 5 geological sections of N–S and NW–SE direction were used for visualization of the alteration patterns.

4 Distribution of the alteration assemblages

Based on the obtained mineral composition of altered rocks, it was possible to define schematically 5 major types of alteration that occur within the deposit and its vicinity: 1) Silicification with predominant quartz; 2) Strong adularia alteration with substantial presence of adularia and illite; 3) Weak adularia alteration with minor presence of adularia and illite accompanied by chlorite and plagioclase, usually affected by albitionation; 4) Strong argillisation with predominant presence of illite and quartz and with increased concentration of pyrite; 5) Propylitisation equally represented by chlorite, illite, quartz, with plagioclase still present, but adularia is absent.

Silicification usually forms a horizon of barren massive or brecciated silicified andesite (Svetozár vein system) that occur at the base of the deposit in the hanging wall of the granodiorite pluton (in W part of the deposit) or in the hanging wall of the large quartz-diorite porphyry sill (in E part of the deposit). Silicification is of variable intensity, while in the less silicified andesite quartz is accompanied mostly by adularia. Less intensive silicification also occurs in the vicinity of other vein systems, especially in the hanging wall of the Agnesa vein system where abundant quartz accompanies strong argillisation.

Strong adularia alteration is the most intensive type of alteration that occurs as a continuous zone in the hanging wall of silicified andesite unit in the thickness of about 20–30 m. This type of alteration is also typical for the vein system Karolina, for the foot wall of the Agnesa vein system and for post-mineralisation horst-related veins.

Weak adularia alteration occurs as a continuous zone that separates strongly adularised rocks in the hanging wall of silicified andesite from the argillised roof of the deposit (in case the Karolina vein system is absent). This type of alteration was determined just at the 15th and 17th levels of the mine, with a characteristic trend of widening of this zone in direction towards the deeper and eastern parts of the deposit.

In SW part of the mine this type of alteration hosts the Krištof vein system.

Argillisation in the roof of the deposit forms a continuous horizon, probably following the upper plane of the shear zone. This alteration zone reaches 10–20 m and it is frequently accompanied by brecciation. At several places it is accompanied by the Agnesa vein system, while argillisation dominates in the hanging wall of these veins. This alteration zone was determined on all levels of the mine, but in direction to depth and to the east of the deposit the distance of this zone from silicified andesite is increasing. Strong argillisation also occurs close to other types of veins if the host rock is strongly brecciated. The largest zone of argillised breccia is located in the hanging wall of major post-mineralisation veins related to the horst uplift. Argillisation affects here both andesite and the quartz-diorite porphyry and illite is typically accompanied by minor kaolinite.

Propylitisation is a regional alteration of weak intensity, located in the hanging wall of the deposit above the argillisation zone, i.e. outside of major vein structures (except of post-mineralisation veins related to the horst uplift). The transition from argillisation towards propylisation is usually gradual with decreasing intensity of alteration with increasing distance from the deposit.

5 Relative timing of the alteration and mineral chemistry

The oldest type of alteration at the deposit is strong silicification, corresponding to the Svetozár vein system. Hydrothermal quartz originated at the expense of andesite, which is indicated by rarely preserved pseudomorphs of quartz after plagioclase phenocrysts.

Plagioclases are overprinted by several generations of alteration, including earlier albite alteration and later more common adularia alteration, while both alteration minerals are overprinted by illite, sometimes also by calcite. Albitionisation can be related to the regional propylitisation and/or to the hydrothermal system that followed the emplacement of the granodiorite pluton (Kodéra et al. 2004). Albitionisation was mostly observed in andesite affected by the weak adularia alteration, including the rock hosting the Krištof vein system. Albite contains from 10.2 to 11.5 wt.% Na₂O. Adularia alteration and relatively
younger illite alteration are alteration patterns that probably originated episodically during all evolutionary stages of the deposit, i.e. from the origin of the Svetozár vein system up to the origin of veins related to the horst uplift. Chemical composition of adularia is of little variability, typically with ~0.4 wt.% of Na₂O and 0.01–0.7 wt.% BaO, but rarely in thin zones (in adularia) it reaches up to 9.2 wt.% BaO. Strongest argillisation apparently corresponds to the stage when the hydrothermal fluids entered the shear zone structures, however, it is likely that some of the illite has already originated during the formation of silicified andesite (in their hanging wall), perhaps later affecting preferential location of shear zone structures. Based on XRD of clay fraction and microprobe analyses of illite in thin sections no significant smectite component is present in alteration.

Mafic minerals (mostly biotite) are typically replaced by chlorite, however, chloritisation has probably also occurred during several stages. Chlorite is most abundant in relatively less altered rocks, including regional propylitisation. Chemically chlorites belong to the clinochlore – chamosite series, close to the clinochlore end-member. Their Mg/Fe ratio is variable and it does not correlate with the type of veins in their vicinity, neither with the distance to the veins. Interestingly, chlorite in rocks hosting Karolina and Krštof vein systems have increased MnO content (up to 5.4 wt.% and 4.9 wt.%, respectively), which corresponds to the presence of Mn-rich minerals in these veins, including Mn-rich chlorite (up to 10.2 wt.% MnO). Chlorite in rocks hosting other vein systems or no vein systems have significantly lower MnO content (Svetozár and Agnesa vein types up to 2.5 wt.%, elsewhere up to 1.6 wt.%).

Carbonates crystallised mainly during younger stages and they are more common in marginal parts of the deposit. They are mostly represented by calcite that locally overprints plagioclase, including those replaced by earlier albite or adularia. Complex Fe-carbonates are also present; however, they are rarer, especially located in the hanging wall of the horst uplift related veins, associated with kaolinite and/or calcite. WDS analyses showed that calcite often contains admixture of MnO (from 0.15 to 1.9 wt.%). Complex Fe-carbonates are rich in FeO (29.6 to 42.8 wt.%), and also contain MgO (5.5 to 12.0 wt.%), MnO (2.8 to 9.7 wt.%), and CaO (1.0 to 9.2 wt.%).

Increased pyrite content was determined just in the roof of the deposit (including the Agnesa vein system) and in the brecciated hanging wall of the post-mineralisation veins related to the horst uplift. Older generation of pyrite is coarse-grained, often forming short veinlets. Sometimes it encloses unaltered basic plagioclase and epidote. Its origin can be attributed to the hydrothermal system that followed the emplacement of the granodiorite pluton. Pyrite contains just trace amounts of admixtures, except for rare samples of euhedral pyrite with resorbed fragments of As-rich pyrite (up to 4.2 wt.%).

Epidote takes part in replacement of plagioclase and mafic minerals, but it is also present in groundmass and in veinlets. Epidote is later than chlorite and its origin is probably related to regional propylitic alteration and/or to the hydrothermal system associated with emplacement of the granodiorite pluton. WDS analyses showed that the epidote minerals have an intermediate position among epidote and clinozoisite with MnO content up to 1.0 wt.%.

Most alteration patterns are accompanied by several generations of veinlets, including oldest pyrite veinlets, cut by frequent quartz, quartz-calcite and youngest adularia-calcite and illite-calcite veinlets.

6 Origin of the vein system and alteration

The widespread adularia alteration and illite alteration at the deposit are characteristic alteration minerals for intermediate- and low sulphidation epithermal vein systems (e.g., Hedenquist et al. 2000). However, their distribution at the deposit is quite unusual with a subhorizontal orientation, corresponding to subhorizontal orientation of the entire deposit along the low-angle normal shear zone (Fig. 1). Consequently, alteration patterns and their mineralogy do not indicate significant changes in temperature, which is consistent with expected relatively small thermal gradient along this palaeohydrothermal system. For example, in argillic alteration nearly no smectite component was found. This indicates that alteration temperatures were always higher than 200–240°C, which is the lower limit of crystallisation of illite and adularia, respectively. These minimum temperatures correspond to fluid inclusion microthermometry data from both parts of the deposit, suggesting the origin of veins in the temperature range from 250 to 310°C from boiling fluids, which caused precipitation of gold and adularia at high fluid/rock ratios (Koděra et al. 2005; Kubač et al. 2016). Predominantly subhorizontal flow of fluids and their extensive boiling can explain the location of argillites in a continuous horizon in the roof of the deposit, which most likely represents a space where condensation of escaping vapour has occurred. The resulting mildly acidic fluids could have migrated along the upper fault plane of the shear zone and alter the vicinity of the fault plane even in a distal position in relationship to the mineralised veins.

Earlier stable isotope research showed that parental fluids were of mixed magmatic and meteoric origin with the source of magmatic components in a shallow, differentiated magma chamber at the base of the volcano (Koděra et al. 2005). Whole-rock geochemical analyses of veins (unpublished data) show changing composition of the magmatic component in the fluids as indicated by decreasing Mn content in vein filling from earlier to later vein systems, also accompanied by the increase in Bi, Sn and Rb-Sr ratio. This change in composition of fluids is probably related to the evolution of the entire magma chamber during the origin of the deposit. The trend of decreasing abundance of Mn in direction to later types of
veins was also determined in this study in the composition of chlorite from the accompanying wall-rock alteration.

Figure 1. Reconstruction of alteration patterns in andesite in the eastern part of the Banská Hodruša deposit prior to the emplacement of sills of quartz-diorite porphyry and post-mineralisation veins related to the horst uplift. a Structural model of the shear zone hosting the mineralised veins; b Schematic 3D visualization of distribution of alteration patterns, based on distribution of alteration in geological maps of 14th, 15th and 17th levels of the mine, as well as in 5 geological sections of N-S and NW-SE direction; c Idealized structural and genetic model showing the relationship among individual vein systems and zonal arrangement of alterations in the shear zone.

According to the distribution of alteration patterns in maps and cross sections, schematically summarised in Figure 1, it is possible to interpret that the main migration of fluids occurred along flat faults of the shear zone, in direction from S to N and later from SE to NW, in which also the planes of the shear zone tend to ascend. Vein systems Karolina and Krištof can be related to the focusing of fluids in the areas where main planes of the shear zone were relatively close together. In these areas, opening of dilatational structures enabled an active suction of fluids and their boiling due to the decreased pressure in these structures (Fig. 1c). In places, where the upper plane of the shear zone was significantly curved and/or affected by the vertically-oriented extension of the continuing underground cauldron subsidence, opening of low-angle structures has probably resulted in the origin of the Agnesa vein system. Later on, master planes of the shear zone were preferentially used for emplacement of post-mineralization quartz-diorite porphyry sills.

7 Conclusions

The presented genetic model of alteration has a potential to be used in effective prognosis of ore mineralisation in the broad vicinity of the studied deposit, but it can be also applied to other similar shallow-dipping intermediate to low sulphidation epithermal systems worldwide. In respect to the model, we can perhaps expect to find extensions to the veins systems in analogous structural-geological positions. Steep ore veins related to dilatational structures of the shear zone (Karolina and Krištof types) can be expected in areas affected by adularia alteration especially in places, where both master planes of the shear zone are relatively close together, i.e. where the subhorizontal zone of argillites is relatively close to the subhorizontal zone of silicified andesite (Svetozár vein system). However, the subhorizontal veins located in the argillised upper plane of the shear zone (Agnesa type) can be also found in areas where both major planes of the shear zone are more remote. However, in future exploration it is also necessary to correctly reconstruct the original spatial arrangement of alterations, i.e. consider the effect of displacement by younger sills of quartz-diorite porphyry and post-mineralisation faults related to the horst uplift.

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Controls on gold distribution at the Horne 5 VMS deposit, Abitibi greenstone belt, Québec

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Abstract. The gold-bearing Horne 5 VMS deposit is located in the Blake River Group of the Abitibi greenstone belt. Hosted within steeply-dipping, north-facing felsic volcaniclastic units, the deposit is fault-bounded and within the boundaries of the Horne block. Mineralization consists of a series of massive to semi-massive sulfide lenses alternating with disseminated and stringer sulfides in coarse felsic volcaniclastic units. The latter often contain massive sulfide clasts. Results from this study show: 1) alteration in the mineralized zones is of moderate intensity and consists of pervasive sericite±quartz; 2) a well-developed foliation is present throughout most of the mineralized zone and is particularly prominent in sericitized zones; 3) sphalerite is associated with massive to disseminated pyrite, whereas chalcopyrite is locally remobilized in secondary sites within the mineralized intervals; 4) gold distribution is relatively variable, but higher gold contents are generally present in the massive to semi-massive sulfide intervals; and 5) less permeable strata within the host volcaniclastic units most likely influenced the distribution of the mineralization interpreted to have formed mostly by sub-seafloor replacement. The Horne 5 deposit represents an opportunity to better understand ore-forming processes in large Archean synvolcanic gold systems.

1 Introduction

The world-class Horne deposit is an Archean gold-rich volcanogenic massive sulfide (VMS) deposit that was exploited by Noranda Mines Ltd. from 1927 to 1976. A total of 53.7 Mt of ore at 6.1 g/t Au (327.6 t, or 11.6 Moz Au), 2.22% Cu and 13.0 g/t Ag was extracted and largely mined from the giant Upper H and Lower H orebodies (Kerr and Mason 1990).

The Horne 5 deposit (often termed “No. 5 zone”), which was only locally mined, was extensively drilled by Noranda Mines Ltd. It is located downdip, but stratigraphically above, the H orebodies (Kerr and Mason 1990). Ongoing drilling by Falco Resources Ltd. has allowed the company to define a new resource for the Horne 5 deposit (including measured, indicated and inferred resources) that amounts to 113.4 Mt at 1.54 g/t Au (174.9 t, or 6.2 Moz Au).

Gold mineralization and grades at the Horne 5 deposit, despite being unusually high for a VMS (Mercier-Langevin et al. 2011a), were never thoroughly investigated. This study will contribute to ongoing research regarding ancient gold-rich VMS deposits and the controls on gold enrichment in synvolcanic systems (e.g., Dubé et al. 2007; Mercier-Langevin et al. 2011a). Specifically, this project aims to determine the precise relationships between gold, sulfides, base metals, host rocks, deformation and metamorphism, in establishing controls on gold distribution at various scales. In doing so, we aim to define the relative timing of gold mineralization at various scales within the Horne 5 deposit.

2 Geological setting

The Horne 5 deposit is located in the 2704 to 2695 Ma Blake River Group (BRG; McNicoll et al. 2014) within the Abitibi greenstone belt, Québec, Canada (Fig. 1). The BRG consists predominantly of submarine mafic to felsic volcanic rocks intruded by numerous syn- to post-volcanic plutons, dikes and sills (McNicoll et al. 2014, and references therein). Known for its significant endowment in VMS and gold-rich VMS deposits, the BRG hosts both the Noranda and Doyon-Bousquet-LaRonde mining camps, and includes 6 of the 11 largest gold-rich VMS deposits in the world. These and other gold-bearing VMS deposits account for 13% of the...
gold production in the Abitibi greenstone belt (Dubre et al. 2007; Mercier-Langevin et al. 2014).

3 Geology of the Horne 5 deposit

The deposit is contained in a tilted, north-facing sequence of felsic to mafic lava flows with associated felsic volcaniclastic units and mafic intrusions within the defined tectono-stratigraphic Horne block (Gibson et al. 2000). The Horne block is bounded by the Horne Creek fault to the north and the Andesite fault to the south (Fig. 1). High-precision U-Pb dating of a coherent rhyolite (Fig. 1, see U-Pb date location) indicates that the rocks in the block are amongst the oldest in the BRG and pre-date the Noranda “central mine sequence” and its archetypal Cu-Zn VMS deposits by approximately four million years (McNicoll et al. 2014). The gold-bearing intervals of the Horne 5 deposit are hosted within felsic lapilli tuff, breccia and minor finely bedded tuff facies and intruded by a swarm of sterile mafic dikes (Sinclair 1970). These volcaniclastic rocks are interpreted as debris flow deposits that accumulated in a fault-bounded graben on the side of a felsic edifice (Kerr and Mason 1990). Mineralized intervals consist predominantly of pyrite with lesser sphalerite, chalcopyrite, and magnetite forming tabular massive to semi-massive sulfide lenses and intercalated with large zones of disseminated and stringer sulfides. Pyrrhotite and galena are present as rare accessory phases (Sinclair 1970).

4 Characteristics of the mineralized zones

The host rocks to the Horne 5 deposit consist of thick, relatively coarse-grained felsic volcaniclastic units that are primarily altered to sericite±quartz (Fig. 2a). Felsic fragments are composed of fine recrystallized quartz and ≤10% sericite, while the matrix consists of sericite, disseminated sulfides and associated trace chlorite, and quartz crystals. The hydrothermal alteration is pervasive and generally of moderate intensity throughout the Horne 5 deposit.

The mineralized envelope varies from 50 to 150 meters in thickness. Two principal types of mineralization are present: 1) relatively compact intervals of massive to semi-massive sulfides (generally ≤10 m thick), and 2) more extensive zones of disseminated to stringer sulfides occurring preferentially in the matrix of the felsic fragmental units. Massive sulfide fragments are present in the felsic breccia facies at several stratigraphic levels (Fig. 2b). Stringer mineralization is more intense near massive sulfide zones, and often occurs in both the hanging wall and footwall where it is associated with very intense hydrothermal alteration (Fig. 2c).

Massive to semi-massive sulfide intervals are composed of a fine to granoblastic pyritic groundmass with variable amounts of interstitial sphalerite (generally ≤15%, locally up to 30%), quartz, sericite, and chlorite. Up to 5% remobilized chalcopyrite is also present along fractures and grain boundaries (Fig. 2d), as well as very rare pyrrhotite inclusions in pyrite. Sphalerite occurs as finely disseminated grains in the matrix of the volcaniclastic rocks and as disseminations and fine foliation-parallel bands in massive sulfide bodies (Fig. 2e). Fine to coarse-grained magnetite appears in the top section of the Horne 5 deposit, and at the bottom of the stratigraphy in a few diamond drill holes (DDH). It is often found in association with chalcopyrite and occasional iron-rich carbonate (Fig. 2f). Several characteristics and textures indicate that emplacement of massive sulfides occurred mostly as sub-seafloor replacement of permeable host rocks. This includes the presence of remnant felsic fragments in massive sulfide bodies; transitional contacts from semi-massive to massive sulfides; and hydrothermal dissolution of felsic fragment margins and replacement by pyrite (Fig. 2g). However, the presence of massive sulfide clasts suggests that some massive sulfide lenses were emplaced at the seafloor or near-seafloor interface and were subsequently eroded and incorporated into debris flows that formed the volcaniclastic units. A combination of both processes contributed to the formation of the deposit.
Figure 2. 

a. Felsic lapilli tuff hosting mineralization in the No. 5 zone. The matrix is dominated by a combination of sericite and pyrite. 
b. Massive sulfide fragments composed of pyrite and clusters of sphalerite. Fragments are flattened into the main foliation. 
c. Stringer and disseminated pyrite zone, located stratigraphically below a massive sulfide body. 
d. Pyrite, disseminated sphalerite and remobilized chalcopyrite in a felsic lapilli tuff. 
e. Fine bands of sphalerite associated with quartz within a massive pyrite interval. 
f. Coarse-grained magnetite, pyrite, chalcopyrite and weathered iron-rich carbonate in the top section of the No. 5 zone. 
g. Replacement of margins of felsic lapilli tuff fragments with fine-grained pyrite. 
h. Well-developed foliation in the mineralized zone. 

Abbreviations: Cb = carbonate, Cp = chalcopyrite, Fol = foliation, LT = lapilli tuff, Mt = magnetite, Py = pyrite, Qtz = quartz, Ser = sericite, Sp = sphalerite, Str = stringer.
Zones of increased sulfide abundance often coincide with coarser-grained volcanioclastic facies (tuff breccia to breccia). Therefore, distribution of the mineralization is likely influenced in part by the permeability of the host volcanic rocks. Controls on distribution include changes from coarse-grained massive beds to overlying fine-grained graded beds and the presence of coherent felsic units directly above massive sulfide bodies. Both act as relatively impermeable cap rocks to ascending fluids, focusing them along specific horizons.

Effects of deformation and metamorphism are noticeable throughout the mineralized zones and include recrystallized alteration and sulfide mineral assemblages, locally remobilized chalcopyrite, a well-developed, roughly E-W striking, sub-vertical foliation with a prominence in sericite-altered zones (Fig. 2h), and flattened volcanioclastic and massive sulfide fragments (Fig. 2b).

5 Gold distribution

Gold grades within the Horne 5 deposit are typically less than 3 g/t and only rarely exceed 10 g/t, as indicated by recent and historical assay data. Gold distribution is relatively variable but there exists a general correlation with pyrite abundance and base metals. Massive to semi-massive sulfide intervals, and to some extent stringer zones, contain the highest gold values (≥1-2 g/t). In four of the five studied DDHs, gold values decrease down-hole in the mineralized zones, whereas Ag, Cu, and Zn values do not change significantly. It remains unclear if this relationship is indicative of a hydrothermal system evolving up-stratigraphy and initially favouring base metal transport over gold precipitation or if it is associated with deformation-induced gold remobilization or “zone refining”.

6 Conclusions and future work

The gold-bearing Horne 5 deposit contains massive to semimassive sulfide lenses and extensive disseminated to stringer mineralization. Gold values are directly associated with base metals and with pyrite occurrence and abundance, suggesting they are genetically linked.

A comparison of the mineralization within the Horne deposit reveals important differences that distinguish the Horne 5 deposit from the Upper and Lower H zones, such as: 1) mineralization within the Horne 5 deposit and the average low gold grades differ significantly from the larger, more gold-rich (6.1 g/t) massive sulfide bodies of the H zones; 2) the pyrite-rich Horne 5 deposit contains only minor chalcopyrite and very rare pyrrhotite, which is in contrast with the pyrite-pyrrhotite-chalcopyrite assemblage of the H zones (Price 1934); and 3) the mostly submicroscopic (“invisible”) gold occurrence in the Horne 5 deposit is unlike the visible to microscopic native gold and Au-tellurides in the Upper and Lower H massive sulfides and their associated chloride-veinlets (Price 1934).

Continuing work will focus on documenting the precise nature of the gold mineralization. This will include laser-ablation inductively-coupled plasma mass spectrometry analysis of sulfide phases, whole rock geochemical analysis of the host volcanic and intrusive rocks, 3-D modelling of metal distribution and alteration, and geochronological analysis. This work will contribute to a better understanding of large Archean synvolcanic gold systems.

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Early Permian magmatic-hydrothermal gold mineral system in Cape York, North Queensland, Australia

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Abstract. This paper presents results of new geochemistry and geochronology for widespread hydrothermal gold mineralisation in Cape York (Australia). Mineralisation commonly occurs in steep quartz veins and breccias, often cutting steep rhyolitic dykes. Gold mostly occurs within massive fine-grained quartz and open-space-growth comb quartz, both with minor sulfides (most commonly pyrite and arsenopyrite, with locally significant galena and sphalerite). Mineralisation is associated with weak sericite alteration. Gold deposits across the entire region have a generally consistent geochemical signature, with strongly anomalous Au-As-Ag-Sb (and locally Pb, Zn), sometimes with elevated Te and Bi. The gold to silver ratio is highly variable, with a common average ratio close to 1:1.

New U-Pb zircon geochronology indicates that mineralised felsic dykes were emplaced in a short magmatic episode in the early Permian (~280-285 Ma), broadly synchronously with the Permian granites and felsic volcanics north of Coen. Ar-Ar geochronology of alteration and vein sericite further suggests that gold mineralisation across the region was emplaced in a single hydrothermal metallogenic event in the early Permian, post-dating felsic magmatism by up to several million years. This event correlates with an episode of spatially extensive magmatism across north-east Queensland, with associated Sn, W, epithermal and intrusion-related Au deposits.

1 Introduction

Gold-quartz vein deposits are widespread across the Cape York Peninsula in north Queensland, Australia. Before the current study, their timing and genesis were poorly constrained. Most significant gold deposits were commonly described as shear-hosted and their genesis was assumed to be related to the emplacement of either Siluro-Devonian batholiths or minor Carboniferous to Permian intrusions (Denaro and Ewers 1995; Bain and Draper 1997).

This study investigated main gold deposits from all significant gold camps in the Cape York region, focusing on multi-element geochemistry and geochronology of gold mineralisation and geochronology of felsic dykes commonly hosting auriferous quartz veins.

2 Geological setting

The Cape York Peninsula represents the north-eastern part of the Proterozoic North Australian Craton, extensively intruded by Siluro-Devonian granites of the Cape York Peninsula Batholith and subsequently affected by more localised Carboniferous and early Permian magmatism (Jell 2013). Proterozoic North Australian Craton over most of the peninsula is covered by the Mesozoic to Cenozoic sedimentary basins. The only area in the eastern part of Cape York where Proterozoic metamorphic and Siluro-Devonian intrusive rocks are extensively exposed at surface is traditionally defined as the Coen Inlier (Bain and Draper 1997). All but one regionally significant gold deposits known in the Cape York region (the Horn Island deposit, off the northern coast of the Cape York Peninsula) occur in this area (Fig. 1).

On the basis of contrasting geological histories, Proterozoic rocks of the Coen Inlier are subdivided into the Etheridge, Savannah and Iron Range provinces (Bain and Draper 1997; Jell 2013). The Etheridge Province in the east of the Coen Inlier is represented by high-grade (upper amphibolite to granulite facies) Paleo- to early Mesoproterozoic metamorphic rocks which experienced peak metamorphism and partial melting at ~1560 Ma. Mesoproterozoic metamorphic rocks of the Savannah Province to the west are composed of shallow marine clastic meta-sediments with minor MORB-like mafic meta-volcanics at the base of the sequence, which has the maximum total stratigraphic thickness exceeding 10 km. The metamorphic grades increase from sub-greenschist in the west to upper amphibolite in the east, with the regional peak metamorphism related to the emplacement of Siluro-Devonian granites, which intruded the boundary between the Etheridge and Savannah provinces in the Coen Inlier (Fig. 1). Structural relationships between the provinces remain unclear. The Neoproterozoic to early Paleozoic Iron Range Province in the north of the Coen Inlier is interpreted as part of the Thomson Orogen, formed along the eastern margin of the North Australian Craton (Jell 2013).

Following multiple regional deformation events in the Proterozoic and early Paleozoic, major steep NW-trending mylonitic shear zones formed or were re-activated across the region after early Devonian, commonly along margins of Siluro-Devonian granites. Gold deposits in the Coen Inlier are typically located in the vicinity of the regional shear zones, along the eastern margin of the Savannah Province (Fig. 1).
3 Characteristics of gold deposits in the Coen Inlier of Cape York

3.1 General characteristics
Regionally significant gold deposits in the Cape York Peninsula cluster in several historic gold fields / camps, the largest of which, in terms of hard-rock historic production, are the Coen (~1.5 t Au and 1.5 t Ag), Ebagooloa, Yarraden, Alice River, Wenlock and Iron Range gold camps in the Coen Inlier (Fig. 1) and the Horn Island camp at the Horn Island (off the northern coast of the Cape York Peninsula). Field examinations of gold deposits and occurrences within the camps confirmed that mineralisation across the region is mostly associated with steep quartz veins and vein breccias (commonly <1 m thick and up to several hundred metres along strike). Auriferous quartz veins are hosted by Proterozoic metamorphic rocks and Devonian granites – most commonly adjacent to sheared contacts between them. In the Coen and Yarraden camps, as well as some deposits at Ebagooloa and several smaller camps, auriferous quartz veins were often observed along sides and cutting steep aphanitic to sparsely porphyritic rhyolitic dykes.

Although gold deposits are often located proximal to mylonitic shear zones, rocks hosting and adjacent to auriferous quartz veins do not display metamorphic fabrics likely to be temporally related to quartz veining. In particular, mineralised rhyolitic dykes commonly display only brittle crackle veining and retain original flow-banding.

3.2 Ore textures, mineralogy and geochemistry
Approximately 200 samples of quartz veins from the main gold camps and some individual isolated historic mines and prospects in the Cape York region were petrographically examined and analysed to investigate their ore textures, mineralogy and multi-element geochemistry. 160 of the analysed samples assayed >0.1 g/t Au, including 40 samples with >5 g/t Au. Auriferous quartz veins often indicate multiple stages of veining, which is particularly common in larger deposits, such as in the Coen and Alice River fields (Fig. 2). Gold occurs in massive fine-grained quartz and open-space-growth comb quartz, both with minor sulfides (most commonly pyrite and arsenopyrite, with locally significant galena and sphalerite). Mineralisation is associated with generally weak sericite alteration.

Gold deposits across the entire region have a generally consistent geochemical signature, with strongly anomalous Au (up to tens of ppm), As (tens to thousands ppm), Ag (up to hundreds of ppm) and Sb (tens of ppm). Horn Island and several smaller deposits are also characterised by anomalous Pb and Zn (up to several per cent). Some deposits also have elevated Te (<0.5 ppm) and Bi (commonly <1 ppm, but sometimes up to 50 ppm).

The gold to silver ratio is highly variable, with a common average ratio in larger ore fields (e.g. Coen) close to 1:1.
3.3 Geochronology of Carboniferous to Permian magmatic rocks and associated gold mineralisation

New U-Pb zircon SHRIMP geochronology (Kositcin et al. 2016; Cross et al. in prep.) indicates that felsic dykes hosting auriferous quartz veins at Coen, Ebagoola, Yarraden and Alice River were all emplaced in a single brief magmatic episode in the early Permian (~280-285 Ma), broadly synchronously with felsic volcanics (284.7 ± 1.7 Ma) and the Wolverton Adamellite (280.4 ± 1.5 Ma, Fig. 1) in the north of the region.

Rhyolitic dykes hosting gold-quartz veins are commonly affected by pervasive sericitic alteration, with fine-grained (<10-20 micron) sericite replacing plagioclase in phenocrysts and the groundmass. Rare muscovite also occurs in gold-quartz veins (inter-grown with sulphides) and in quartz-wolframite veins in the Archer River tin field. Ar-Ar geochronology of three sericite-rich samples of pervasively altered dykes, one sample of muscovite from an auriferous quartz vein at Coen and one sample of muscovite from a quartz-wolframite vein at Archer River all indicate formation at 275-280 Ma – post-dating felsic magmatism in the region (including immediate host rocks) by up to several million years. These new results provide the first reliable geochronological constraints on the age of gold mineralisation in the region.

4 Discussion

All gold deposits within the Coen Inlier of Cape York in north Queensland (Australia) share similar deposit characteristics and represent products of the same distinct early Permian hydrothermal gold mineral system. Spatial distribution of gold deposits and their main characteristics indicate the existence of various metallogenic controls which operated at a wide range of scales – from broad regional to the scale of individual deposits and orebodies.

New geochronology indicates that, at the broad regional scale, felsic magmatism and spatially and (broadly) temporally associated gold mineralisation in the Coen Inlier of Cape York is part of an extensive early Permian (285-275 Ma) magmatic-hydrothermal system, documented across the entire north-east Queensland, extending > 800 km from north to south and up to 200 km east to west (Morrison et al. 2015; Chang et al. 2016; this study). This system produced: (i) epithermal and intrusion-related gold deposits associated with volcanic and sub-volcanic magmatic complexes in the Etheridge Province (Agate Creek low-sulfidation epithermal deposit, intrusion-related gold occurrences at Gilberton) and northern Bowen Basin (Mt Carlton high-sulfidation epithermal Au-Ag deposit); (ii) tin and tungsten deposits associated with plutonic highly fractionated granites in the Hodgkinson Province (Watershed, Mt Carbine) and in Cape York (Archer River tin field).

Within the Coen Inlier, almost all regionally significant gold deposits and their clusters occur within 10-20 km to the west of the approximate boundary between the Savannah and Etheridge provinces (Fig. 1). Such spatial distribution suggests that this Proterozoic province boundary possibly acted as a metallogenic zone-scale mineralisation control, similar to deep crustal boundaries and structures inferred as significant metallogenic controls in other regions and mineral systems (McCuaig and Hronsky 2014; Hagemann et al. 2016).

Regional shear zones were often developed along lithological contacts of Siluro-Devonian granites and Proterozoic metamorphic rocks. They are interpreted as more local-scale structural controls on the emplacement of rhyolitic dykes and subsequent focused circulation of mineralising fluids along zones of rheological contrast (which was not accompanied by any significant faulting).

Auriferous quartz veins across the region were emplaced in a brittle (epizonal) crustal environment, from moderate-temperature fluids causing sericitic alteration of host rocks. They have similarities with both low-sulfidation epithermal deposits and distal veins associated with intrusion-related gold systems. More detailed investigations to better constrain potential sources of auriferous fluids (including oxygen isotope geochemistry, fluid inclusion investigations) are currently under way.

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Geochemical assemblages in orogenic gold deposits of the Abitibi greenstone belt, Canada: constraints from PCA analysis

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Abstract. Major and trace element composition of ore-bearing rocks from ten orogenic gold deposits in Canada was systematically analyzed. These data were used to unravel the relationship among elements, as well as the host rock, alteration and mineralization by principal component analysis (PCA). Results show that Re is coupled with Au but decoupled from Mo, indicating that Re is associated with Au-bearing phases rather than molybdenite. This demonstrates that Re-Os age of pyrite in gold deposits can represent the timing of Au mineralization. The lithophile elements and alteration minerals can be discriminated from each other by the defined principle components with characteristic element assemblages. The visible close association of PGE, Hg, and W implies that they were formed by the hydrothermal process. PGE were mobilized at around 300°C. Importantly, the size-fraction analyses provide detailed information on the nature and extent of the alteration associated with orogenic gold deposits.

1 Introduction

Orogenic lode gold deposits are typically distributed along first-order compressional to transpressional crustal-scale fault zones in Archean greenstone belt. Numerous gold deposits of this type are distributed along the Destor-Porcupine and the Larder Lake-Cadillac fault zones, in the Archean Abitibi greenstone belt of the Superior Craton, Canada.

Numerous studies have been carried out on the origin, chronology, tectonic evolution, and ore forming process for the metallogenic systems of Archean greenstone-hosted orogenic gold deposits (e.g., Wong et al. 1991; Beaudoin and Pitre 2005; Goldfarb et al. 2005; Rabeau et al. 2013; McNicoll et al. 2014; Beaudoin and Chiaradia 2016; Fayol et al. 2016; Rezeau et al. 2016). However, the origin of Au and the genetic relationship between gold mineralization and hydrothermal alteration remain matters of debate. The orogenic gold deposits are characterized by strongly deformed and metamorphosed host rocks and gold mineralization is closely related to characteristic alteration. Alteration vectoring is thus a crucial aspect for the research and exploration. Meanwhile, the relationship between Au and other elements is not clear enough, which makes the origin of gold ambiguous. Early works underline the specificity of the gold dominant vein-type deposits, but the orogenic concept has progressively broadened the number of associated elements (Hutchinson 1987; Colvine et al. 1989; Goldfarb et al. 2005). This work mainly documents the elemental composition of ore-bearing rocks from ten orogenic gold deposits based on the size-fraction mineral separation method. Principal component analysis was used to unravel the relationship among elements, particularly the relationship between Au and other elements. The relationship between gold mineralization and the hydrothermal alteration was also established, which may be used to guide the exploration for orogenic gold deposits.

2 Sample location and description

Fourteen ore-bearing rocks of ten deposits from the three corridors, Cadillac, Wedding-Lamarck, and Belleterre, were selected for X-ray fluorescence (XRF) analysis and PCA (Fig. 2). Three samples from Lapa, Goldex, and Beaufor mines in the Larder Lake-Cadillac fault zones were studied in detail to discuss the relationship between major elemental composition and host rocks (Fig. 3). The Goldex gold mine is located 4 km west of the town of Val-d’Or in the Abitibi region of northwest Québec. It is a quartz-tourmaline gold-bearing vein type deposit, hosted in a sill of granodiorite rocks (Hudyma et al. 2010). The Beaufor mine is located in the same district, and belongs to the same clan, east of the Bourlamaque TTG pluton (Tremblay 2001). The Lapa deposit is hosted in mafic to ultramafic rocks belonging to the Piché Group, within the the Larder Lake-Cadillac fault zone (Simard et al. 2013).

3 Methodology

3.1 Sample separation based on size fraction

The methodology used in this study is inspired from Clauer and Chaudhuri (1999). Samples were crushed by manual jaw crushe firstly and disaggregated by grinding for 1-2 minutes in an electric rotary mortar. Samples were sorted by size. Before sieving, a small part of materiel was reserved as a whole rock sample. The remaining part was sieved with USA standard test sieves and divided into 8
size-fractions, i.e., >1000 μm, 500-1000 μm, 250-500 μm, 100-250 μm, 60-100 μm, 40-60 μm, and <40 μm. Every fraction should keep a dry part for the XRF analyses. Separation of heavy part from light part was done by crossflow method (Kohmuenchn et al. 2005). The detailed flow chart is shown in figure 1.

![Flow chart diagram](image)

**Figure 1.** The flow diagram of the main protocols.

### 3.2 XRF analysis

A total of 96 size distribution fractions and whole rock samples were analyzed by a Bruker S-4 Pioneer XRF at University of Quebec at Montreal. Five grams of sample powders (size 30-40 microns) were mixed with 10% of Boric Acid (from Chemplex) and pressed at 25t (metric). The error is 0.5% using standardless method.

### 3.3 PCA statistical method

PCA was carried out using the function factor analysis in the statistical software SPSS 16.0 (Norusis, 2008). Data used for PCA are log-centred. During the analysis, factor was extracted using principal components by correlation matrix without rotation. In general, two principal components were extracted and factor (component) scores for each sample are calculated using Regression method and saved as variables.

### 4 Results and discussion

Twenty-nine of fifty-four elements analyzed by XRF can be used for PCA because all the major elements and nearly all trace elements contain more than 40% censored data. Two principal components (PC1 and PC2) were extracted for all XRF data, which accounts for 39% and 14% of variance, respectively. The loading plot of variables (elements) in PC1-PC2 space is illustrated in figure 2. These loading plots show correlations among different elements in gold-bearing rocks from ten deposits.

Different elemental assemblages reflect different alteration types, host rock types, and mineralization information. PC1 is opposing Zr, P, Mn, Mg to Cu, S, W, Hg, therefore lithological elements (Mn-Mg from ferromagnesian minerals, Ba-Sr from feldspars, Zr from zircon, P from apatite) to hydrothermal elements. The position of Ti and Mo reflect specific association during the separation process.

PC2 is opposing Mo, Re, Pt, Hg, W to Al, Ca, and K (= feldspars) and Fe: fresh feldspars are opposed to mobile elements. One of the interesting aspects of this analysis is that the PGE are associated with W and Hg, and clearly separated both with sulfide and heavy minerals (Ta, Mo).

![Plot of PCA results](image)

**Figure 2.** PCA results of XRF data of ore-bearing rocks from ten orogenic gold deposits of the Abitibi greenstone belt, Canada (Lamaque, Beaufor, Lac Herbin, Goldex, Lapa, Francoeur, Wasamac, Astoria, Belleterre, Bachelor).

The size fractions of three gold mines with different host rocks show different major elements normalized spider diagrams (Fig. 3). According to the spider diagram, the smaller size-fractions (0-40, 40-60, and 60-100 μm) of sample from the Beaufor mine are relatively depleted in K and Ti, whereas the larger size-fractions (200-500 and 500-1000 μm) are rich in Na relative to the whole rock (Fig. 3a). The smaller size-fractions (0-100 μm) of sample from Goldex mine show thoroughly contrasting trend of major elements with those larger size-fractions (100-1000 μm). All the size-fractions of the sample from Lapa mine show the same trend with only very slight differences in Ti, Mn, Ca, and K contents.
Figure 3. Major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P) concentrations of size-fractions (SF) normalized to those of whole rock (WR) samples. a) Beaufor mine hosted by felsic rocks. b) Goldex mine hosted by diorite. c) Lapa mine hosted by ultramafic rocks.

5 Implications

From what we have discussed above, the size-fraction and PCA method are very useful, and we can get three principle implications:

1) PCA of all the samples of ten deposits shows a clear distinction between lithophile and alteration minerals;

2) The association of PGE, Hg, and W implies that they were emplaced during the hydrothermal process, indicating mobility around 300°C for PGE.

3) The size-fraction method showed more detailed information about the alteration type of different host rocks.

Acknowledgements

We are thankful to Lucille Daver whose size fraction preparing work contributed significantly to this work. We are grateful to Michel Preda and Xiao-Wen Huang for their contribution to the work of XRF analyses. Finally, this work would not be possible without the support of FORNT, Géology Québec and the contribution of industrial partners to the Corridor Project and China Scholarship Council (CSC).

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Geology, Geochemistry and U-Pb Geochronology of Arc-Related Granitoids of the Alta Floresta Gold Province and implications to the Orosirian gold metallogeny of SW Amazon craton, Brazil

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Abstract. The Alta Floresta Gold Province (AFGP) is located in the southwestern part of the Amazon craton, between two geochronological provinces Tapajos-Parima (easternmost AFGP) and Rondonia-Juruena. The Tapajos-Parima province is one of the best preserved Paleoproterozoic orogenic belt of South America. In the southwestern part of this orogenic belt several foliated granitoids occur associated with four NW-SE first order shear zones as part of the Peru-Traião system, which host several Au-Cu ore zones. The adakitic, high K, Rb and LILE Gringo granitoids (2037±5.9Ma) are the oldest in the province. The Braço Norte garnet leucogranites (2006±4.7Ma) are related to the peraluminous crustal leucocratic association, and garnet-kyanite xenoliths indicate high pressure formation. Biotite tonalites, Naiuram granodiorites, micro-granodiorite dikes (2012 ±13Ma) and hornblende-quartz-diorites (1981±8.1Ma) are geochemically similar, metaluminous, magnesian, medium-K calc-alkaline. Naiuram granodiorites have adakitic composition. Features as: (a) heterogeneous ductile deformation, from high T igneous, to amphibolite facies metamorphic foliation, to mylonitic foliation; (b) medium to high-K calc-alkaline rocks and (c) kyanite-garnet xenoliths in garnet leucogranites may represent a magmatic arc roof present in the Peixoto de Azevedo region. The new findings regarding geological framework and adakitic composition of some of the granitoids can contribute to a better understanding of the evolution of the area, Au-Cu fertility of the magma, and geological connections between AFGP and the northern counterpart of the Tapajos Gold Province.

1 Introduction

The Amazon Craton has two important gold provinces: Alta Floresta Gold Province (AFGP) and Tapajós Gold Province (TGP), which share geological similarities in terms of rock ages, deposit types and structures. The easternmost AFGP and TGP, are included in the Tapajos-Parima province (2.10~1.87 Ga, Fig. 1), which extends throughout the Amazon Craton in Brazil and is one of the largest preserved Rhyacian-Orosirian orogenic belts in the world. AFGP and TGP consist of several arc-related plutono-volcanic sequences of ages varying from 2.04 to 1.75 Ga (Santos et al. 2001).

The main mineral exploration models for both gold provinces are (Santos et al. 2001): (1) Au and Au-Cu orogenic-gold deposits (turbidite and magmatic arc-hosted); (2) intrusion-centered (Cu-Au porphyry, and Au +Zn + Pb ± Cu epithermal deposits); and (3) paleoplacer. Three groups of primary gold deposits have been identified in the host AFGP granitoids (Assis, 2015, Mesquita, et al. 2015): (1) disseminated Au ± Cu; (2) ductile shear vein-type Au ± Cu; and (3) brittle vein-type Au + base metals deposits. Most of the type (2) mineralization is hosted by foliated granitoids at the easternmost part of the AFGP (focus here), in the Peixoto de Azevedo region.

2 Geology and petrography of the Peixoto de Azevedo rocks

A new geological map for the Peixoto de Azevedo region (Santos et al. 2000, AFGP- Alta Floresta Gold Province, TPG-Tapajos Gold Province. White circle-Manaus city.

The lack of structural, geochemical, and isotopic data for the host foliated granitoids makes the discussion of the geotectonic evolution and Au-Cu fertility of the magma, and consequently the improvement of exploration models for AFGP difficult. In this context, the our goal is to summarize the petrogenetic characteristics of the 2.04 to 1.81 Ga foliated granitoids of easternmost AFGP, and discuss magma fertility.

Figure 1. Geochronological Provinces of the Amazon craton (Santos et al. 2000). AFGP- Alta Floresta Gold Province, TPG-Tapajos Gold Province. White circle-Manaus city.
zones, which form biotite, chlorite, sericite, carbonate phyllonites, and host several vein-type Au and Au-Cu deposits.

The foliated granitoid rocks comprise: (a) the Gringo granitoids; (b) Biotite tonalites; (c) the Naiuram granodiorites and cross-cut (d) micro-granodiorite dikes; (e) the Braço Norte leucogranites; and (f) Hornblende quartz-diorites.

The foliated granitoids host the Peteca and Gringo deposits. The anastomosing S_n is marked by feldspars and hornblende rimmed by matrix (Fig. 3d).

**Figure 3.** Foliated granitoids: Gringo porphyritic biotite granite with a weak and b strong foliation (Sn). c biotite schlieren mark Sn in Biotite tonalite. d Naiuram Hornblende granodiorite with mylonitic Sn. e foliated micro-granodiorite dike crosscuts the Naiuram granodiorite mylonitic Sn. f Braço Norte leucogranite, exhibiting a garnet-kyanite xenolith (arrow). g diffuse contact between the Braço Norte leucogranite and the Naiuram granodiorite. h Hornblende-quartz diorite.

Hornblende is rimmed by epidote, titanite, chalcopyrite, and pyrite (Fig. 4d). The Naiuram granodiorites are crosscut by micro-granodiorite dikes (Fig. 3e). The Sn+1 foliation in micro-granodiorites is defined by plagioclase phenocrysts and an aphanitic matrix (Fig. 4e).

The Braço Norte garnet-muscovite leucogranites are in tectonic contact with the Naiuram granodiorites (Fig. 3g). They show a mylonitic S_n defined by elongated feldspar and fractured garnet grains rimmed by muscovite and biotite. The irregular, elongated xenoliths (Fig. 3f) are composed of garnet and kyanite.

The Hornblende quartz-diorites occur as small elongated bodies. The rocks are heterograined, medium-to fine-grained (Fig. 3g). S_n is well-developed and marked by the alignment of plagioclase, and a recrystallized hornblende-plagioclase matrix. Plagioclase megacrysts keep their igneous prismatic euhedral form, besides its intracrystalline deformation (Fig. 4f).

### 3 Geochemistry and U-Pb geochronology of the foliated granitoids

The Gringo granitoids are calc-alkaline to alkali-calcic, high-K, peraluminous, and transitional magnesian to ferroan (Fig. 5, Table 1). Primitive mantle-normalized patterns (Fig. 6a) show LREE enrichment and HREE depletion, resulting in high fractionation patterns. Eu anomalies are slightly negative to none. High Rb and LILE, and low Y and Nb contents suggest that the Gringo...
granitoids formed from a magma source characteristic of a mature volcanic arc to post-collisional setting (Pearce et al. 1984).

Nine zircon grains yield an upper intercept crystallization age of 2037±5.9 Ma (U-Pb Fig.7a).

**Table 1.** Mean chemical composition of the Peixoto de Azevedo rocks. $\Sigma$FeO = FeO$_T$+MgO+MnO+TiO$_2$. GG-Gringo granitoids, BNL-Braço Norte leucogranite, BT-biotite tonalite, HD-hornblende quartz-diorite, NG-Naiuran granodiorite, MG-microgranodiorite.

<table>
<thead>
<tr>
<th>Elem</th>
<th>Na$_2$O</th>
<th>$\Sigma$FeO</th>
<th>Rb</th>
<th>Sr</th>
<th>Nb</th>
<th>Ni</th>
<th>Cr</th>
<th>Yb</th>
<th>Y</th>
<th>(La/Yb)$_N$</th>
<th>Eu/Eu*</th>
</tr>
</thead>
<tbody>
<tr>
<td>GG</td>
<td>3.6</td>
<td>3.1</td>
<td>115</td>
<td>254</td>
<td>8</td>
<td>24</td>
<td>54</td>
<td>0.67</td>
<td>7</td>
<td>54</td>
<td>0.8</td>
</tr>
<tr>
<td>BNL</td>
<td>3.5</td>
<td>1.5</td>
<td>109</td>
<td>221</td>
<td>1</td>
<td>1</td>
<td>8</td>
<td>0.5</td>
<td>2</td>
<td>14</td>
<td>1.9</td>
</tr>
<tr>
<td>BT</td>
<td>4.1</td>
<td>6.4</td>
<td>104</td>
<td>424</td>
<td>10</td>
<td>17</td>
<td>17</td>
<td>0.8</td>
<td>14</td>
<td>70</td>
<td>0.4</td>
</tr>
<tr>
<td>HD</td>
<td>4.5</td>
<td>13.9</td>
<td>56</td>
<td>731</td>
<td>19</td>
<td>62</td>
<td>17</td>
<td>2.7</td>
<td>27</td>
<td>12</td>
<td>0.8</td>
</tr>
<tr>
<td>NG</td>
<td>4.2</td>
<td>10.9</td>
<td>97</td>
<td>460</td>
<td>31</td>
<td>34</td>
<td>21</td>
<td>1.9</td>
<td>19</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>MG</td>
<td>4.6</td>
<td>4.6</td>
<td>54</td>
<td>352</td>
<td>20</td>
<td>27</td>
<td>0.2</td>
<td>13</td>
<td>2</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>

Low fractionation patterns and positive Eu anomaly are expected for crustal leucogranites. Also high Rb and low Nb and Y contents are expected for crustal granites, which indicate magma sources from mature volcanic-arc to syn- collisional fields. Eleven zircon grains yielded an upper intercept crystallization age of 2006±7.1 Ma (Fig.7c).

**Figure 4.** Photomicrographs (cross polarized light). a Gringo granite: igneous biotite aggregate. b Gringo granodiorite: mylonitic Sn marked by garnet and quartz ribbons. c biotite tonalite: large subgrains in plagioclase. d Naiuran granodiorite: recrystallized rim around hornblende megacryst. Quartz chess-board pattern (red arrow). e plagioclase mark Sn in micro-granodiorite dike. f subgrain in euhedral igneous plagioclase (arrow) plus polygonal hornblende in hornblende quartz-diorite.

**Figure 5.** Frost et al. (2001) diagrams. a Na$_2$O+K$_2$O-CaO vs SiO$_2$. b SiO$_2$ vs K$_2$O diagram. c A/NK vs ASI (alumina saturation index) diagram. d FeO$_T$/FeO$_T$+MgO vs SiO$_2$ diagram.

**Figure 6.** Primitive mantle-normalized REE patterns (McDonough & Sun 1995) for a Gringo granitoids, Braço Norte Leucogranites and b hornblende diorite, biotite tonalite, Naiuran granodiorites and microgranodiorite dyke. c (La/Yb)$_N$ vs. Yb$_N$ (Martin 1999) and d Y vs. Sr/Y (Drummond & Defant 1990) diagrams discriminating between adakitic (grey field) and calc-alkaline (white fields compositions.

The Naiuran granodiorites, biotite tonalites, hornblende quartz-diorites and microgranodiorite dikes are calc-alkaline, metaluminous to slightly peraluminous, medium-K, and magnesian (Fig. 5). Biotite tonalites are the most LREE enriched, yielding a fractionation pattern with a pronounced Eu negative anomaly (Fig. 6b). The Naiuran granodiorites and hornblende quartz-diorite are moderate to highly LREE enriched and yield lower fractionation patterns with a slightly negative Eu anomaly.

**Micro-granodiorites** show very low REE enrichment, similarly to the Braço Norte leucogranites, resulting in moderate fractionation patterns, flat HREE patterns, and a slightly positive Eu anomaly. The lowest Rb, Y and Nb content suggest less evolved source magmas. Ten zircon grains from the micro-granodiorites
yield an upper intercept crystallization age of 120±13 Ma (Fig.7b), and twenty three zircon grains of the Hornblende quartz-diorites yield an upper intercept crystallization age of 1981.2±8.1 Ma (Fig.7d).

The moderate Rb, low to moderate Nb and Y suggest that Biotite tonalites, Naiuram granodiorites, Micro-granodiorite, hornblende quartz-diorites are crystallized from evolved or continental volcanic arc magmas (Pearce et al. 1984).

![Image](image-url)  
**Figure 7.** U-Pb Concordia diagrams for zircon grains. **a** Sample PFS-022 of Gringo equigranular biotite granite. **b** sample PET-005 of micro-granodiorite. **c** sample PET-002 of Braço Norte leucogranites. **d** PFS-066 of hornblende quartz-diorites.

4 Discussion and conclusions

The present paper identifies several foliated granitoids hosting vein-type gold deposits. The Gringo granitoids (2037Ma) are the oldest foliated granitoids. The parallelism of their granitoids’ REE patterns suggests they are cogenetic (Fig. 6a), and since the less differentiated granodiorites are REE richer than syenogranites, this could suggest different amounts of crustal melt assimilation.

The peraluminous character (Fig.5c), presence of Al-rich minerals, high SiO₂, K₂O, and Rb contents; depletion of HSFE; and presence of kyanite and garnet xenoliths, indicate that the Braço Norte leucogranites can be part of the peraluminous leucocratic association, resulting from the melting of the lower crust. The 2006 Ma crustal melting source for the magmatism, may correlate these rocks to the ~2000 Ma Cuiu-Cuiu arc-crustal parallelism of their granitoids’ REE patterns suggests they are cogenetic (Fig. 6a), and since the less differentiated granodiorites are REE richer than syenogranites, this could suggest different amounts of crustal melt assimilation.

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As presented above, biotite tonalites (2014 Ma, Trevisan 2015), Naiuram granodiorites, 2012 Ma micro-granodiorite, and 1981 Ma hornblende quartz-diorites show similar geochemical features, and considering high alumina contents (14.5-20 wt.%), and the presence of apatite, titanite, and zircon as accessory minerals, they could be part of the same magmatic arc evolution.

The constant NW-SE high-T mylonitic foliation and development of HSFE; and presence of kyanite and garnet suggest that rocks be part of the same magmatic arc evolution. The peraluminous character (Fig.5c), presence of Al-rich minerals, high SiO₂, K₂O, and Rb contents; depletion of HSFE; and presence of kyanite and garnet xenoliths, indicate that the Braço Norte leucogranites can be part of the peraluminous leucocratic association, resulting from the melting of the lower crust. The 2006 Ma crustal melting source for the magmatism, may correlate these rocks to the ~2000 Ma Cuiu-Cuiu arc-crustal parallelism of their granitoids’ REE patterns suggests they are cogenetic (Fig. 6a), and since the less differentiated granodiorites are REE richer than syenogranites, this could suggest different amounts of crustal melt assimilation.

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The constant NW-SE high-T mylonitic foliation and deformational microstructures, such as large subgrain in igneous plagioclase, and chessboard pattern in quartz (Kruhl 1996) besides recrystallized matrix side by side to igneous textures, specially Naiuram granodiorites and hornblende quartz-diorite, could indicate that the rocks result from a complex mixtures of processes, such as shearing, amphibolite facies metamorphism, and subsolidus deformation during magma emplacement. These characteristics are typical of a magmatic arc roof, which is corroborated by the deep setting of some of the gold mineralizations, as the Paraiba gold deposit (Trevisan, 2015). The host Gringo and Naiuram granitoids have adakitic geochemical characteristics (Martin 1999), such as high Na₂O (>3.5%), Sr (>300ppm), Ni (≥ 20 ppm), Cr (≥ 30 ppm) contents, and high fractionation patterns ((La/Yb)>10) (Fig. 6c-d, Table 1). Our follow-up goal is to investigate the association between these adakitic rocks and their correlation with magma fertility for Au-Cu (Charadía et al. 2012). We believe it is capital step to develop genetic models that can be used for exploration purposes.

Acknowledgements

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References

Geological characteristics of Carlin-type gold mineralization prospects in a ‘frontier’ area, Rackla belt, Yukon, Canada

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Abstract. Carbonate replacement-type gold prospects were recently discovered in a >80 km-long corridor known as the Rackla belt. The belt strikes parallel to major regional faults and to the Selwyn Basin – Mackenzie Platform boundary in north central Yukon (Canada). In the eastern Rackla belt, Carlin-type mineralization is hosted in three main units composed of limestone, dolostone and calcareous siltstone and shale that range in age from Neoproterozoic to Devonian. Several of these prospects share characteristics commonly associated with Carlin-type deposits of western United States. Similarities include zones of decarbonatization, local vuggy silica, extremely fine pyrite with auriferous arsenian overgrowths, locally abundant realgar and orpiment, and a strong As-Hg-Sb-Tl enrichment. At the prospect scale, the structural controls on gold distribution (faults and folds) are clear, but the geometry, kinematics and timing of structures remain to be documented in detail. Host-rock porosity/permeability and reactivity also influence the distribution of mineralized zones.

The gold prospects of the Rackla belt are considered as some of the best examples of Carlin-type mineralization outside western United States, which provides us with a unique opportunity to further study the key geological elements in the genesis, distribution and preservation of this major gold deposit type.

Figure 1. a Geological setting of the Rackla belt in east-central Yukon (modified from Colpron et al. 2013). b Geological map of the eastern Rackla Belt (simplified from Moynihan 2016). The blue dotted line is a marker horizon corresponding to the contact between the Nadaleen and Gametrail formations.
1 Introduction

Carbonate-hosted Carlin-type deposits represent one of the world’s most important source of gold but, except for a few potential analogues, all deposits of this type are located in the Great Basin of western United States (Cline et al. 2005). For this reason, most of the available description and understanding of Carlin-type deposits comes from this region and it remains unclear if geological and exploration models can be exported elsewhere.

The Rackla belt in north-central Yukon (Canada) hosts mineralized zones with distinct characteristics, including gold prospects considered as “true” Carlin-type mineralization (Poulsen 1996; Tucker et al. 2013; Arehart et al. 2013; Tucker 2015; Palmer and Kuiper 2016). These prospects are the aim of the present contribution.

2 Geological setting

The Rackla belt in north-central Yukon forms a 5-15 km-wide east-trending zone bounded to the S by the Dawson Thrust and to the N by the Kathleen Lakes Fault (Fig. 1A). This area marks the northern boundary of the Selwyn Basin in this region (Fig. 1A). The Dawson Thrust is a major Mesozoic fault associated with the building of the Cordillera (Abbott 1997). The present-day location of the thrust roughly coincides with the location of facies boundaries during the Neoproterozoic and Paleozoic, suggesting that depositional patterns were controlled by a major, probably deep-seated, structure. Evidence of syn-sedimentary tectonism in sedimentary units from mid-Proterozoic to mid-Paleozoic supports this hypothesis. Toward the eastern end of the Rackla belt, where the Carlin-type prospects are located, both the Dawson Thrust and Kathleen Lakes Fault split in several faults suggesting that the displacement is distributed through several branching splays («horsetail structure») in this area (Moynihan 2016).

The sedimentary succession consists of a relatively diversified assemblage of Neoproterozoic (Windermere Supergroup and Hyland Group) and overlying Cambrian to Carboniferous strata. Igneous rocks are scarce in the belt and limited to a poorly outcropping gabbroic pluton and dykes.

The succession is complexly faulted and folded (Fig. 1B) and several phases of deformation can locally be documented. Major faults were classically interpreted as thrusts or backthrusts, but some of them likely bear a significant strike-slip component.

3 Mineralization

The Rackla belt hosts several mineralization types tentatively classified as skarn, SEDEX, Mississippi Valley Type (MVT) and epithermal on regional metallogenic synthesis and compilations (e.g., Goodfellow 2007; Yukon Geological Survey 2017).

In the most advanced prospect (Conrad; Fig. 1) several mineralized zones have been intersected over a vertical interval of 0.8 km, including an upper zone extending along strike for more than 800 m.

The potential for carbonate-hosted Carlin-type mineralization in the Canadian Cordillera was first proposed by Poulsen (1996), but it is only in 2010 that Carlin-type mineralization was discovered in the eastern Rackla belt through follow-up work by ATAC Resources Ltd on a stream sediment survey conducted by the Geological Survey of Canada (Goodfellow and Lynch 1978) that indicated arsenic anomalies. Subsequent drilling resulted in the discovery of four main mineralized zones located in a relatively restricted area (< 50 km²; Fig. 1B).

Mineralization preferentially occurs in antclinal hinge zones or close to steeply-dipping faults. At Conrad, argillaceous mudstones and siltstones in fault contact with the limestone unit hosting the mineralization probably acted as an aquitard and contributed to focus fluid flow in the fault footwall. At Anubis, mineralization is hosted by highly fractured, strongly folded siltstone and shale at the fault contact with a limestone unit. Preliminary observations indicate that some of the faults were active after the mineralizing event.

Gabbroic dykes that are altered and locally mineralized were dated at 74.4 ± 1.0 Ma (Tucker 2015) and provide a maximum age for the mineralization.

Gold is hosted in arsenic-rich pyrite growth rims around pre-existing pyrite (Tucker et al. 2013; Sack et al. 2014). Realgar and orpiment are key spatial indicators of gold mineralization (Figs. 2 and 3). These minerals occur as irregular patches (Fig. 2C) and/or as replacement of selective cm limestone beds (Fig. 3B) as well as in veinlets. They also occur as late-stage filling in fractures or voids, in brecciated intervals, in the matrix of local high-grade hydrothermal breccia (Fig. 2D) or as replacement of calcite clasts within cavity fill breccia (Fig. 3A). Locally, realgar and orpiment form striae on fault surfaces attesting to their syn-tectonic emplacement.

Decarbonatization is the principal type of alteration. Mineralized intervals yielding the highest gold values are often dark grey, featureless and friable (Fig. 2A). Calcium is strongly leached in mineralized intervals.

Significant calcite veining (up to 30 vol. %) is often developed up to tens of meters away from the mineralized zone. The calcite veins may be the product of the strong decarbonatization recorded by the immediate host to the gold mineralization. Several episodes of veining and brecciation are identified indicating protracted hydrothermal/tectonic activity (Fig. 3). Alteration products also include narrow high-grade vuggy silica intervals (Fig. 3A) formed by low-pH acid leaching.

Gold rich zones are significantly enriched in pathfinder elements such as As, Hg, Ti, Sb and depleted in Ca, Mg and Sr.
Figure 2. High-grade gold intervals. a Typical decarbonatized interval characterized by a dark grey color and the lack of macroscopic features. b Decarbonatized interval characterized by late stage calcite and realgar. c Decarbonatized interval associated with realgar patches and seams. d Hydrothermal breccia with partly replaced angular limestone clasts in a realgar-rich matrix. e Vuggy-textured, silica breccia; All Samples came from 1.04 to 1.40 m-long intervals yielding values > 7.9 ppm Au.

Figure 3. Typical features associated with mineralization. a Breccia showing selective replacement of calcite-rich clasts. b Realgar replacement of selected limestone beds and filling fracture at high-angle to bedding. c Late stage vein with realgar cross-cutting sheeted mm-scale calcite veinlets. d Brecciated limestone with fractures filled with realgar.

4 Discussion

The gold prospects in the eastern part of the Rackla belt show striking similarities with Carlin-type deposits of western United States.

At the regional scale, both areas belong to the passive margin of Laurentia during the Neoproterozoic/Paleozoic and were part of the Cordilleran accretionary wedge during the Mesozoic/early Tertiary. The sedimentary succession includes impure carbonate rocks that acted as preferential host units to mineralization in both the western United States and Yukon. However, in the eastern Rackla belt, based on the available data, evidence of crustal-scale extension and normal fault systems such as those documented in the Basin and Range province are not recognized. In Yukon, preliminary interpretation suggests that structures that may have contributed to permeability enhancement, fluid emplacement and orebody geometry are contemporaneous with fault motion with a significant strike-slip component and are associated with local dilational zones related to relay zones, fault bends and fault terminations.
Figure 4. Example of a high-grade interval (Conrad prospect) showing a correlation between high gold and mercury grades and decarbonatization (low Ca content). Note the variable distribution and density of calcite veining.

At the district scale, the occurrence of diverse styles of gold mineralization and their structural control are common to both the SW United States and Yukon. The clustering of gold prospects in relatively restricted areas is another common characteristic.

At the prospect scale, the association of gold with arsenic-rich pyrite, the common occurrence of realgar/orpiment, structurally and stratigraphically controlled alteration styles including decarbonatization and vuggy silica breccia, the very low base metal content and the enrichment in a series of diagnostic pathfinder elements (Au, As, Hg, Tl, Sb) are key characteristics found in Carlin-type mineralization in both the type area and north-central Yukon.

In summary, characteristics of carbonate replacement gold prospects in the eastern Rackla belt support their interpretation as one of the rare and best examples of a “true” Carlin-type system outside western United States. The study of these prospects thus provides a unique opportunity to review the geological elements that are necessary to form Carlin-type deposits, outside of their type area in Nevada, but in a geological setting that shares many similarities. A better understanding of the Rackla belt prospects will help refine geological and genetic models for the study area, but perhaps elsewhere as well.

Acknowledgements

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Gold epichrons in the Abitibi greenstone belt, Canada, and the impact of early Proterozoic Matachewan LIP event

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Abstract. The Cadillac – Larder Lake Fault zone (CLLFZ) constitutes one of the largest gold districts in the world. Despite U/Pb, 40Ar/39Ar, and Sm/Nd isotopic time constraints along the fault, the timing of gold mineralisation remains poorly defined. This abstract summarises results from a new methodological approach. The method allows to analyse the isotopic signatures of gold mineralisation on seven mineralization sites along the CLLFZ. It combines detailed mineralogical, geochemical and Re/Os isotopic systematics of sample size-fractions. Breaking down samples into eight size-fractions allows systematic analysis of gold distribution and related alteration minerals. SEM coupled with EDX allows defining mineralogy of size-fractions. XRF and XRD allowed the chemical compositions and mineralogy of the various size-fractions to be determined. Isotopic analyses of rhenium (by ICP-MS) and osmium (by NTIMS) were performed, with Re and Os concentrations determined by isotope dilution technique. 187Re/187Os isochrons were calculated from 37 size-fractions from seven samples. Properly sampling for Re/Os geochronology appears critical in understanding ore forming processes. The concept of epichron is introduce in order defining an isochron resulting from epigenetic mineralisation within an ore system.

1 Context

Most of the gold deposits in Archean greenstone belts are associated with large structural fault corridors (Kerrich 1986; Goldfarb et al. 2001). The exact timing of the formation of the gold mineralization remains however poorly understood: Is the gold concentration progressively constructed by successive enrichment from early VMS or porphyry concentrations to late shear zones, or is it deposited at the very end of the deformation, in association with the stabilization of the craton (Goldfarb et al. 2001; Large et al. 2011)? Detailed understanding of these processes remains essential to all exploration projects within the Superior Province.

In order to advance on the dating of gold events, a three year project was developed as a partnership between the mining industry – Géologie Québec/FRQNT and UQÀM. The main goal of the project is to provide robust time constraints on gold mineralisation and crustal evolution of the Eastern part of the Superior Craton. Four mineralized corridors were selected: 1) The East-West trending Cadillac – Larder Lake Fault zone (CLLFZ), 2) the Northeast-Southwest trending Wedding-Lamarck Corridor, 3) the Belleterre sector in the Pontiac Sub-Provience, and the Rex corridor in the Minto Province. This paper summarizes results from CLLFZ (Fig. 1).

Figure 1. Geological sketch of the Cadillac-Larder-Lake Fault zone (CLLFZ) illustrating the location and 187Re/187Os isochron ages of seven samples.
The Cadillac –Larder Lake Fault zone constitutes one of the largest gold systems in the world with more than 100 Moz produced in the last century (Pilote et al. 2014). It display a protracted evolution from ductile to brittle. The Sigma-Lamaque mine, in Val d’Or (Québec), represents one of the most studied mines along the CLLFZ and is archetypal of the concept of orogenic gold deposit (Groves et al. 1996). Many isotopic systems have been used in this district in establishing time constraints on alteration minerals (U/Pb, 40Ar/39Ar, and Sm/Nd), resulting in contrasting results (Wong et al. 1991; Hanes et al. 1992; Anglin et al. 1996). Previous ages obtained range from ca. 2.3*10^2704 Ma to ca 2286 Ma. We summarizes hereafter district in establishing time constraints on alteration minerals (U/Pb, 40Ar/39Ar, and Sm/Nd), resulting in contrasting results (Wong et al. 1991; Hanes et al. 1992; Anglin et al. 1996). Previous ages obtained range from ca. 2.3*10^2704 Ma to ca 2286 Ma. We summarizes hereafter

187Re/187Os isochrons calculates from seven samples from gold mines along the Quebec portion of the CLLFZ (Figure 1): 1 Wasamac, 2, Zulapa, 3 Lapa, 4 Goldex, 5 Lamaque Triangle zone, 6 Lamaque Parallel zone, 7 Beaufor. These deposit represent different styles of gold deposit as classified by Rafni (2013). Wasamac belongs to the Kirkland Lake style of mineralization, associated with alkaline dykes (Mériaud and Jébrak, 2017). Lapa and Zulapa illustrate a deeper style of ultramafic-hosted ductile shear-zone (Simard et al. 2013); Goldex, Lamaque and Beaufor belong to the Val d’Or quartz-carbonate-tourmaline district (Robert et al, 2005; Beaudoin et Pitre, 2005).

2 Methodology

Samples were subjected to methodology illustrated in Figure 2, inspired form Clauer and Chaudhuri (1999). Samples were disaggregated by grinding for 2 minutes in a rotary agate-mortar. Size-fractions were then produced by sieving disaggregated samples for 20 minutes (Figure 2). A dry portion of each size-fraction was preserved dry for further XRF and XRD analysis. The remaining portion was soaked for an hour prior to a 5-minute ultrasonic bath treatment, thereby, promoting grain liberation.

Cross-flow separation inspired from (Kohmuench et al. 2005) provided quick and reliable heavy mineral separation with a density cutoff near five. Magnetite was used as density indicator (i.e, density between 5and 6) using a magnet in monitoring magnetite occurrence during heavy minerals concentration process. Therefore, no mineral with density lighter than five was involved in the following Re/Os procedures.

Magnetic phases, magnetite, specular hematite, hematite, and pyrrhotite were removed from heavy mineral concentrate with strong magnet coveted with weighing paper. Prior to Re/Os analysis, concentrates were homogenized using agate pestle and mortar. Approximately 200 mg of concentrates were digested in Carius tube according to Shirey and Walker (1995). Single 187Os and 186Re spike was used. Nitric acid was prepared according to Yang et al. (2015). Samples were digested 24 hours at 250°C. Osmium extraction was performed according to Birck et al. (1997).

Osmium analysis were performed in negative ion mode using a Thermo Triton Plus mass spectrometer by ion counting in peak jumping mode. Fourteen procedural blank runs returned an average of 1.8*10^-16 mole 187Os and 2.3*10^-12 187Re. Thirteen runs using in average 3µL of the DROsO standard returned an average 187Os/188Os ratio of 0.1615 ± 0.0003. Compared to Meisel et al (2003), Pearson and Woodland (2000) protocol for rhenium extraction using HCI+HF greatly helped eluting tungsten. This approach greatly helped increasing rhenium precision, accuracy, and reproducibility. Rhenium data were obtained using a magnetic sector ICP-MS using the SRM 3143 international standard for control. Isochron were calculated using Isoplot 4.0 (Ludwig, 2012).

Size-fraction geochemistry was done by XRF and is the object of Meng et al. (This volume) abstract.

3 Results

Isochron were calculated both at the mine site as well as at the CLLZF scale. This paper reports regional isochron calculated from 37 size-fractions from 7 samples (Table 1 and 2). By this approach, the CLLFZ is considered as a unique system; the regional isochron best illustrates the system variation.

Table 1 displays isochron ages with 95% confidence interval, intercept with 95% confidence interval, MSWD, number of size-fraction involved for calculation. Four isochron were calculated: 2575±7 Ma, 2505±20 Ma, 2398±11 Ma, and 2267±21 Ma. On one hand, Table 2 displays from west to east along the CLLFZ the site contribution to each isochron. On the other hand, Figure 1 illustrates site locations along the CLLFZ as well as isochron ages for each site. From Table 2 one can observe a significant aging trend from 2267 to 2575 Ma. Zulapa and Lamaque sites contribute to the oldest isochron at 2575 Ma. The 2505 Ma isochron is restricted to Val d’Or district both at Lamaque zones and Goldex mines (Figure 1). All deposits with the exception of Wasamac and Beaufor are contributing to the 2393 Ma isochron. Finally, all mines,
but Lapa and Triangle zone from Lamaque are contributing to the 2267 Ma isochron.

Figure 3 illustrates $^{187}$Re/$^{187}$Os isochron intervals compared to U/Pb and $^{40}$Ar/$^{39}$Ar intervals documented in Abitibi on various alteration minerals (c.f., Lemarchand, 2012; Percival and West, 1994; Powell et al. 1995). Isochron ages coincides systematically with $^{40}$Ar/$^{39}$Ar data. $2575 \pm 7, 2505 \pm 20$, and $2398 \pm 11$ Ma $^{187}$Re/$^{187}$Os isochrons are coeval to the transition between amphiboles and white micas. $2267 \pm 11$ Ma $^{187}$Re/$^{187}$Os isochron is coeval to biotite. Figure 3 helps estimating closure temperature of $^{187}$Re/$^{187}$Os between 500 ºC and 400 ºC for this approach according to hornblende and muscovite closure temperature.

Table 1: Isochrones data

<table>
<thead>
<tr>
<th>Isochron (Ma)</th>
<th>±2δ</th>
<th>$^{187}$Os initial (ppt)</th>
<th>±2δ</th>
<th>MSWD</th>
<th>N (fraction)</th>
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<tr>
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<td>-0.3</td>
<td>6</td>
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<td>2267</td>
<td>21</td>
<td>-0.44</td>
<td>0.32</td>
<td>0.92</td>
<td>9</td>
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Table 2: Sample contribution to isochrones

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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isochron (Ma)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2575.1</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>2398</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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<td>X</td>
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</table>

4 Isochron and epichron

We define an epichron as an isochron derived for authigenic mineralisation developed within mineralisation zone. Authigenic mineralisation may result from remobilisation or enrichment from existing mineralisation or resulting from distinct mineralisation event and source.

Nature and age of source can be evaluated by calculating initial $^{187}$Os/$^{188}$Os ratio based on isochron age. High initial ratios are indicative of crustal source whereas low initial ratios approaching 1 are suggestive of mafic source.

The Lamaque gold deposit shows clear variations in the initial ratio: The Triangle zone. South of Lamaque Mine contributes to the 2575, 2505, and 2398 Ma isochrons exhibiting high initial $^{187}$Os/$^{188}$Os ratios ranging from 312 to 6. On one hand, model ages for the 2575 Ma isochron are ranging from 2592 to 2894 Ma with initial ratios averaging 156. On the other hand, model ages relating to the 2398 Ma isochron are ranging between $2379 \pm 34$ and $2443 \pm 34$ with lower initial ratio of 6.2 and 17.4, respectively. Therefore, the older age would reflect a crustal contribution whereas the younger one would indicate a mafic source that would fit with the emplacement of the Matachewan event (Ciborowski et al. 2015). The mantle plume head underlying this Large Igneous Province was probably located immediately south the Abitibi between 2491 and 2437 Ma; it has been correlated with the Great Oxidation Event. This would have also been recorded in the isotopic signatures of the gold mineralization along the Cadillac break. The question of a gold input remains open as a number of gold and Cu-Au deposits are related to potassic rocks in within-plate plume-related setting (Muller and Groves, 2016).

5 Conclusions

The Re-Os isotopic analysis of the pyrite in several gold deposits along the CLLFZ, south of the Abitibi greenstone belt, reveal that the area had suffered several thermic pulses during more than 100 Ma after the emplacement of the syn-tectonic sanukitoïds plutons and S-type post-tectonic magmatism. Between 2575 Ma and 2267 Ma, numerous isotopic systems were reopen indicating the intensity and the large extend of the reworking. All styles of gold
mineralization were concerned. This paradox (Kerrich and Kyser, 1994) could probably be explained by the onset of the Matachewan LIP, during the Lower Paleoproterozoic. This major pulsative event could also have been recorded in the low initial osmium ratio of some of the pyrites.

Therefore, the construction of the gold deposits in the Southern Abitibi belt would be span on over several tenth of millions years, recorded by ephichrons. The very notion of one unique age for orogenic-type late Archean gold mineralization would be a non-sense. Several detailed studies have recently shown that pyrite crystallization in gold deposits was almost always a step process (Large et al. 2011; Bigot and Jébrak, 2015; Mills et al. 2015, Daver 2016). We now need to correlate these steps with the isotopic signatures of the minerals association to gold mineralization.

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Abstact. Major, minor and trace elements composition of tourmaline from 18 orogenic gold deposits and districts has been measured by EPMA and LA-ICP-MS. Deposits were selected to compare the composition of tourmaline from deposits in various hostrocks and metamorphic grade, and age of mineralization from Archean to Carboniferous. Tourmaline from orogenic gold deposits is dravitic in composition, with less common schorlitic composition. Tourmaline displays 3 REE patterns including 1) a flat pattern, 2) a fractionated pattern, 3) a HREE enriched pattern. REE patterns do not correlate to the hostrock composition, metamorphic grade, or age of mineralization, suggesting they are dominantly derived from the fluid source rocks. PCA of LA-ICP-MS data shows that tourmaline hosted in felsic and intermediate volcanic and plutonic rocks have similar trace element signatures that differ from those from deposits hosted in metasedimentary rocks. Tourmaline from deposits at various metamorphic facies have similar trace element compositions. Tourmaline from Phanerozoic deposits has a distinct trace element signature. Thus, the geological setting of the deposits has a weak control tourmaline trace element composition that can be distinguished from that of other mineral deposit types or geological environments.

2 Geological setting of selected orogenic gold deposits

Tourmaline was investigated from 18 orogenic gold deposits and districts including deposits from the Abitibi greenstone belt (Canada), the James Bay district (Canada), the Meliadine district (Canada), the Sierra Nevada Foothills (USA), the Rosebel district in the Guyana shield, the Salsigne deposit from the Massif Central (France), the West Africa craton (Burkina Faso), the Damara orogen (Namibia), the Kaapvaal (RSA), the Dharwar (India) and the Yilgarn (Australia) cratons.

Deposits were selected to provide a range of geological settings for orogenic gold deposits, and comprise classical examples of this deposit type. Hostrocks are commonly clastic sedimentary rocks or mafic rocks such as basalt or gabbro. Several deposits from the Abitibi belt are hosted in intermediate to felsic intrusions. The metamorphic facies of the selected gold deposit ranges from lower greenschist to upper amphibolite. Most of the deposits studied formed during the Archean, with the exception of Essakane and Navachab, which formed during the Proterozoic and Salsigne, which formed during the Carboniferous.

3 Tourmaline texture and mineral assemblages

In orogenic gold deposits, tourmaline is most commonly found in quartz-carbonate veins, or disseminated in vein selvages. Tourmaline presents a wide range of size, texture, color, optical zoning and mineral associations. Tourmaline forms aggregates of very fine anhedral grains in some deposits. In others, tourmaline forms aggregates of tabular to acicular, medium size grains in quartz, or forms fibrous aggregates perpendicular to vein selvages.
The most common tourmaline color is bluish-green to brown under microscope. In a few deposits, tourmaline is light blue or orange. Tourmaline commonly shows a rim with various color shades from orange to brown to dark green from a few to 50 µm in thickness. In some complex grains, oscillatory zoning and/or sector zoning are found.

4 Analytical methods

Major and minor elements were measured with a Cameca SX-100 Electron Probe Micro-Analyzer (EPMA) at Université Laval with the analytical method described in Grzela (2017). Minor and trace elements were measured using a RESOlution M-50 Excimer 193 nm laser coupled to an Agilent 7700x ICP-MS at UQAC (Québec, Canada) with the analytical method described in Grzela (2017). Principal Component Analysis (PCA) was performed on imputed, and CLR-transformed, data using the method described in Makvandi et al. (2016).

5 Results

Tourmaline from orogenic gold deposit is alkalic and more commonly has a dravitic composition. Some tourmaline samples plot in the field for schorl, with few exceptions in the foitite and the magnesio-foitite fields (Fig. 1). Tourmaline from orogenic gold deposits from various geological settings, including composition and metamorphic facies of the hostrocks, and age of mineralization, has similar major element composition.

Tourmaline from orogenic gold deposits display 3 distinctly different Rare Earth Elements (REE) patterns. The tourmaline/chondrite ratio ranges from 0.01 to 100 and the Eu anomaly is commonly positive in all patterns (Figure 2): 1) a flat REE pattern, 2) a fractionated REE pattern and, 3) a HREE enriched pattern. The 3 REE patterns are found in tourmaline cores. The REE patterns are not unique within a deposit. For instance, at the Hoyle Pond and Roberto deposits, REE patterns vary with the tourmaline texture and the core color. At Roberto, orange tourmaline has a HREE enriched pattern, whereas brown tourmaline has a fractionated pattern. At Hoyle Pond, aggregates of orange tourmaline has a flat pattern whereas blue tourmaline has a HREE enriched pattern. At Beaufor, tourmaline cores are characterized by HREE enriched patterns, whereas tourmaline rims are characterized by a flat pattern. However, REE patterns are not systematically related to the geological setting of the deposits.

The results of PCA for tourmaline trace elements in orogenic gold deposits is shown in figure 3. The principal components PC1 and PC2 for orogenic gold deposit tourmaline represent 22.6 % and 14.4 respectively, of the total variance of the dataset. PC1 is defined by positive contributions of Ni, Co, V and negative contributions of...
Figure 4. PCA using Cr, Zn, Ga, Sr, Zr, Sn, Ba and Pb for tourmaline from different deposit types and rocks.

Mn, Ti, Ca, (La/Sm)_CN, \( \sum \)REE and Li. PC2 is defined by positive contributions of the Y, \( \sum \)REE, Ba and K and negative contributions of Eu anomaly (Fig. 3). Tourmaline from Archean and Proterozoic orogenic gold deposits are not discriminated by PC1 and PC2. Tourmaline from Phanerozoic deposits have negative PC1 and positive PC2 (Figure 3a). Tourmaline from deposits hosted in metasedimentary rocks has negative PC1, with the exception of Rosebel (Fig. 3b). Tourmaline from deposits hosted in felsic to intermediate rocks has positive PC1 (Fig. 3b). Tourmaline from deposits hosted in rocks metamorphosed to greenschist facies and those from deposits hosted in rocks metamorphosed at upper greenschist to lower amphibolite facies are not distinguished by PC1 and PC2 (Figure 3c).

PCA of tourmaline from orogenic gold deposits from this study and from various deposit types and geological environment from the literature, using two different sets of trace elements, is shown in figures 4 and 5. In figure 4, the principal components PC1 and PC2 represent 32.5 % and 24.4 % respectively, of the total variance. PC1 is defined by positive contributions of Zn, Ga and Sr and negative contributions of Zr and Ba. PC2 is defined by positive contributions of Sn and Pb and negative contributions of Cr and Sr. Tourmaline from orogenic gold deposits has dominantly positive PC1 but is not discriminated by PC2. Tourmalines from the Berry-Havey pegmatite (Maine, USA), the Tsa da Glisza Emerald deposit (Yukon, Canada) and the Scharzwald hydrothermal veins (Germany) have negative PC1 and positive PC2. Tourmaline from the Roberto pegmatite has negative PC1 and negative PC2. The Yunlong Sn skarn deposit (Yunnan, China) tourmaline has negative PC1 and negative PC2.

6 Discussion and preliminary conclusion

In tourmaline from the Val-d’Or district, Grzela (2017) noted a variation in the REE patterns in the rim and the core of tourmaline. However, both patterns are present in tourmaline cores from other orogenic gold deposits. The HREE enriched pattern was recognized in the Hutt (Hazarika et al. 2015) and Mt Gibson (Jiang et al. 2002) Mo porphyry (Washington, USA). Tourmalines from Volcanogenic Massive Sulfides (VMS) and from the Dachang Sn-Pb-Zn stratiform deposit (Guangxi, China) have negative PC1, and positive PC2, whereas those from the Qitianling batholith (Guangxi, China) have positive PC1 and positive PC2. In Figure 5, the principal components PC1 and PC2 represent 29.0 % and 16.2 % respectively, of the total variance. PC1 is defined by positive contributions of V, Sc, Sr and Co and negative contributions of Zr and Y. PC2 is defined by positive contributions of Zn, Pb and Cu and negative contributions of Y and Zr. Tourmaline from orogenic gold deposits has dominantly positive PC1 but is not discriminated by PC2. Tourmalines from the Berry-Havey pegmatite (Maine, USA), the Tsa da Glisza Emerald deposit (Yukon, Canada) and the Scharzwald hydrothermal veins (Germany) have negative PC1 and positive PC2. Tourmaline from the Roberto pegmatite has negative PC1 and negative PC2. The Yunlong Sn skarn deposit (Yunnan, China) tourmaline has negative PC1 and negative PC2.

Figure 5. PCA with Sc, V, Co, Cu, Zn, Sr, Y, Zr, Sn and Pb for tourmaline from different deposit types.
orogenic gold deposits. The 3 REE patterns from orogenic gold deposit tourmaline are also found in various mineral deposits and geological environment including Cu-Mo porphyry (Iveson et al. 2016), Sn deposit (Jiang et al. 2004), VMS deposits (Roberts et al. 2006) and granitic batholiths (Duchoslav et al. 2017; Yang et al. 2015). The REE patterns in tourmaline from orogenic gold deposits contrast strongly with those from pegmatite that have a strong HREE depleted pattern, with a strong negative europium anomaly (Copjakova et al. 2015; Bacik et al. 2012).

Based on the Mg content in tourmaline from the Big Bell and the Mount Gibson orogenic gold deposits, Jiang et al. (2002) suggested that tourmaline trace element composition is dominated by that of the fluid rather than that of the hostrocks. Hydrothermal fluids in orogenic gold typically consist of aqueous-carbonic fluid with a low salinity (Goldfarb et al. 2005). Thus, we infer that the similar trace element composition in tourmaline from orogenic gold deposits, formed in different hostrocks of felsic to mafic composition reflects the gold-bearing-hydrothermal fluid composition and that the various geological parameters such as composition and metamorphic facies of the hostrock and age of mineralization are not major controls on the trace element signature of orogenic gold deposit tourmaline, consistent with Jiang’s et al. (2002) assertions. Therefore, the 3 REE patterns must then indicate different types of fluid sources that can be found in various orogenic gold deposits. Tourmaline from orogenic gold deposits have different trace element compositions compared to tourmaline from other deposit types and host rocks (Figs. 4 and 5), formed under different conditions and in different geological settings. Thus, trace element composition allows to discriminate between tourmaline from orogenic gold deposits and from other environments. Tourmaline trace element composition could be used for provenance studies using indicator minerals in overburdened sediments.

Acknowledgements

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Petrographic and μ-XRF study of the Kam Group lithologies in the Au-bearing Yellowknife greenstone belt, Northwest Territories, Canada

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Abstract. The Yellowknife greenstone belt (YGB) is located in the southwestern portion of the Archean Slave craton in the Northwest Territories, Canada. It is host to the historic Giant and Con mines which have produced a combined 13.5 Moz (383 t) of gold. Both of these deposits occur in the metavolcanic sequences of the Kam Group, which is part of the larger Yellowknife Supergroup. North of the Giant and Con deposits there are other gold showings that are also hosted by the Kam Group. To gain a better understanding of this unit, six major lithologies were sampled and studied. The study began with felsic porphyries from the Hebert-Brent gold showing, but also includes mafic flows, felsic tuffs, cherts, mudstones, and gabbro dykes. Optical petrography was used in conjunction with micro X-Ray Fluorescence to identify the dominant mineralogy and textural relationships in polished thin sections. Multi-element distribution maps display the relationships between the dominant phases of the porphyry samples, in this case quartz and sericitized feldspar phenocrysts set in a microcrystalline groundmass of quartz, calcite, and muscovite. Zirconium distribution maps indicate grains of zircon that may be further analysed to establish the timing of these porphyries in relation to the Kam Group.

1 Introduction

The Archean Slave craton is dominated by granitoid and supracrustal rock assemblages ranging from 4.05 to 2.55 Ga (Bleeker et al. 1999 and references therein). The Yellowknife greenstone belt (YGB) is located within the southwestern part of the craton in the Northwest Territories, Canada. The Archean Slave craton has been divided into the Central Slave Basement Complex which is overlain by the Yellowknife Supergroup. The Yellowknife Supergroup is host to the YGB and is further divided, from west to east, into the Central Slave Cover Group, Kam Group, Banting Group, Duncan Lake Group, and finally an Unnamed Group that partly consists of the unconformable Jackson Lake Formation (Bleeker et al. 1999). The Jackson Lake Formation is a Timiskaming-type sequence of polymictic conglomerates, cross-bedded sandstone, and argillite that occurs on the eastern margin of the belt (Martel and Lin 2006). Overall the stratigraphy trends northeast, dips vertically to south-easterly, and youngs to the southeast. The western margin of the Kam Group is intruded by the Ryan Lake pluton (2675 Ma), Defeat plutonic suite (2630-2620 Ma), and the Duckfish Granite (2608 Ma).

The YGB has been extensively explored and mined since the initial gold rush in the 1930’s and 1940’s and is still part of an active exploration program carried out by TerraX Minerals Inc. Historic mining includes the Giant and Con gold mines, which have produced a total of more than 13.5 Moz (383 t) gold and the Discovery Mine which produced just over 1 Moz (28 t; Bullen and Robb 2006). Both free-milling and refractory gold can be found at the Giant and Con deposits. The free-milling gold is part of a native gold, gold-pyrite, gold-pyrrophotite, or gold-base metal assemblage while the refractory gold is dominantly hosted by arsenopyrite, and pyrite to a lesser extent (Siddorn et al. 2006). The Giant deposit contains mainly refractory gold in arsenopyrite that is disseminated in quartz-ankerite-paragonite schists or laminated quartz veins. The Con deposit hosts both types of gold in a series of quartz-carbonate veins and schists.

While the Discovery mine is hosted in a turbidite sequence, the Giant and Con deposits are hosted in sericite- and chlorite-rich alteration and deformation zones in the metavolcanic sequences of the Kam Group, separated by the Proterozoic West Bay Fault (Siddorn et al. 2006). This study will focus on the major lithologies of the Kam Group found within TerraX Minerals’ Northbelt property. Petrographic and mineral chemistry studies will be used to characterize the various mafic and felsic metavolcanics, as well as cross-cutting mafic dykes and felsic intrusions.

2 Methods

Surface and core samples were collected from six major lithologies throughout the Northbelt property, which include: massive and pillow mafic flows, felsic tuffs, gabbro dykes, felsic porphyries, cherts and mudstones. Each sample was photographed and submitted for thin section preparation at the University of New Brunswick; select samples were made into polished slabs.

Micro X-Ray Fluorescence (μ-XRF) is a non-destructive technique that was used for the initial textural analysis of the dominant mineralogy of each thin section. The sample is placed in a vacuum sealed chamber and a Rh
tube is used to produce X-rays that are rastered across the sample to generate a characteristic X-ray fluorescence. A full spectrum of elemental data is collected for each analysed spot. The complete µ-XRF analysis took 3-3.5 hours to finish using 30-50 kV and 300-400 A; the conditions vary based on the size of the area being analysed. The images shown in the results section are multi-element images that show each selected element as a specific colour, in areas where two or more elements occur together, the colours will add.

In conjunction with the µ-XRF technique, optical petrography and image analysis software were used to fully identify the minerals present and take accurate measurements of individual grains (ImageJ; Abramoff et al. 2004). Petrography was carried out on a Nikon Eclipse E600 polarizing microscope and subsequent photomicrographs were taken using a Zeiss AxioImager microscope. Plain polarized light (PPL), cross-polarized light (XPL) and reflected light (RFL) were all required to identify and describe the silicates, sulphides and oxides in each thin section.

3 Preliminary results

Although this study is ongoing, some preliminary results regarding felsic porphyries are detailed below. The investigation began with porphyries from one target within the YGB, the Hebert-Brent gold showing. The showing is located < 2 km northeast of the Crestaurum mine shaft and is hosted in bleached mafic volcanics that are locally pillowed, with associated deformed chert and mudstone horizons. There are two types of porphyries present, quartz feldspar porphyries (QFP) and feldspar quartz porphyries (FQP), as well as gabbro intrusions. This area is of particular interest because of the style mineralization that was found. Within the YGB, the historic Con and Giant mines consist of shear-zone and quartz vein-hosted gold, which is also the case for the Crestaurum deposit that is less than 2 km away from the Hebert-Brent showing which consists of replacement-style mineralization. Porphyries from the Hebert-Brent showing were chosen as the first to be examined because of their proximity to mineralization and their potential for age dating. As the study continues, the remaining mafic and sedimentary lithologies at the Hebert-Brent showing will be examined and then compared to other samples from the belt.

One of the benefits of the µ-XRF technique is the ability to analyse multiple samples at once, which allows us to compare textures in one image. Figures 1 and 2 are qualitative element distribution maps of two felsic porphyry samples from the Hebert-Brent showing.

The elements shown in figure 1 include Si, K and Ca and dominantly correspond to quartz, muscovite and calcite, respectively. The dominant phenocryst in the QFP is quartz with abundant aggregates of calcite and minor muscovite disseminated throughout the matrix (Fig. 1a). The quartz phenocrysts have a subrounded to amoeboid shape. In contrast to this, the FQP in figure 1b has phenocrysts that are dominantly potassic with a subangular and often rectangular shape. Calcite is almost exclusively associated with a quartz vein on the right margin of the thin section. Upon petrographic examination of the FQP, the potassic phenocrysts were found to be sericitized feldspars.

Figure 1. Multi-element µ-XRF images illustrating the distribution of Si (green), K (pink), and Ca (orange) in two thin sections from the Hebert-Brent showing. The corresponding elements and colours are shown in the bottom left corner of Figure 1a. Images are 2.5 cm by 4 cm. a QFP, b FQP.

Figure 2 shows the distribution of Fe and S which is of particular interest when searching for sulphides. When Fe and S are found in the same mineral, the colours will ‘add’ together. In this case the yellow and blue add together and display a blue-grey colour which represents Fe-sulphides in the thin sections. Fe-sulphides are less abundant in the QFP sample (Fig. 2a) compared to the FQP (Fig. 2b), however there are many areas of the thin sections that are simply Fe-rich. The thin sections were further examined microscopically to determine which phases are represented by the remaining Fe shown in figure 2a. The Fe present in the QFP sample corresponds to Fe-Ti oxides and chlorite. The remaining Fe observed the FQP sample was almost exclusively found to be Fe-Ti oxides.
Finally, µ-XRF data was collected on a second QFP sample from the Hebert-Brent showing and processed to show the relative abundance of Zr and P (Fig. 3a and b). This is illustrated on a sliding scale where reds represent areas that the selected element is detected, and blues indicate areas that the element was not detected. In this case, Zr and P were chosen because they are abundant elements found in zircons and apatite, two minerals that can be dated by U-Pb geochronology (Jackson et al. 2004; Chew et al. 2011). Therefore, the red ‘hot spots’ disseminated throughout figures 3a and 3b represent possible zircon and apatite grains. µ-XRF images such as these show the textural context of zircon and apatite grains before they are analysed in situ by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). Figure 3 also illustrates the size distribution of zircons and apatite grains in the field of view. Zircon grains range in size from 20 to 110 µm and apatites range from 50 to 260 µm in width. Grain size is an important feature to characterize as it is a limiting factor in LA-ICP-MS analysis.

Examining µ-XRF images processed in this manner is particularly helpful in altered and microcrystalline samples such as these felsic units. Subsequent analysis of the zircon and apatite grains by SEM-EDS will confirm their size and composition before in situ U-Pb geochronology by LA-ICP-MS takes place. This will help establish the timing of each felsic unit and relate them to the overlying volcaniclastic units of the Townsite and Banting formations.

4 Discussion and future work

The focus of this study is to characterize the major lithologies of the Kam Group within TerraX Minerals’ Northbelt property through petrographic and mineral chemistry studies. At this point, the study has focused on felsic porphyries from the Hebert-Brent showing, north of the Crestaurum mine shaft. µ-XRF data collected from polished thin sections can show elemental associations when multi-element images are generated from the data. When used in conjunction with optical petrography, the same µ-XRF images are indicative of the dominant mineralogy in a sample. In this case, the phenocrystic phases (quartz and sericitized feldspar), groundmass (quartz, calcite, and muscovite), Fe-sulphides, and possible zircons can all be observed in three images (Figs. 1-3). However, due to the microcrystalline nature of the samples, additional microanalytical techniques will be
required to identify all of the phases present.

Future work for this study will include: (1) detailed imaging and textural analysis of lithologies that are either proximal to or hosting gold mineralization. This may allow us to define specific events that are related to mineralization which is important in narrowing the list of exploration targets; (2) the collection of mineral chemistry data of silicates, sulphides, and oxides to establish any differentiating characteristics between the Kam Group lithologies; (3) evaluation of zircons and apatites identified through μ-XRF for U-Pb geochronology, and subsequent analysis of those grains.

Acknowledgements

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References

The Gaching Au mineralization in the Maletoivayam ore field, Kamchatka, Russia

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Abstract. Samples from the Gaching Au mineralization from the Maletoivayam ore field, Kamchatka, were studied. The vein hosted and disseminated pyrite at Gaching is associated with Au-bearing minerals in intensely oxidized quartzite and quartz-alunite altered rocks. Noble metal mineralization is represented by native gold (15%) and Au compounds with Te, Sb, As, Se, and S (85%). Gold forms xenomorphic grains (10-50 μm), orange-brown in color, and with porous structure, which is known as “mustard” gold. The gold may contain minor Fe occurring as pore filling iron hydroxides. The main Au- and Ag-bearing minerals are calaverite, krennerite, unnamed \(\text{Au}_2\text{Te}_4(\text{Se},\text{S})_3\) and Au-Fe-Ag-Sb-As-Te oxide with variable element ratios (grains up to 60 μm). The \(\text{Au}_2\text{Te}_4(\text{Se},\text{S})_3\) phases (both Se-, and S-rich) found at Gaching, have not been reported before in nature. However, the synthetic analogue of the phase \(\text{Au}_2\text{Te}_4\text{Se}_3\) was reported. The phase \((\text{Au,Fe})_3(\text{Sb,As})\text{O}_6\) exists as a stable Au-Ag oxide. Gold mineralization is associated with tetrahedrite, tennantite, goldfieldite, native tellurium, bismite, guanajuatite, rooseveltite, and tripuhyite. The sequence of crystallization for the Au-Ag mineralization is as follows: (1) Au-Ag alloys and Au-Ag-sulfo-seleno-telluride with associated fahlore; (2) complex Au-Ag-oxides containing Sb and As, unnamed \(\text{Au}_2\text{Te}_4(\text{Se},\text{S})_3\), and hessite in association with native tellurium and fahlore; and (3) high-grade mustard gold.

1 Introduction

The Gaching Au mineralization in the Maletoivayam ore field is located in the Eocene-Oligocene central Kamchatka volcanic belt. Gold-silver mineralization in the Maletoivayam ore field belongs to high-sulfidation epithermal type (Okrugin 2003, Melkomukov et al. 2010, Kalinin et al. 2012). The vein and disseminated mineralization in the ore field includes pyrite, native gold and Au-Ag-tellurides in association with various sulfosalts of Cu, Fe, and Zn in quartzites and quartz-alunite altered rocks. The ore zones in epithermal deposits typically contain as much as several hundreds of ppm Au. The Au grade of occurrences in the Maletoivayam ore field locally reaches 8.8 ppm (Melkomukov et al. 2010) and ranges between 0.1 and 144 ppm according to data of the Karamkenskaya Geological and Geophysical Expedition (http://kgge.ru/?page_id=443). The deposit was formed in multiple-stages such that the mode of the gold occurrences varied during the evolution of the ore-forming system and under the influence of long-term superimposed processes such as oxidation and secondary enrichment.

We have studied gravity concentrates and also high oxidized samples from our gravity enrichment experiments collected from the Maletoivayam ore field. In this contribution, we present the first mineralogical data from the Gaching mineralization.

2 The Gaching gold ores

2.1 Characteristics of the Gaching gold occurrence

The studied samples were collected from intensely oxidized quartzite and quartz-alunite altered rocks. The Gaching area within the Maletoivayam ore field is located in the southwestern part of the Koryak Highland, Kamchatka. Structurally, it belongs to the central part of the Vetrovayam volcanic zone of the northeastern Central Kamchatka volcanic belt. The Gaching occurrence, located at the head of the Gachingalhovayam River, represents a quartz stockwork hosted by the secondary quartzites and intensely oxidized quartz-alunite rocks. The vein quartz contains Au concentrations that are unevenly distributed and can vary over a wide range from 0.1 to 140 ppm. The study of the heavy fractions of Au- and Ag-bearing rocks has shown that there is a high pyrite content. More than 80% of pyrite is present as coarse grains ranging from a few tens of micrometers to 0.25 mm in diameter. The ore minerals at the Gaching are always associated with white quartz, whereas grey quartz, which is common in other parts of the Maletoivayam ore field, is absent. The degree of oxidation of the rocks varies from medium to high.
2.2 The mode of Au occurrence

Gold mineralization at Gaching occurs in two main forms. Native gold (15%) is predominantly intergrown with fahlore and complex Au-bearing oxides. More commonly, gold forms compounds with Te, Sb, As, Se, and S that are generally oxidized to varying degrees (85%). Native gold is brown-yellow to brown under reflected light and occurs in grains up to 10-20 or locally 50 μm in diameter (Fig. 1). Grains of native gold are xenomorphic with a lumpy shape, porous, and have loose structure (mustard-gold). Gold grains often are intergrown with other minerals, such as tetrahedrite and goldfildite (Fig. 1d).

Table 1. Composition of gold (wt.%)

<table>
<thead>
<tr>
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<th>Fe</th>
<th>Total</th>
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<td>99.51</td>
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<td>7</td>
<td>96.21</td>
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</tr>
</tbody>
</table>

Figure 1. Native gold from the Gaching occurrence (polished sections). a reflected light. b-d SEM images. b high-grade oxidized. d gold-silver alloy intergrown with tetrahedrite.

Native gold at Gaching is subordinate in abundance compared to other Au- and Ag-bearing minerals. High-purity native gold is common, but may contain minor amounts of Ag and Fe (Table 1). Therefore, the fineness of gold varies in the range of 931-1000. The minor concentration of Ag in gold is of a primary character, whereas the Fe is due to mechanical impurities of iron hydroxides that fill the pores in mustard gold.

The main minerals from the Gaching Au±Ag association are Au (±Ag) -selenotellurides that include calaverite, krennerite, and an unnamed Au$_2$Te$_4$(Se,S)$_3$ (Table 2-3.). They are commonly intergrown with each other, and are found in association with tetrahedrite, Se-rich tellurium, and triphyllite (Table 2). The grain sizes for the Au (±Ag) -selenotellurides do not exceed 60 μm. Krennerite contains up to 3.94 wt.% Ag (Table. 3), and both minerals (calaverite, krennerite) contain 1.25-1.97 wt.% Se. The Au$_2$Te$_4$(Se,S)$_3$ is a new phase, which has not been reported before in nature. However, the synthetic phase Au$_2$Te$_3$Se$_2$ was reported from the experimental study of Wang (2000). This phase is a potentially new mineral, that seems to have both Se- and S-rich end-members (Table 3).

Table 2. Au-Ag minerals and unnamed phases from the Gaching mineralization

<table>
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<tr>
<th>Minerals</th>
<th>Compositions</th>
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<td>Gold</td>
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<tr>
<td>Calaverite</td>
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<td>Krennerite</td>
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<tr>
<td>Non-stoichiometric</td>
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* - unnamed phases repeatedly found

Table 3. Composition of Au-Ag minerals from the Gaching ore occurrence

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<tr>
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The data were obtained from the EDS spectrometer. 1-4 - krennerite, 5,6 - calaverite, 7-11 unnamed phase Au$_2$Te$_4$(Se,S)$_3$.
1. \((\text{Au}_{0.95}\text{Ag}_{0.05})_{0.01}(\text{Te}_{1.02}\text{Se}_{0.98})_{1.00}\)
2. \((\text{Au}_{0.95}\text{Ag}_{0.05})_{0.01}(\text{Te}_{1.02}\text{Se}_{0.98})_{1.00}\)
3. \((\text{Au}_{0.95}\text{Ag}_{0.05})_{0.01}(\text{Te}_{1.02}\text{Se}_{0.98})_{1.00}\)
4. \((\text{Au}_{0.95}\text{Ag}_{0.05})_{0.01}(\text{Te}_{1.02}\text{Se}_{0.98})_{1.00}\)
5. \(\text{Au}_{0.99}\text{Te}_{0.01}\)
6. \(\text{Au}_{0.01}\text{Te}_{0.01}\text{Se}_{0.99}\)
7. \(\text{Au}_{1.00}\text{Te}_{4.12}(\text{Se}_{1.45}\text{S}_{0.57})_{2.84}\)
8. \(\text{Au}_{1.95}\text{Te}_{4.14}(\text{Se}_{2.02}\text{S}_{0.77})_{2.79}\)
9. \(\text{Au}_{2.07}\text{Te}_{4.14}(\text{Se}_{2.45}\text{S}_{0.52})_{2.70}\)
10. \(\text{Au}_{1.98}\text{Te}_{4.14}(\text{Se}_{2.52}\text{S}_{0.79})_{2.03}\)
11. \(\text{Au}_{2.01}\text{Te}_{4.01}(\text{Se}_{2.02}\text{S}_{0.92})_{2.97}\)

Figure 2. SEM images of Au (±Ag) minerals from the Gaching mineralization. a krennerite \((\text{Au,Ag})(\text{Te,Se})\); intergrown with S-bearing tellurium and goldfildite. b intergrowth of krennerite \((\text{Au,Ag})(\text{Te,Se})\); and unnamed \(\text{Au,Te}_2(\text{Se,S})\). c krennerite with complex Au-oxide. d calaverite partly replaced by Au-oxide and tripuhyite \((\text{FeSbO}_3)\).

The majority of Au compounds occur in oxidized forms of complex composition \((\text{Au-Fe-Ag-Sb-As-Te-O})\) with variable element ratios (Table 2). They are characterized by replacement textures with relicts of primary minerals (Fig. 2 c,d). The colloform aggregates of Au-oxides are also common (Fig. 1c). In addition to non-stoichiometric compositions \(\left[(\text{Au,Ag})-(\text{Sb,Te})-\text{O}\right]_\text{c,d}; \text{Te}}\), there are oxides with compositions that are almost identical from grain to grain and have the general formula \((\text{Au,Fe})_2(\text{Sb,As})\text{O}_6\). They may contain minor amounts of Cu, Ag, Te and Se. This stable composition can be interpreted as potentially defining a new mineral. Its stoichiometric formulas are:

\begin{align*}
(\text{Au}_{1.10}\text{Fe}_{0.89}\text{Sb}_{0.89}\text{As}_{0.08})_{0.01}(\text{Sb}_{0.67}\text{As}_{0.24}\text{Te}_{0.08}\text{S}_{0.06})_{0.01} & \text{O}_{6.02} \\
(\text{Au}_{1.10}\text{Fe}_{0.64}\text{Sb}_{0.64}\text{As}_{0.08}\text{Te}_{0.12})_{0.01}(\text{Sb}_{0.65}\text{As}_{0.19}\text{Te}_{0.10}\text{S}_{0.08})_{0.01} & \text{O}_{6.02} \\
(\text{Au}_{1.10}\text{Fe}_{0.93})_{0.01}(\text{Sb}_{0.70}\text{As}_{0.21})_{0.01} & \text{O}_{6.01}
\end{align*}

2.3 Associated minerals

Pyrite is the most common mineral in all studied samples. It is characterized by an irregular distribution in quartzite. It may occur in the form of isolated single grains or as clustered disseminations. Intergrowths of pyrite with gold or Au- and Ag-bearing tellurides were not observed because the pyrite was formed, most likely, during the early stage of the ore-forming process. However, Au-Ag- minerals were found in close association with fahlores: tetrahedrite \((\text{Cu}_{10.50}\text{Zn}_{0.03})\text{Fe}_{0.03}\text{Fe}_{0.07})_{11.96}(\text{Sb}_{2.60}\text{As}_{0.75}\text{Te}_{0.63})_{3.96}\text{S}_{12.82}\), tennantite \((\text{Cu}_{9.89}\text{Fe}_{0.07})_{0.96}(\text{As}_{3.43}\text{Te}_{0.49}\text{Sb}_{0.22})_{4.14}\text{S}_{13.90}\), goldfildite \(\text{Cu}_{10.97}(\text{Te}_{1.91}\text{As}_{1.42}\text{Sb}_{0.71})_{4.14}(\text{S}_{11.15}\text{Se}_{3.86})_{12.99}\), as well as with other rare minerals such as native tellurium and its compounds with boron \((\text{Bi}_{2.83})\text{Te}_{2.83}\text{S}_{0.09}\), and selenium \(\text{Te}_{0.83}\text{Se}_{1.17}\), native bismuth, bismite \((\text{Bi}_{2.01}\text{O}_{3.98})\), guanajautite \((\text{Bi}_{2.01}\text{Se}_{1.17})\), rooseveltite \((\text{BiAsO}_4)\), tripuhyite \((\text{FeSbO}_4)\), and different unnamed phases: \(\text{Fe}_2(\text{Sb,Te,As})_4\text{O}_{13}\), \((\text{Fe,Fe}_{1/2}\text{As,Te})\text{O}_{13}\), \((\text{Fe,Fe}_{1/2}\text{As,Te})\text{O}_{13}\).

3 Discussion

The mineral associations from the Gaching ores of the Malatoivayam ore field have been studied in detail for the first time. The study showed that the mineral association at Gaching is comparable with other previously studied deposits of Kamchatka, such as Aginskoye and Ozernovskoye (Kudaeva and Andreeva 2012). In these deposits, and similar to Malatoivayam, a significant proportion of the precious metals are hosted as Au-Ag- tellurides that are associated with fahlores and native mustard gold, and that formed from the destruction of early-stage Au-tellurides (Kudaeva and Andreeva 2012).

The mustard gold is formed in the supergene environment in gold-silver-telluride deposits during the oxidation of the gold-bearing tellurides (Nekrasov 1991). It appears as a porous and powdery brown and brick-red...
mass, although with some more metallic-like fragments (Fig. 1a). It is composed of aggregates of microparticles, up to 1-5 μm in diameter and with low reflectivity. Iron hydroxides may form precipitates in numerous pores of mustard gold in the supergene zone, thus causing the formation of mechanical impurities in what can be termed “Fe-bearing gold”. Petersen et al. (1999) and Zhao et al. (2009) found that mustard gold is formed by the destruction of Au- and Ag-bearing tellurides.

Experiments on the kinetics of transformation of Au-rich tellurides showed that oxidation of calaverite (AuTe$_2$) takes place at 220°C and Au is redeposited as mustard gold (Zhao et al. 2009), whereas Te is precipitated in native form. This process is, most likely, responsible for the formation of mustard gold in the Gaching ores. This process may occur in several stages, because the primary Au-Ag-tellurides (krennerite, calaverite) are first oxidized to form complex oxides. The oxides involve the addition of Fe, Sb, As, and (or) S, which were probably remobilized by the later stage hydrothermal fluids. At the same time, Ag and Te in krennerite are released to form newly precipitated native tellurium, BTe$_3$ and hessite. The observed mineralogical sequence differs from that described for similar epithermal gold-telluride deposits such as Kochbulak-Karagach in Uzbekistan and Bereznyakovskoe deposit in the southern Urals (Plotinskaya and Kovalenker, 2008). In those deposits native tellurium and high-grade gold are interpreted to have crystallized in the early hydrothermal stage.

It should be emphasized that in addition to the above-listed oxides, some new phases, such as the unnamed phase Au$_4$Te$_4$(Se,S), which had not been previously reported from other gold deposits, appear in the Gaching ores. This particular new phase is characterized by the mutual substitution between S and Se and thus both sulfur- and selenium-rich species are present (Table 3).

4 Conclusions

Mineralogical study of the Gaching ores of the Maletoivayam ore field resulted in the definition of three paragenetic stages:
- first, Au and Ag are concentrated in two forms, as Au-Ag-tellurides (seleno-tellurides) and Au-Ag alloys with low Ag content (2-3 wt.%)
- second, the noble metals are present as complex (Au,Ag) - (Sb,As,Se,S) - O compounds and as newly-formed sulfide- and seleno-gold tellurides and hessite
- third, all of the Au-bearing minerals are transformed into high-grade mustard gold.

Acknowledgements

Financial support through an internal project from the Czech Geological Survey is gratefully acknowledged.

References

Geology of the 4.2 Moz Au Amaruq project, Nunavut

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Abstract. The Amaruq gold project is located 50 kilometers NW of the Meadowbank gold mine, within the Rae Domain of the Churchill Province, in Nunavut, Canada. The Amaruq area consists of Archean supracrustal rocks of the Woodburn Lake group (ca. 2.71 Ga), which comprises intercalated mafic-ultramafic rocks, greywacke, chert and silicate-facies iron formation. Two principal gold zones are recognized and comprise different types of ore. The Whale Tail zone is primarily characterized by stratabound to locally discordant, disseminated to semi-massive pyrrhotite – arsenopyrite – loellingite – gold associated with “silica flooding” in chert and iron formation. The IVR zone, north of the Whale Tail zone, outcrops in a fold hinge zone where three phases of deformation are documented. Although chert and iron formation replacements are present, the IVR zone predominantly consists of shallowly SE-dipping quartz ± carbonate veins associated with potassic and carbonate alteration along high strain corridors. At the IVR zone, several sets of veins are documented and contain gold, arsenopyrite, and traces of galena. Crosscutting relationships indicate that the quartz ± carbonate veins predate or are coeval with the development of the main foliation (S_p). Folded mafic-ultramafic and chemical sedimentary rocks, and deformation corridors are the main controls on ore distribution at Amaruq.

1 Introduction

The Amaruq gold project is 100% owned by Agnico Eagle Mines Ltd. (AEM), with a total resource of 4.23 million ounces of gold at 4.59 g/t. The Amaruq project, currently in a development phase, is located 50 kilometers NW of the Meadowbank mine and 120 kilometers NW of Baker Lake in the Kivalliq region of Nunavut, Canada (Fig. 1).

Early work in the area showed that the mineralized zones have a complex geometry, are structurally controlled and are hosted in complexly folded and faulted volcanic and sedimentary rocks, including chert and iron formation (Côté-Mantha et al. 2015). Ongoing research at Amaruq aims at documenting the geology of the deposit and at establishing the principal lithologic and structural controls on ore genesis and gold distribution, and at defining the relative timing of events. Relevant observations about the structural setting of the mineralized zones at Amaruq, and preliminary interpretations about the controls on ore, are presented here.

Figure 1. Location of the Amaruq project, 50 km NNW of the Meadowbank mine in Nunavut.
2 Local geological setting

The Amaruq area is underlain by the Archean supracrustal rocks of the Woodburn Lake group (ca. 2.72-2.71 Ga), within the Rae Domain of the Churchill Province. The Woodburn Lake group is part of a greenstone belt that was deformed and metamorphosed at Archean and Paleoproterozoic times (Pehrsson et al. 2013).

In the study area, the Woodburn Lake group comprises a complexly deformed, ~250 m-thick band of mafic and ultramafic volcanic and intrusive rocks intercalated with greywacke, chert and silicate-facies iron formation (Fig. 2). This volcano-sedimentary succession is bounded by plagioclase-quartz-biotite-sericite greywacke.

Two principal gold zones, located in distinct structural domains, are present on the Amaruq property, i.e. the Whale Tail and IVR zones (Fig. 2), which comprise distinct types of ore and alteration.

![Figure 2. Simplified geological map a and cross section b of the Amaruq area, with the location of the Whale tail and IVR zones (modified from AEM 2016).](image)

3 Hydrothermal alteration and veins

The Whale Tail zone is primarily characterized by stratabound (Fig. 3a) to locally discordant, disseminated to semi-massive pyrrhotite - arsenopyrite - loellingite - gold associated with replacement-style zones of “silica flooding” in chert and silicate-facies iron formation layers (Fig. 3b). These mineralized zones are folded and form steeply dipping to subvertical ore bodies up to 90 m-thick. Gold is spatially associated with arsenopyrite, loellingite (Lauzon et al. 2017) and pyrrhotite (Fig. 3c).

The IVR zone outcrops 300 meters NE of the Whale Tail zone (Fig. 2), in a fold hinge zone where three phases of deformation are documented. Although chert and iron formation replacement-type mineralization is present, the IVR zone predominantly consists of folded, shallow SE-dipping sulphide-poor quartz ± carbonate veins in mafic to ultramafic and sedimentary rocks. Sericite, biotite and carbonate (calcite and ferroan dolomite) alteration affects the host rocks (Fig. 3d).

There are several types of auriferous veins at IVR: 1) fine-grained greyish, and deformed quartz ± carbonate veins containing arsenopyrite along the vein selvages, and locally visible gold; 2) medium- to coarse-grained whitish to greyish recrystallized and laminated quartz ± galena - visible gold veins; and 3) less frequent, and often barren, undeformed coarse-grained white quartz veins (Fig. 3e, f).
Preliminary structural analysis of the IVR zone shows that the main phase of deformation ($D_p$) is represented by a moderately to steeply SE-dipping schistosity ($S_p$), by shallow-plunging ($0-30^\circ$) tight to isoclinal folds (Fig. 4a), and by NW-verging thrust faults. $D_p$ is affected by a shallow dipping crenulation cleavage associated to $D_{p+1}$ (Fig. 4b, c), and by open to closed folds and crenulation lineation plunging towards the NE or the SW.

In this structural context, the main auriferous veins are deformed (Fig. 4d, e), while the relative timing of emplacement of the other vein sets remains under investigation. Both the vein- and replacement-style orebodies are characterized by east-plunging ore shoots. Correlations between the IVR and Whale Tail zones, or structural domains, are still under study.

4 Structural geology

At Amaruq, the mineralized zones are affected by at least two phases of deformation, which seems to correspond to the Paleoproterozoic deformation described in the region, with peak metamorphic conditions at upper greenschist to lower amphibolite facies (Zaleski 2005).
Figure 4. Photographs of rocks and structures present at Amaruq. a Isoclinally folded (F_p) stratification (S_0) with axial planar pressure-solution cleavage (S_p). b Subhorizontal S_{p+1} crenulation cleavage affecting S_p schistosity. c Intersection lineations between S_{p}/S_{p+1} and S_{p}/S_{p+1}. d and e Folded and boudinaged recrystallized quartz veins are subparallel to S_p suggesting that they are pre-to syn-D_p.

5 Discussion and conclusion

The Amaruq property comprises major auriferous zones that are clearly distinct in style from other known gold occurrences in the region. Preliminary results indicate that the Amaruq gold system exhibits contrasting ore styles, with dominantly stratabound, replacement-style ore in the Whale Tail zone, and quartz ± veins in the IVR zone.

Crosscutting relationships indicate protracted hydrothermal activity, with extensive zones of silicification, and zones of carbonate, sericite and biotite alteration associated with deformed and recrystallized quartz ± carbonate veins. The relative timing of other vein sets is still under investigation and any genetic relationship with gold is under study. Mafic, ultramafic and chemical sedimentary rocks, together with the presence of arsenopyrite and folds and thrust faults are key controlling elements at Amaruq.

Ongoing research at Amaruq aims at better understanding the key ore-forming processes active in the area, and at defining their diagnostic characteristics, to help vector towards favourable environments for gold mineralization in the Churchill Province and other Archean terranes.

Acknowledgements

This work is part of a Ph.D thesis research by the senior author as part of the Targeted Geoscience Initiative (Gold project) of Natural Resources Canada. We thank Agnico Eagle Mines Ltd. for access to the property, to drill core and data, and for logistical and scientific support. MV acknowledges MITACS for financial support.

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Petrogenesis of scheelite at the Timmins West mine, Timmins, Ontario

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Abstract. Gold mineralization at the Timmins West Mine is hosted along the 144-trend. This is a structural zone that extends to the southwest from the Timmins deposit area. Mineralization at the Thunder Creek and Gap deposits is comprised of multiple generations of quartz-carbonate +/- scheelite and molybdenite veins, and is associated with syenitic and monzonitic intrusions. Gold is often found within scheelite and molybdenite veins, and is associated with mineralization. Here we propose to use the geochemistry of scheelite to place constraints on the origin of the gold mineralization.

Gold mineralization at the Thunder Creek and Gap deposits at the Timmins West Mine (TWM), Ontario, occurs largely within quartz veins that are hosted by syenitic-monzonitic intrusions. These intrusions have feldspathic and carbonate alteration. There are two main hypotheses, either the gold is genetically related to the syenite or it is related to later orogenic events that preferentially produced brittle fractures in the monzonite-syenite host. Scheelite is a common hydrothermal mineral found in gold deposits (Anglin et al. 1996; Raju et al. 2016). In this study the trace element geochemistry of scheelite will be used to constrain the source of W, and possibly the Au associated with it.

1 Introduction

Gold distribution in Archean gold deposits has a tendency to be highly erratic, this can often lead to erroneous deposit assessments (Raju et al. 2016). The strong deformation present in this deposit type makes it difficult to establish the relationships between magmatism, metamorphism and mineralization. Here we propose to use the geochemistry of scheelite to place constraints on the origin of the gold mineralization.

Gold mineralization at the Thunder Creek and Gap deposits at the Timmins West Mine (TWM), Ontario, occurs largely within quartz veins that are hosted by syenitic-monzonitic intrusions. These intrusions have feldspathic and carbonate alteration. There are two main hypotheses, either the gold is genetically related to the syenite or it is related to later orogenic events that preferentially produced brittle fractures in the monzonite-syenite host. Scheelite is a common hydrothermal mineral found in gold deposits (Anglin et al. 1996; Raju et al. 2016). In this study the trace element geochemistry of scheelite will be used to constrain the source of W, and possibly the Au associated with it.

2 Geology

The Timmins West Mine is comprised of three deposits: Timmins, 144-Gap and Thunder Creek (Fig 1). Both the Timmins and Thunder Creek deposits lies on the border of a north-east trending contact between the 2.7 Ga Tisdale assemblage to the northwest and the 2.6 Ga Porcupine assemblage to the southeast (Kallio and Vaz. 2016). This contact dips steeply to the northwest and is intruded by several alkaline ultramafic intrusions, as well as equigranular K-feldspar intrusions which range from monzonitic to syenitic in composition (Kallio and Vaz. 2016). These alkaline intrusive complexes are ~2687 Ma, similar in age to the Timiskaming assemblage (Kallio and Vaz. 2016). Samples were taken from the Thunder Creek and 144-Gap deposits. These two deposits are 1.5km apart (Campbell 2014; Kallio and Vaz 2016) but the mineralization in both are hosted by the same syenitic intrusions.

The syenitic intrusions are polyphase and range in texture from equigranular to porphyritic (Kallio and Vaz. 2016). Compositionally the intrusions have been labelled quartz-monzonite to syenite, though it is difficult to pinpoint due to the intense deformation (Kallio and Vaz. 2016). Alteration types include carbonate, potassic, feldspathic and silicic.

3 Mineralization

Gold mineralization at Thunder Creek and the 144-Gap deposit is hosted by multiple generations of quartz veins cross-cutting syenitic intrusions. Campbell (2014), describes the veins as V1 quartz veins, V2 extensional quartz veins, and V3 subvertical quartz veins. Quartz veins sampled in this study contained pyrite +/- molybdenite and scheelite. This fits the description of the V2 vein series in Campbell (2014). Although there is no intergrowth of the scheelite and gold, their spatial relationship is suggested to be temporal. V2 veins are the most important hosts of gold, thus the scheelite samples are also representative of the main stage of mineralization.

Scheelite (CaWO4), is a common hydrothermal mineral associated with quartz-carbonate gold deposits (Dube & Gosselin 2007). It is very useful for this application as it allows for the substitution of elements, particularly REE’s, into the Ca²⁺ bonding site (Anglin et al. 1996; Ghaderi 1999). This, along with the widespread presence of scheelite in Archean gold deposits, makes it an ideal candidate for tracing gold mineralization. By conducting various analyses the geochemistry of scheelite can reveal the source of the ore forming fluid, mechanisms of mineral growth and even the genetic type of deposit (Ghaderi et al. 1999).
Figure 1. Geology of the Timmins West Complex (Kallio and Vaz 2016).

Figure 2. Left: Scheelite in quartz vein cross cutting syenitic host rock. Right: Scheelite under short-wave ultra violet light. Sc = scheelite, Sy = syenite, Py = pyrite, Qz = quartz.

Figure 3. Scheelite and visible gold in a quartz vein cross-cutting syenitic host rock. Sc = scheelite, Sy = syenite, Qz = quartz. VG circled in red.
4 Methods

Four scheelite grains from V₂ quartz veins cross-cutting the syenite were selected based on size, spatial relationship to Au and lack of inclusions. Powdered whole rock samples from the syenite were also taken. Samples were collected from wall rock at 555m depth at the Thunder Creek deposit, and from drill core at both the Gap and Thunder Creek deposits.

The four selected scheelites were first analysed using JEOL (benchtop-SEM) to make an inventory for inclusions in the grains. Thick sections were then analysed by cathodoluminescence (CL) and wavelength dispersive spectroscopy (WDS) mapping using a JEOL JXA-8530F electron microprobe at Western University. Trace elements of the scheelites were then determined by laser ablation ICP-MS using a NWR 193 UC laser ablation system and an Agilent 7900 ICP-MS using thick sections at the University of Toronto. A beam size of 49µm at 10Hz with dwell times of .05s to .02s for Hf measurements and 10ms to 20ms for Th and U.

Three whole rock samples were produced from the crushing and milling of syenitic host rock cut from cores. Samples were dissolved using acid digestion on a hot plate. A combination of HCl, HNO₃, and HF were used to completely dissolve rock samples over the course of 4 days. HClO₄ was then used to dissolve any remaining fluorides. Samples were then dried down and taken up in 2% HNO₃ and analyzed by quadrupole inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo Scientific iCAP Q in the GEOMETRIC lab at Western University for trace element concentrations. Powdered samples were analysed by x-ray fluorescence (XRF) to obtain major element concentrations.

5 Results

Cathodoluminescence mapping revealed a lack of zoning and minimal inclusions in 3 of the 4 grains. Overall element concentrations from WDS mapping were homogeneous throughout scheelite crystals. Inclusions were plagioclase (albite) and tended to be very small (<100µm). Concentric zoning was seen in one of the scheelite grains (Fig 4). Later analysis of a transect taken through the grain revealed no consistent patterns in the major or trace element data throughout the zonations. Therefore, this is likely a growth zonation pattern.

Trace element data measured by LA-ICP-MS and quadrupole ICP-MS were normalized to CI chondrite values from Sun and McDonough (1989), results can be seen in Fig 5. In the scheelite samples a convex REE pattern is observed, the maximum being at Eu-Gd. No Eu anomaly is observed or a minor positive, which could imply an oxidizing environment during formation.

The whole rock data shows a smooth, almost concave form of the graph. Lower concentrations of REE in the whole rock where there is enrichment in scheelite could imply movement between the two. Trace element data was compared to the range of concentrations found in orogenic (metamorphic) scheelites from the study of Poulin (2016), this data can be seen in table 1 below. The patterns seen in the Thunder Creek and Gap deposit scheelites are very similar in that they follow the high Sr and low Mo concentration pattern. This was inverse for both porphyry related and other hydrothermal scheelites. Since the orogenic gold deposits study in Poulin (2016) are not intrusion related results from the Thunder Creek and 144-Gap zone scheelites are closely related to metamorphic fluids rather than genetically related to the syenitic intrusion.
Table 1. Comparison of Sr and Mo data from Thunder Creek and 144-Gap zone scheelites and Poulin (2016) scheelites.

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4 Conclusions

Scheelite from Thunder Creek and 144-Gap have high Sr and low Mo concentrations, relative to scheelite from other deposit types. This indicates that the scheelites from Thunder Creek and 144-Gap syenite are genetically similar to metamorphic fluids. Much of the mineralization is vein-hosted, therefore it is likely that the monzonite-syenite host rock preferentially fractured and acted as a conduit for later mineralizing fluids that had a strong metamorphic component, supporting the second hypothesis.

References

Telluride mineralogy of the San Martín de Loba gold deposit, South of Bolívar - Colombia

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Abstract. Gold deposits in the south of Bolívar, Serranía de San Lucas, are recognized as the finest gold deposit in Colombia. Mineral recovery processes of these deposits use low technology, with limited mineralogical information available. Hence it has a lot of recovery problems, with gold recovery rates between 40 - 60%.

Mineralogical studies show that there are two gold mineralizing stages, the first one with native gold, disseminated with coarse-grained sulfides and the second one as electrum gold in growth zoning with galena and sporadic sphalerite, at the last part of this stage hessite is found. These minerals were used to understand the forming conditions, comparing the results with previous studies. Using scanning electron microscope (SEM) analysis on, the minerals in equilibrium with gold; hessite, sphalerite and galena, we calculated the temperature range of this stage (i.e. 150 – 250 °C) and the tellurium and sulfur fugacities, key conditions in the precipitation of minerals. (i.e. log fTe2: -13.4 to -17.4 y log fS2: -10 to -16.5).

1 Introduction

Gold production in Colombia is primarily from alluvial and epithermal deposits within which the south of Bolivar Mining District is an important epithermal one, even though it has an artisanal exploitation and the fact that it has a low recovery rate (i.e. 40 - 60%). It provided 22.5% of the national gold production (Pantorrilla et al. 2007) (i.e. 3.7 MOz Au during the last decade). In addition, it is the first deposit with tellurides reported in Colombia (Maria 1995), which makes it an interesting object of study.

Au-Ag-Te deposits are related to a wide variety of ore deposits; epithermal, orogenic and intrusion related (Afifi et al. 1988a; Cook et al. 2009). The paragenetic association of gold silver tellurides and thermodynamic data of the minerals in equilibrium with them, can be used to establish conditions of deposition of the mineral assemblages found in the deposit (Bortnikov et al. 1988).

2 Regional tectonic setting

San Martín de Loba’s gold deposit is located in the northern part of the Central Cordillera of Colombia in a place known as Serranía de San Lucas (Fig. 1). It is an isolated block, detached cinematically from the main fault system of Palestina (Duque-Caro 1990; Cediel and Shaw 2003; Sarmiento-Rojas et al. 2006). Gold at the San Martín de Loba is considered as coeval with an early Jurassic magmatic event (Leal-Mejía 2011), nevertheless the mineralization has not been dated and there are other subsequent magmatic events that could provide the conditions to generate this deposit, during the complex tectonostratigraphic evolution of the area (Aspden et al. 1987; Royero 1996; Sarmiento-Rojas et al. 2006; Clavijo et al. 2008).

3 Geological description of the deposit

Gold mining in the San Martín de Loba deposit is reported since the XVIII century (Restrepo 1888). Historically the deposit has produced 1.75MOz Au over 300 years and has a total calculated resource of 3.5MOz (Leal-Mejía 2011).

The deposit is located north of the San Martín batholith and is associated with some apophyses of this one (Leal-Mejía 2011) (Fig. 1). Gold mineralization is found in veins. These are mainly hosted by the San Martín de Loba batholith, primarily composed by granodiorites although it is also locally hosted by volcanoclastic sequences of the Norean Formation, which shows a strong phillic alteration. Cretaceous to early Eocene sediments unconformably cover older rocks, being responsible for a flat topography (Etayo 1985; Rolon and Toro 2003). The veins occur along 260-300° striking and 60-70°SW dipping. Data on ore grades vary from 2.5 up to 311 g/t Au (Romero et al. 1994).
4 Analytical

4.1 Ore petrography

An optical study of the textural relationship between ore minerals was done in 25 polished and polished thin sections from the deposit and to determine mineral assemblages and paragenetic sequence of the mineralization.

4.2 Scanning electron microscope (SEM)

A scanning electron microscope FEI Quanta 200 -r at the Universidad Nacional de Colombia, was used to analyse the composition of gold, tellurides and sulfurs in equilibrium using back-scattering electrons (BSE) spectrometry. Operating conditions were an accelerated voltage of 30KV and a vacuum of 0.009Pa.

5 Results and discussion

A brief paragenetic sequence was developed for the deposit based on textural relationships between ore and gangue minerals in the samples, using a reflected light polarizing microscope (Fig. 2). Two gold mineralizing stages were defined, the first one with native gold (Gold I), disseminated with coarse-grained sulfides (i.e. Sphalerite I and Galena I) and the second one in growth zoning of electrum (Gold II) with galena (Galena II) and sporadic sphalerites (Sphalerite II) (Figs. 3 and 4). The only telluride found was hessite. It is the last mineral to appear in equilibrium with electrum during the stage 2 (Fig. 5).

The chemical potential of sulfur and telluride (i.e. sulfur and tellurium fugacity; log $f_S^2$ and log $f_{Te}^2$), are factors that control directly the mineral assemblage found in the deposit (Barton and Toulmin 1964; Bortnikov et al. 1988), and it can be calculated from the composition of minerals in equilibrium in stage 2 using equations that have been widely studied for decades (Barton and Toulmin 1964; Barton 1980; Afifi et al. 1988a, b; Bortnikov et al. 1988). At the early stage 2 a high content of sulfur in the galena composition and a high content of silver in electrum was found (i.e. S=57% and Ag=48%). As a result the chemical potential of sulfur was calculated, (i.e. log $f_S^2$=-10 to -16.5), whereas in the late part of this stage hessite was found in equilibrium with electrum (i.e Ag=27%). This mineral was used to calculate the chemical potential of telluride, (i.e. log $f_{Te}^2$=-13.4 to -17.4) with a formation temperatures for the reactions between 150 – 250°C.

There are some reports of gold tellurides in the deposit like calaverite and sylvanite (Maria 1995), however according to the thermodynamic data of these minerals and the conditions of formation that were determinated in this work, the presence of them is not possible.

(Leal-Mejia 2011) proposes a paragenetic sequence for this area in which two mineralizing stages are presented with electrum, differentiated by the silver content (i.e. Ag=79% and Ag: 45% respectively). Although native and electrum gold were found in two different stages in this work, the chemical composition of gold described by Leal-Mejia (2011), seems to correspond to electrum previously described in stage 2. The greater fineness found at the late part of the stage 2 may be related to high tellurium activity, as described by Bortnikov et al. (1988).

6 Conclusions

Gold at San Martín de Loba gold deposit precipitates at relatively low temperatures (i.e. 150 – 250°C). Tellurium activity and electrum fineness are greater with presence of hessite, when hessite is present. During the telluride an electrum precipitation process, Te$_2$ only incorporate Ag to precipitate hessite. The low content of Te$_2$ in the mineralizing fluid, leads to the consumption of the entire Te$_2$ and does not allow others tellurides to form.
Figure 4. BSE image showing growth zoning of galena (Gn) with gold (Au) and sporadic apparition of sphalerite II (Sph II) in pyrite (Py) and sphalerite I (Sph I).

Figure 5. BSE image showing Gold (Au) in equilibrium with hessite (Hss) in pyrite (Py).

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Geochemistry and chronology of magmatic intrusions related to the Jinba gold mineralization, Xinjiang, China

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Abstract. The Jinba gold deposit, located in the inner contact zone of the Habhae Intrusion, occurs in plagiogranite of the Habhae intrusion and in the Middle Devonian the Ashele group subgroup. The gold mineralizations occur in the central part of the ductile shear deformation metamorphic belt in the Markacurry giant fault belt, closely related to early ductile shear activity. This paper discusses the characteristics of wall rock alteration, which generally-developed pyritization, sericitization, silification. Gold mineralization in the area is closely related to plagioclase granite and diorite, the drilling rock samples from the center to the outside mineralization and alteration gradually weakened, change significantly. According to the geochemistry study, gabbro-diorite may be the product of magma intrusion and crystallization of the deep mantle. Plagiogranite indicated that it may be the products of the magmatic activity. Through the LA-ICP-MS zircon U-Pb dating experiment on plagiogranite in Jinba gold deposit, a weighted average age of 431±3.4 Ma was obtained which may represent the early intrusion. Due to the deeper depth of ore-controlling and the larger ore-bearing structure space, the deep ore-forming fluids can migrate upwards. At the same time, frequent volcanic magmatic activity may provide heat and ore-forming materials and result in remobilization and migration of gold. The Markacurry ductile shear zone had provided a space for gold mineralization where gold-bearing quartz veins were emplaced.

1 Introduction

The Jinba gold deposit, located in the Habhae county north of about 25° azimuth 16km is Altay region Habhae County Salta wood Township jurisdiction. A great number of previous studies indicate that gold deposits in the Ertix Tectonic Belt are closely related to structures and ductile shear zones (Dong Y G et al. 2000). The main ore bodies of the Jinba gold deposit occur in the Maerkekuli shear zone which is the Northwest part of the regional Ertix Fault. Although geological studies had been done since the discovery of the gold deposit in 2004, there remain exist problems concerning ore genesis, including the relationship between magmatic activities and gold deposits, as well as ore-forming fluids and their evolution during gold deposition. In order to understand the genesis of the gold deposits and predict potencial prospecting area we carried out geochemistry and chronology of the magmatic intrusions related to gold mineralization.

2 Geological setting

There are up to a thousand meters wide extrusion fracture zone or mylonitized belt along both sides of regional Markacurry fault controlling the Jinba gold deposit. The Markacurry fault has obvious characteristics of multi-stages ductile shearing in the Ashele-Tuokuzibai area. The Jinba gold deposit occurs in the plagiogranite massif of Habhae intrusion and in second lithologic section of Middle Devonian Ashele Formation (D1-2as) subgroup second lithologic layer (Fig.1). The main lithology includes variable crystal tuff, rhyolitic ignimbrite, rhyolite, metamorphic sandstone, sericite chlorite phyllite and quartz crystal limestone. The Habhae intrusion is mainly composed of porphyritic plagioclase granite, coarse-grain plagioclase granite, granitic migmatite in the northern and northeast of the mining area. The granite-porphry, plagiogranite, diorite and quartz veins are mainly distributed in the inner and outer contacts of the Habhae intrusion. Gold-bearing ore bodies are composed of altered diorite and quartz veins filled in the fractures. Based on ore mineral associations and host rocks, ore types can be divided into altered rock type, including altered diorite, altered sandstone and phyllite, altered mylonite, as well as quartz veins filling in various wall rocks.

3 Petrological characteristics

Plagioclase granite, the main wall rock of gold-bearing veins, is composed of quartz, plagioclase, and hornblende with massive structure and homograniular texture. Quartz grains (20–30%) are mostly lenticular, and fine grained (1-2mm). Plagioclase (55%~65%) which can be further identified as oligoclase (An=20~30%) occurs as anhedral (2mm). Local potassium feldspar with tartan twinning and plate shape microcline are also present. Hornblende (5–10%) appears columnar and replaced by chlorite at edge. Minor minerals are biotite. Gabbro-diorite has massive structure and homoeoblastic texture, with main minerals composed of plagioclase, amphibole, biotite clinzoisite and epidote. Hornblende (20–30%) its nematoblastic is greater than 50%. Biotite (10%) is flake
Six plagiogranite and six gabbro-diorite samples were selected for geochemical analysis, in order to understand how the Jinba gold mineralization is related with these intrusions.

The petrochemical analysis indicates that K$_2$O and MgO contents in the samples of fresh (or weakly altered) gabbro-diorite are relatively lower, whereas SiO$_2$ is higher. The trace elements in altered gabbro-diorite are higher than fresh gabbro-diorite. The major and trace elements in the altered and unaltered plagiogranites are not significant.

The REE of gabbro-diorite samples distribution curve is relatively slow, and the light and heavy rare earth fractionation is not obvious which indicate that gabbro-diorite may be the product of magma intrusion and crystallization of the deep mantle. Plagiogranite samples show a light REE enrichment curve (Fig.3). It indicates that they may be the products of the magmatic activity.

The composition of the intrusion is complex, and the source and the formation of the rock mass are various. In this area, plagiogranite samples are located in the peraluminous area of the A/NK-A/CNK scheme (Fig.4) and the calc-alkaline series of rocks in the K$_2$O-SiO$_2$ diagram (Fig.5). Plagiogranite belongs to peraluminous calc alkalic rocks, which is the product of partial melting of the typical crustal rocks.

**5 Chronology of Habae intrusion**

Cai (2007) obtained a zircon U-Pb SHRIMP age of 390 ± 5Ma of zircon SHRIMP U-Pb age for granite in Habae intrusion, and Li (2012) obtained an LA-ICP-MS U-Pb zircon age of 406Ma for the monzonite granite. However, Chen et al. (2000) got 284.4-277.3Ma of whole rock K-Ar
age for plagiogranite, and (297 + 11) Ma of Rb-Sr isochron age. These data are much younger and may represent the age of late tectonic events. In this study, we carried out LA-ICP-MS zircon U-Pb (Institute of Geochemistry Chinese Academy of Science) dating analysis for plagiogranite of Habahe intrusion. The results show that Th/U ratios of 17 effective data have typical characteristics of the magmatic zircon Th/U ratios (>0.4, Rubatto, 2002). Zircon concordant diagram shows that the U-Pb zircon age of the plagiogranite is 431 ± 3.4 Ma (Fig. 6), which is older than the data from Cai (2007) and Li (2012) and might represent an early intrusion event.

6 Discussion

The Habahe plagiogranite intrusion, located in the north and east of the mining area, was intruded by various dikes, including granite porphyry, anorthosite, diorite dikes, as well as quartz veins. The altered diorite dikes and quartz veins are associated with gold mineralization. The geochronological data of the Habahe intrusion shows various results. The experiments were already carried out by different experimental methods. Such as zircon SHRIMP U-Pb age of granite in Habahe intrusion was 390 ± 5 Ma (Cai 2007), the LA-ICP-MS zircon U-Pb age of monzonitic granite was 406 Ma (Li 2012), whole rock K-Ar age of plagiogranite was 284.4–277.3 Ma and Rb-Sr isochron age was 297 ± 11 Ma. The U-Pb zircon age of the plagiogranite is 431 ± 3.4 Ma in this study may represent an early intrusion event.
The Habhe plagiogranite results from an early magmatic event, and emplaced in the island arc environment related to plate subduction for partial melting of continental crust rocks product. In the Nb-Y and Ta-Yb diagrams (Fig. 6.7), all samples are located in the area of volcanic arc+syn-collision granite and volcanic-arc granite. It indicates diorite and plagiogranite intrusion could suggest that it has been formed in the subduction zone. Plagiogranite might provide a source of gold mineralization.

![Figure 6](image6.png)

**Figure 6.** The Nb-Y and Ta-Yb diagrams of diorite (base map cited from Pearce et al. 1984). WPG: within-plate granite; ORG: Ocean ridge granite; VAG: Volcanic-arc granite; syn-COLG: syn-collisional granite; VAG+syn-COLG: Volcanic-arc granite + syn-collisional granite

![Figure 7](image7.png)

**Figure 7.** The Nb-Y and Ta-Yb diagrams of plagioclase granite (base map cited from Pearce et al. 1984).

Ertix tectonic belt with strong magmatic activity, and the volcano eruption and magmatic intrusion is frequently, especially in the western part (Markacurry fault). The Jinba gold deposit was closely related with early ductile shear event of the Markacurry fault. The ore bodies occur in the core of intensive ductile shear zones.

7 Conclusions

1) Geochemistry studies show that the trace elements of the altered gabbro-diorite are overall high, and its light and heavy rare earth fractionation is not obvious with easy REE curve. Major and trace elements of altered and fresh plagiogranite shows little change. Light rare earth elements of plagiogranite sample show relative enrichment distribution patterns. Gabbro-diorite may be the product of magma intrusion and crystallization of the deep mantle.

2) Through the U-Pb LA-ICP-MS zircon dating of the present plagiogranite within Jinba gold deposit, a weighted average age of 431 ± 3.4 Ma was obtained which may represent the age of early intrusion.

3) Gold mineralization in the Jinba area was closely related to various dikes (such as diorite dikes) and quartz veins in plagiogranite intrusion. Markacurry ductile shear zone provides a space for mineralization. Preliminary gold enrichment of quartz veins in the diorite and plagiogranite maybe the source of the gold mineralization within the Jinba deposit.

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Quartz phenocrysts and fluid inclusions in porphyritic granite, Dongping gold deposit, Northern Hebei, China

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Abstract. The giant Dongping gold deposit was the first discovered among the alkaline complex-hosted gold ores in China. Porphyritic granite at the Dongping deposit, controlled by a NEE-SWW striking shear zone, is characterized by abundant quartz phenocrysts. Tiny feldspar crystals occurring as solid inclusions within the porphyritic quartz were identified as both potassium feldspar and albite. Isolated fluid inclusions in the porphyritic quartz have higher homogenization temperatures than those in gold-rich vein quartz, indicating the initial fluids yielding gold-forming fluids with much more CO₂.

1 Introduction

The giant Dongping gold deposit, situated in northern Hebei Province, was the first recognized among the alkaline rock-related gold deposits because they are hosted by the Middle Devonian Shuiquangou Alkaline Complex (SAC) (Song and Zhao, 1996; Nie et al., 2004). However, geochronological data show that these gold deposits were formed in Late Jurassic (Jiang and Nie, 2000; Luo et al., 2001; Li et al., 2010).

A porphyritic granite body was recently recognized within the SAC and strikes NEE-SWW with a width of 15-20m. The quartz phenocrysts in the granite have unique features, including rounded shapes, surrounding feldspar and recrystallized quartz grains, small plagioclase inclusions, and various types of fluid inclusions. Exploratory drilling indicated that gold grades of as much as 5.96g/t characterized granite. Important questions include: what is the origin of quartz phenocrysts, and how is the gold mineralization in the porphyritic granite in the Dongping deposit? It is necessary to study the quartz phenocrysts and fluid inclusions to better understand the origin of gold deposits in this area.

2 Geological setting

Located 50km east of Zhangjiakou city, the Dongping gold deposit (152Ma, Hart et al., 2002) is one of the large gold deposits in the North China Craton, with more than 70 tonnages of gold. The regional strata in this area are mainly the Mesoarchean Chongli Group composed of biotite plagioclase gneiss, plagioclase granulite, and marble; the Paleoproterozoic Hongqiyingzi Group composed of plagioclase gneiss, amphibolite, and biotite granulite, and Jurassic volcanoclastic rocks. The gold-bearing vein systems are mainly hosted in the Hercynian Shuiquangou alkaline complex (390±6–386±6 Ma, Luo et al., 2001; 382.8±3.3Ma, Li et al., 2010), which is composed of syenite, monzonite, and alkali feldspar syenite (Fig.1). There is a K-feldspar-rich granite on the southern side of the mine area (Shangshuiquan). The porphyritic granite is located in the Zhuanzhilian area 5km to the northeast of the Dongping deposit.

Figure 1. Simplified geological map of the Shuiquangou Alkali Complex in the Zhangjiakou area, Hebei Province, China (modified after Song et al. (1996) and Li et al. (2010))

1-Quaternary; 2-Yanshanian medium acidic volcanoclastic rock; 3-Neoproterozoic and Mesoproterozoic cover rock; 4-Paleoproterozoic Hongqiyingzi Group; 5-Archean Chongli Group; 6-Shangshuiquan K-feldspar granite; 7-Honghuangling biotite granite; 8-monzonitic granite; 9-porphyritic granite; 10-Shuiquangou alkaline complex; 11-Wenquan macrophyric granite; 12-ultrabasic rock; 13-Archean granitic gneiss; 14-fault; 15-gold deposit

Gold mineralization in the Dongping deposit includes both disseminated ore and quartz vein-hosted ore. The metallic minerals are mainly native gold, calaverite and pyrite, with small amounts of sphalerite, galena and chalcopyrite; the gangue minerals are K-feldspar and quartz. There are four mineralization stages at the Dongping gold deposit that include (I) (K-feldspar)-white quartz, (II) pyrite-quartz, (III) polymetallic sulfides (chalcopyrite, pyrite, galena)-smoky quartz, and (IV) calcite-quartz stage. Stages II and III are the main gold mineralizing stages. Gold-rich veinlets contain relatively abundant polymetallic sulfides and they fill fractures in the early white quartz veins. The Number 70 vein system is
the largest in the Dongping area. Hydrothermal alteration is mainly potassic alteration, silicification and pyritization.

3 Porphyritic granite

The NEE-striking porphyritic granite occurs in the Shuiquangou Alkaline Complex. The major minerals in the granite are potassium feldspar (~55%), plagioclase (~20%), and quartz (~25%) (Fig. 2A and B). Plagioclase is mainly albite and occurs as fine aggregate (0.05~0.1mm). The K-feldspar seems dirty on the surface in thin section, and garnet can be seen between some grains of the K-feldspar. Quartz occurs mainly as phenocrysts or aggregates with sizes ranging from 0.5~10mm. They are not true phenocrysts, so we sometimes prefer to call them porphyritic quartz. Single porphyritic quartz aggregates are composed of one or several quartz crystals surrounded by fine recrystallized quartz. Tiny feldspar crystals can be seen as solid inclusions within grains of porphyritic quartz (Fig.2D and E).

Electron microprobe analyses (EMPA) have been carried out on the feldspar inclusions (Fig.3) in porphyritic quartz at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG-CAS) and the Beijing Research Institute of Uranium Geology, China National Nuclear Corporation. The work was done using the SXFive and JXA-8100 instruments, respectively.

The results show that feldspar inclusions in porphyritic quartz can be classified as two types. One is mainly composed of K2O (15.45~16.37 wt%), Na2O (0.30~1.09 wt%), CaO (0~0.03 wt%), SiO2 (64.06~65.31 wt%), and Al2O3 (17.79~19.12 wt%), which can be identified as potassium feldspar or orthoclase. The other is composed of Na2O (11.18~12.03 wt%), K2O (0.08~0.20 wt%), CaO (0.03~0.11 wt%), SiO2 (67.88~68.64 wt%), and Al2O3 (19.05~20.66 wt%), which can be identified as albite. The typical back scattering electron images of orthoclase and albite are shown in figure 3. The crystal chemical formula for each can be calculated based on the EMPA data, such as (K0.957Na0.027Ca0.001)m.089[A1.02Si2.98O8] for K-feldspar, and (Na1.004K0.008Ca0.001).017[A1.013Si2.95O8] for albite (Fig.3, ZK102 (4)7, 8). Albite and orthoclase typically occur as stripe feldspar in one inclusion. It is still a question as to whether they were crystallized from supersaturated SiO2-rich fluids or they replaced porphyritic quartz during a later event.

4 Fluid inclusions in porphyritic quartz

Abundant fluid inclusions in porphyritic quartz show various types and generations (Fig.4). They can be classified as W-type (L-V aqueous inclusions, with L:V ratios >70%), V-type (V-L inclusions, with L:V ratios <30%), CW-type (H2O-CO2 inclusions, some with three phases), and WS-type (L-V-S, with daughter salt mineral-bearing water inclusions), based upon phases observed at room temperature.

Several aggregates of quartz phenocrysts were selected for fluid inclusion microthermometry. The first generation of fluid inclusions can be identified in porphyritic quartz. The first generation of inclusions occurs as isolated V, CW, and less commonly WS-types. The second generation of fluid inclusions occurs as FIA (fluid inclusion assemblages) composed of W-type inclusions. The third generation is also composed of tiny W-type FIA that cut across the second generation of FIA (Fig.4A and 4B).
of fluid inclusions, occurring as isolated L-V or V-L inclusions, have relatively higher homogenization temperatures from 355 to 400 (L-V inclusions, homogenized into liquid phases) and 390 to 400 (V-L inclusions, homogenized into critical phases) (Fig.5). The melting temperatures of ice for these inclusions are from -5.5~ -1.5 with salinities of 8.55~2.57 wt%NaCl equiv. (after Bodnar, 1993). Most inclusions homogenized into the critical phase, so the critical pressures can be estimated to be about 30MPa.

**Figure 5.** Homogenization temperatures for the first generation fluid inclusions in porphyritic quartz.

### 4 Discussion

#### 4.1 Comparison to the Dongping gold deposit

What is relationship between the porphyritic granite and the Dongping gold mineralization? Are there differences among the fluid inclusions in the porphyritic quartz and various vein quartz generations of the Dongping gold deposit, particularly those rich in gold?

As mentioned above, gold-rich ores typically occur in polymetallic sulfides-quartz veinlets (stages III). We studied gold-rich ore samples containing visible gold grains. They were collected from the 1220m level of the Dongping gold mine, where the pyrite and chalcopyrite-bearing veinlets and smoky grey quartz veins fill a thick white quartz vein. The $\text{H}_2\text{O}-\text{CO}_2$ fluid inclusions are abundant in the smoky grey quartz near gold grains (Fig.6).

Micro thermometry shows that the bubbles in the $\text{H}_2\text{O}-\text{CO}_2$ fluid inclusions are mainly vapor $\text{CO}_2$; a few $\text{H}_2\text{O}-\text{CO}_2$ inclusions have thin films of liquid $\text{CO}_2$ surrounding the bubbles, with $\text{CO}_2$ melting at -58.3~57.6 and $\text{CO}_2$ homogenizations from 27.8~30.9. The densities for the $\text{CO}_2$ phase in the $\text{H}_2\text{O}-\text{CO}_2$ inclusions are 0.58~0.67g/cm3. The final homogenization temperatures are 191~373, and mainly between 270~330 (Fig.7). The melting temperatures of ice are -5.6~0.8, and the melting temperatures of clathrate are 8.5~9.1, defining salinities of 1.2~8.7%NaCl equiv. and densities of 0.60~0.92 g/cm³. Based upon critical temperatures of $\text{H}_2\text{O}-\text{CO}_2$-NaCl system (Frantz et al, 1992), critical pressures of the fluids are calculated as 70-160MPa. In conclusion, gold-rich ores were formed under at minimum depths of 2.8km based on lithostatic pressures.

The results from the above research show that the fluids both in the porphyritic quartz and gold-rich ores of the Dongping gold deposit have similar characteristics of mesothermal-hypothermal conditions and are low salinity $\text{H}_2\text{O}-\text{CO}_2$-NaCl fluids. However, the final homogenization temperatures for the porphyritic quartz are higher than those for the gold-rich ores.

**Figure 6.** Gold-rich quartz veins and the characteristics of fluid inclusions in the deep portion of the Dongping gold deposit, northern Hebei, China. a Gold grain and fluid inclusions in stage II quartz of the Dongping gold deposit, DP12-C. b Exposed surface of gold in stage II quartz in photo A (reflective light). c $\text{H}_2\text{O}-\text{CO}_2$ inclusions in area C of photo A. d $\text{H}_2\text{O}-\text{CO}_2$ inclusions in area D of photo A. e $\text{H}_2\text{O}-\text{CO}_2$ inclusions in area E of the photo A.

**Figure 7.** Histograms of homogenization temperatures (left) and salinities (right) for fluid inclusions in vein quartz of gold-rich ores in the Dongping gold deposit, northern Hebei.

#### 4.2 Geological significance of data for porphyritic quartz and from fluid inclusions

The genesis of the Dongping gold deposit is controversial. The source of the gold is a key problem of ore genesis. The early opinion was that gold was mainly derived from the Shuiquangou Alkaline Complex host rocks (Song and Zhao, 1996), and partly from Mesoarchean metamorphic rocks of the Chongli Group. Jiang and Nie (1994) argued that gold was partly derived from the upper mantle during the upward movement of the Shuiquangou Alkaline Complex. It is possible that rocks of the Chongli Group were a source of gold because they contain background concentrations of 7.0~9.3ppb of Au, which is higher than the average Au content of the crust. However, recent studies show that the ore-forming age of the Dongping gold mineralization is much younger than the age of host Shuiquangou Alkaline Complex. Age data include...
140.3±1.4Ma and 140.2±1.3Ma from U-Pb analyses of hydrothermal zircon in potassically altered rock and a potassium feldspar-quartz vein, respectively (Li et al., 2010), as well as 152Ma from 40Ar-39Ar measurements of sericite in altered rock (Hart et al., 2002). It is noteworthy that there is an Early Jurassic granite intrusion with an age of 135±0.4Ma (Mo, 1997) to the south of the Dongping gold deposit (Fig.8). We also obtained a 138±0.82Ma of zircon U-Pb age for the K-feldspar-rich granite in the Dongping area (Zhang et al., 2012). These data indicate that the Dongping gold mineralization may be related to Late Jurassic – Early Cretaceous granite magmatism.

The source of the ore-forming fluids is also a debated question. Mao et al. (2001) emphasized the role of mantle fluids, whereas Fan et al. (2001) considered ore-forming fluids to be magmatic fluids that mixed with ancient meteoric water. Hart et al. (2002) believed that the ore-forming fluids were similar to those of orogenic gold in metamorphic terrane.

Fluid inclusion study indicates that the homogenization temperatures of isolated L-V or V-L inclusions in quartz phenocrysts of mineralizing porphyritic granite are higher than for inclusions in gold-rich ores. On the other hand, the gold mineralizing porphyritic granite is controlled by a NEE-SWW shear zone based on drill core information (Fig.8). Our study shows that the porphyritic granite has 361±12Ma and 364.5±8.4Ma U-Pb ages for residual zircon, so the porphyritic quartz and gold mineralization might be products of a late hydrothermal event. We assume that this event was the same as the mineralizing event occurring in the Dongping gold deposit. Isolated inclusions having higher homogenization temperatures in quartz phenocrysts might represent the initial fluids from which gold-forming fluids with much more CO₂ were derived when temperatures deceased.

Abundant albite and orthoclase inclusions occurring in porphyritic quartz may also indicate a late hydrothermal event after emplacement of the porphyritic granite. The porphyritic quartz may be crystallized from supersaturated SiO₂ fluids rich in K and Na, or replaced by hydrothermal fluids rich in K and Na.

5 Conclusions

Porphyritic granite, newly identified in the Shuiquangou Alkaline Complex, is controlled by a NEE-SWW shear zone. Porphyritic quartz composed of one or several quartz crystals is abundant in the granite. Tiny feldspar crystals seen as solid inclusions within grains of porphyritic quartz were identified as potassium feldspar and albite. Isolated fluid inclusions trapped in porphyritic quartz have higher homogenization temperatures than those in gold-rich vein quartz and might represent the initial fluids that later yielded gold-forming fluids with much more CO₂.

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References


Alteration halo and lithostratigraphy of the Pine Cove orogenic gold deposit, Baie Verte Peninsula, Newfoundland, Canada

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Abstract. The Pine Cove gold mine is hosted within Ordovician gabbro sills and volcano-sedimentary rocks of the Venam’s Bight Formation, Snooks Arm Group, on the Baie Verte Peninsula, Newfoundland. Gold mineralization occurs with disseminated pyrite contemporaneous with quartz-calcite-albite breccia-veins that occur along contacts between gabbro sills and volcano-sedimentary strata. Two distinct alteration assemblages are identified at Pine Cove: proximal sericite-rutile and distal epidote±titanite. A less consistently-developed, spatially-intermediate alteration zone consists of carbonate as pervasive ground mass alteration ± porphyroblasts. Short wave infrared (SWIR) spectra of white micas show muscovitic to paragonitic compositions proximal to mineralization, whereas white micas in less altered rocks are phengitic. Mass balance calculations for altered wall rock show enrichments in CO₂, K₂O, S, Rb, W, In, Pb, Bi, Te, Se, Cs, and Ba, and depletions in As, Sb, and locally Na₂O, similar to orogenic Au deposits globally.

1 Introduction

The geology of orogenic gold deposits on the Baie Verte Peninsula, north-central Newfoundland, has been summarized by Evans (2004). However, the hydrothermal alteration patterns and lithostratigraphy of these deposits have not been comprehensively documented. It is therefore difficult to fully assess factors that influenced the formation of these deposits or apply alteration models during exploration in the district. In light of recent tectonostratigraphic studies on the Baie Verte Peninsula (Skuls& et al. 2010) and global models for orogenic gold deposits (Dubé and Gosselin 2007), characterization of alteration patterns and the stratigraphic setting of mineralization could significantly improve exploration targeting in the region. Using integrated core logging, lithogeochemistry, petrography, and short-wave infrared (SWIR) spectroscopy, this study aims to characterize host rock composition and hydrothermal alteration at the currently-operating Pine Cove gold mine, to better define exploration criteria on the Baie Verte Peninsula.

2 Geologic setting

Williams (1979) identified four tectonostratigraphic zones within Newfoundland; these are the Avalon, Gander, Dunning, and Humber zones from east to west, respectively (Fig. 1a). The amalgamation of these tectonostratigraphic zones is the result of diachronous Paleozioc accretionary orogenies during the closing of the Iapetus and Rheic Oceans, which culminated in the collision of Laurentia and Gondwana to form the supercontinent Pangea (van Staal 2007; van Staal and Barr 2012).

Figure 1. a Tectonostratigraphic map of Newfoundland. b Generalized geologic map of the Baie Verte Peninsula. Modified from Skuls& et al. (2015).

The Baie Verte Peninsula straddles a suture belt between the Humber Zone and Notre Dame Subzone of the Dunning Zone, termed the Baie Verte-Brompton Line (BVBL) (Fig. 1b). The Baie Verte-Brompton Line extends through much of the Canadian Appalachians as a belt of disrupted ultramafic bodies and mélanges along a steeply-dipping structural zone interpreted to represent the tectonic interface between the Laurentian continent and the ancient Iapetus ocean (Williams and St. Julien 1982). On the Baie
Verte Peninsula, the BVBL is a north-northeast to east trending fault zone that juxtaposes oceanic terranes of the Notre Dame Subzone against continentally-derived rocks of the Humber Zone (Hibbard 1983). Pine Cove is located within a dismembered ophiolite cover sequence in the Notre Dame Subzone, just east of the BVBL (Evans 2004; Skulski et al. 2015).

The Betts Cove Complex and overlying Snooks Arm Group are the best preserved of the Ordovician oceanic terranes on the Baie Verte Peninsula (Fig. 1b). As such, the stratigraphy defined by Bédard (2000) for the Betts Cove area provides a stratigraphic template for the other sequences on the peninsula (Skulski et al. 2010).

3 Geology of the Pine Cove gold deposit

The Pine Cove ore body occurs approximately 50 to 200 meters (m) above of the Scrape Thrust Fault (STF), a regional fault associated with Silurian sinistral transpression (Castonguay et al. 2009; Skulski et al. 2010). In the mine area, rocks below the STF are fine-grained amphibolite (Fig. 2a). Structurally overlying the amphibolite is a 25 to >90 m zone of contorted ± brecciated quartz-chlorite-sericite-carbonate schist. Separating the amphibolite and contorted greenschist is 1 to 2 m of deformed wall rock and clay gouge. The contorted schist transitions upwards into pervasively carbonate altered mafic tuffs, flows, and sedimentary rocks. These metavolcanic rocks are here interpreted to be Venam’s Bight Formation (see Lithogeochemistry). Above the Venam’s Bight Formation is a lithic greywacke, which is overlain by hematitic argillite. This sedimentary sequence is a marker unit throughout the deposit. The uppermost rocks are relatively gold-poor and consist of mafic tuff, lapilli tuff, greywacke, and argillite. These rocks are interpreted to correlate with the Bobby Cove Formation. Bobby Cove Formation rocks are in para-conformable contact with the underlying hematitic argillite, although this contact is commonly faulted.

Host rocks and mineralized zones are broadly subparallel to the STF, which dips approximately 30 to 35 degrees northward (Fig. 2b). Mineralization is associated with pyrite disseminated in the selvages of quartz-carbonate-albite breccia-veins that are best developed along the contacts between gabbro sills and sedimentary rocks.

Visible mineral mapping, petrographic, and SEM observations reveal distal mineral assemblages are dominated by epidote, Fe-Mg chlorite, calcite, and titanite after titanomagnetite. Intermediate alteration assemblages consist of pervasive carbonate alteration, and locally carbonate porphyroblasts. Proximal alteration consists of pyrite, muscovite, Fe-chlorite, Fe-calcite, and fine-grained rutile after titanomagnetite. Native gold, chalcopyrite, and galena occur as micron-sized inclusions in pyrite and/or as fracture fillings in brecciated pyrite grains.

Figure 2. a Geologic cross section of the Pine Cove deposit. b Cross section showing generalized gold mineralization and alteration patterns.

3.1 Lithogeochemistry

Immobile element ratios (Al₂O₃/TiO₂, Al₂O₃/Zr, Ti/Sc, and Th/Yb) were used to classify rock types and make subdivisions of FW and HW rocks (e.g., Maclean and Barrett 1993; Ross and Bedard 2009). Venam’s Bight Formation basalts have enriched mid-ocean ridge basalt immobile element signatures, with tholeiitic to transitional
Th/Yb values. Gabbros also have tholeiitic, enriched mid-ocean ridge basalt signatures. Two geochemically-distinct subdivisions are apparent in the Bobby Cove Formation tuffs. Bobby Cove Formation – A (BCF-A) tuffs have a transitional island-arc basalt signature, whereas Bobby Cove Formation – B (BCF-B) tuffs have a calc-alkaline ocean-floor basalt signature.

A comparison of Ti/V and Ti/Zr data from Bédard (2000) shows that basalts below the sedimentary sequence likely correlate to the Venam’s Bight Formation (Fig. 3). BCF-A is similar to the low-Ti Bobby Cove Formation, whereas BCF-B may be a locally distinct unit within the Bobby Cove Formation.

3.2 Hydrothermal alteration geochemistry

Mass balance calculations using the MacLean and Barrett (1993) single-precursor method show that hydrothermal alteration is defined by addition of CO₂, K₂O, S, Au, Rb, W, In, Pb, Bi, Te, Se, Cs, and Ba. Molar element ratios indicate that gold is associated with the formation of sericite and calcite (Fig. 4a). Carbonate and sericite alteration is accompanied by depletion in As, Sb, and locally Na₂O (Fig 4b).

3.3 Short Wave Infrared Reflectance (SWIR) spectroscopy

The wavelength position of the 2200nm AIOH absorption features at Pine Cove vary from 2189 to 2227 nm. Gold mineralization is associated with muscovitic AIOH absorption features (~ 2195 to 2205 nm) (Fig. 5). Shorter wavelengths are characteristic of paragonitic mica, whereas longer wavelengths are typically diagnostic of phengitic mica (Herrmann et al. 2001; AusSpec International 2008). Mica crystallinity, as measured by the depth of the 2200 nm feature divided by the depth of the 1900 nm feature, broadly increases with proximity to mineralization, but there are exceptions and the pattern is not well defined. The wavelength position of the FeOH (2255 nm) and MgOH (2335 nm) SWIR absorption features do not show systematic variation with alteration.

Figure 4. a Carbonate alteration index versus sericite alteration index diagram (e.g. Eilu 1998). The line CO₂/Ca = 1 represents all available Ca has been used to form calcite. Samples that plot above the line CO₂/Ca = 1 contain Fe-, Mg-, and/or Mn-bearing carbonates, such as ankerite. b Alkali + carbonate alteration index (e.g. Bierlein et al. 2000) versus As variation diagram, illustrating depletion of As with increasing alteration and Au mineralization.

Figure 5. Carbonate alteration index versus position of the 2200nm AIOH absorption feature, illustrating the correlation of muscovite and calcite formation with gold mineralization.

4 Discussion and conclusions

The Venam’s Bight Formation is younger than the Bobby Cove Formation (Bédard 2000); however, lithogeochemoical data suggest that the Bobby Cove Formation is overlying the Venam’s Bight Formation at Pine Cove. This, in addition to reverse-graded bedding in some greywacke and argillite, suggests that the deposit is situated within an overturned stratigraphic sequence. Alternatively, this relationship may represent a variation in the regional volcanic stratigraphy.

Visible alteration, molar element ratios, and SWIR spectra significantly extend the footprint of the deposit than previously identified visually. SWIR spectra of white micas show that the position of the AIOH absorption feature can be used to differentiate proximal muscovite alteration from distal/background micas. This may be particularly useful in sedimentary rocks that have detrital and/or metamorphic white mica. The lack of a shift in the FeOH absorption feature, despite the occurrence of Fe-chlorite (as shown by SEM) is likely due to the relatively limited extent of Fe-
chlorite alteration.

Ore-forming fluids were enriched in CO$_2$, K$_2$O, S, Au, Rb, W, Pb, Bi, Te, and Se. The interaction of the CO$_2$- and K$_2$O-rich fluids with feldspar- and titanite-bearing wall rocks resulted in the formation of muscovite and rutile, respectively. The formation of vein albite was likely sourced from the breakdown of wall rock albite during sericite alteration.

Mineralizing quartz breccia veins represent injections into discrete shear zones developed in response to movement along the Scraper Thrust Fault during Silurian transpression (D$_3$ of Calon and Weick 1990; D$_2$ and D$_3$ of Castonguay et al. 2009). Contorted schist and cataclastite overprint these veins, and may be related to reactivation of the STF as an extensional fault (D$_3$ of Castonguay et al. 2009). Quartz breccia veins are most abundant near contacts of gabbro sills, and mineralization dominantly occurs within Fe-rich gabbros and basalts of the Venam’s Bight Formation. This indicates two fundamental controls on mineralization: 1) hydrofracturing assisted by anisotropic deformation of rigid gabbro sills within softer country rocks, and 2) sulfidation of the Fe-rich gabbros and Venam’s Bight Formation basalts (e.g., Williams-Jones et al. 2009). Comparatively, the tuffs of the Bobby Cove Formation lack abundant gabbro intrusions and are relatively Fe-poor, and were thus a less receptive host rock at Pine Cove. This relationship illustrates the important controls of both chemically-favourable host rock and structurally-favourable rheological contrast between host units.

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S01 – Geology, geodynamics and metallogeny of the Rhyacian (2.35 – 2.05 Ga)

Convenors:
Marc Bardoux
Richard Ernst
James Sears

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Keynote presentation

Calibrating the early Paleoproterozoic glacial period

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Abstract. The Great Oxidation Event (GOE) began in the early Paleoproterozoic in association with global glaciations and emplacement of numerous large igneous provinces (LIPs). However, the exact timing of, and relationships among these events are debated because of poor age constraints. Here we show that the first Paleoproterozoic global glaciation occurred between 2442 Ma and 2435 Ma, and is documented on at least four cratons: Kaapvaal, Superior, Wyoming and Kola-Karelia. This is reinforced by a new age presented herein of 2,426 ± 3 Ma for Ongeluk LIP from the Kaapvaal Craton of southern Africa. This necessitates a stratigraphic revision for the Transvaal Supergroup between the volcanic Ongeluk and Hekpoort formations in its two main sub-basins. This new age also helps define a key paleomagnetic pole that positions the Kaapvaal Craton at equatorial latitudes of 11° ±6° at this time. Furthermore, the rise of atmospheric oxygen is now shown to be oscillatory, which together with climatic instabilities may have continued over the next ∼200 Myr. The Ongeluk LIP represents a waning stage in the succession of several LIPs across a large low-latitude supercontinent (Kenorland?). These LIPs played critical, albeit complex, roles in the rise of oxygen and in both initiating and terminating global glaciations.

1 How to date an early Paleoproterozoic volcanic succession

Sedimentary basins are host to important redox indicators that demonstrate what the Earth’s climate was like in deep time. However, without accurate spatial and temporal resolution of these climatic proxies, the ability to make larger models and interpretations becomes increasingly difficult and subjective. Relative age dating includes the law of superposition and various cross-cutting age relationships with readily dateable magmatic intrusions. However, detrital zircon records, and U-Pb ages on volcanic successions and tuffs remain the most realistic means of obtaining ages to bracket a sedimentary succession. Zircon can be extracted with some difficulty from rhyolites, but xenocrysts can be problematic when defining an age within the succession for volcanism. Basalts are even more difficult to target for age dating due to the rarity of zircon. However, baddeleyite is known to occur in such silica-undersaturated rocks, but it is usually too small to separate unless the rocks are coarse-grained, making it a difficult target to date by U-Pb methods. With modern instrumental techniques, however, combining the search and imaging capabilities of a scanning electron microscope and the high mass resolution dating capabilities of secondary ion mass spectrometry (SIMS), baddeleyite and zircon can be analysed in-situ using U-Pb, overcoming these difficulties. Small but otherwise pristine baddeleyite (and zircon) can be accurately dated down to approximately 5 µm, albeit at lower precision (Chamberlain et al. 2010). Using these techniques in conjunction with high-precision isotope dilution-thermal ionization mass spectrometry (TIMS) U-Pb dating of coarser-grained dolerite feeders (dykes and sills), an accurate and precise age of a volcanic succession can be established, especially when combined further with paleomagnetic or geochemical studies. In this study (Gumsley et al. 2017), we obtained in-situ U-Pb SIMS baddeleyite dates from a coarse-grained basaltic flow unit from an early Paleoproterozoic volcanic succession in southern Africa on the Kaapvaal Craton in the Ongeluk Formation (Transvaal Supergroup). We combined this with ages from a coeval N-trending dolerite dyke swarm, and sills of the Westerberg Province emplaced stratigraphically below the Ongeluk Formation (Kampmann et al. 2015; Gumsley et al. 2017) in the larger region, producing a 2426 ± 3 Ma weighted mean age (Gumsley et al. 2017), which defines a new, near-equatorial (Evans et al. 1997) large igneous province (LIP) at this time, which is nearly 200 Myr older than previous age calculations.

2 The Transvaal Supergroup, South Africa

The Neoarchean to Paleoproterozoic Transvaal Supergroup of the Kaapvaal Craton in southern Africa comprises one of the best-preserved and most complete stratigraphic records spanning a critical interval in Earth history. This time interval witnessed the successive growth and progressive emergence of the first continents, emplacement of numerous LIPs across this supercontinent (Kenorland?), as well as the first significant rise in atmospheric oxygen levels or Great Oxidation Event (GOE). Further events associated with the GOE include glaciations and the first known global glaciation, or Snowball Earth (Kirschvink et al. 2000), and one of the largest seawater carbon isotopic excursions, the Lomagundi-Jatuli Event. However, since the earliest documentation and interpretation of South African geology, a key correlation line for interpreting the Transvaal Supergroup stratigraphy and these associated events has been to equate the two main volcanic formations within the larger Transvaal Supergroup: the mostly submarine Ongeluk Formation basalts in the western Griqualand West sub-basin, and the subaerial Hekpoort Formation basalts in the eastern Transvaal sub-basin (Fig. 1). Older Rb-Sr and Pb-Pb whole-rock isochron data have indicated that these volcanic
formations are ca. 2.22 Ga in age, and more specifically 2222 ±13 Ma for the Ongeluk Formation basalts (Cornell et al. 1996), and ≤2250-2240 Ma for the Hekpoort Formation basalts (Schröder et al. 2016), although this has been questioned based on arguments from basin architecture (Moore et al. 2001). These contrary arguments have now been validated with our new 2,426 ±3 Ma age for the Ongeluk Formation basalts and its associated dykes and sills (Gumsley et al. 2017), which requires a reinterpretation of the Transvaal Supergroup stratigraphy.

In addition, as the Ongeluk Formation basalts overlie and interfinger with the paleo-equatorial glacial Makganyene Formation diamictites (Evans et al. 1997; Kirschvink et al. 2000), and straddles the onset of GOE, so the 2,426 ±3 Ma age also dates the termination of the first of four possible Paleoproterozoic glaciations (Rasmussen et al. 2013; Gumsley et al. 2017). Previous paleomagnetic work has also shown that the Ongeluk Formation basalts erupted at low latitude (Evans et al. 1997), a key observation re-confirmed by (Gumsley et al. 2017) and implying that the Makganyene Formation glacial event was likely global, i.e., a ‘Snowball Earth glaciation’, as the two successions are conformable. The new Ongeluk Formation basalt age (and the greater LIP age) in conjunction with other critical observations, forces a significant reinterpretation of the Transvaal Supergroup stratigraphy (Fig. 1, Gumsley et al. 2017). We propose that the Postmasburg Group of the Griqualand West sub-basin is entirely older than the upper part of the Transvaal sub-basin, i.e., older than the Duitschland Formation and lower Pretoria Group. If the Makganyene, Ongeluk, and overlying Hotazel and Mooidraai formations (Postmasburg Group) ever extended into the Transvaal sub-basin, their record has been erased by erosion below the base of the Duitschland Formation, which is marked by a significant angular unconformity that represents the demise, folding, and subsequent uplift of the of the Ghaap Group and Chuniespoort Group depositional system. Following this
main tectonic disturbance, there was a shift in depocentre to the northeast, and the initiation of a lithologically different (successor?) basin represented by the Duitschland Formation and the unconformably overlying Pretoria Group. Combining this new stratigraphic framework with the published record of redox indicators suggests that the onset of GOE was not characterized by a single transition and rise of atmospheric oxygen levels, but rather by one or more ‘oscillations’ in oxygen levels before final complete oxygenation of the atmosphere and the first appearance of red-bed sandstones in the Dwaaiheuwel Formation (Gumsley et al. 2017). Our new Ongeluk Formation basalt age eliminates the >200 Myr hiatus below the Makganyene Formation diamictites, and argues for an essentially continuous depositional record leading up to the Makganyene Snowball Earth glaciation with only a minor unconformity associated with sea-level fall (Polteau et al. 2006).

3 Global Correlation

This leads us to interpret the Makganyene Formation glaciation as the first Paleoproterozoic glaciation, and we correlate it with the diamictites of the Ramsay Lake Formation of the Huronian Supergroup in Canada (Gumsley et al. 2017). Cap carbonates are lacking above this first glaciation in both supergroups. We correlate the lower Duitschland Formation glaciation with the Bruce Formation glaciation, identifying it as the second glaciation. It is overlain in both basins by a unique level of cap carbonates of potentially global significance. Glaciations within the Huronian Supergroup of the Superior Craton are bracketed in age between 2460 Ma and 2308 Ma (Ketchum et al. 2013; Rasmussen et al. 2013; Bleeker et al. 2015), with the Ramsay Lake Formation glaciation occurring between 2460 Ma and 2426 Ma (Gumsley et al. 2017). This in turn correlates with the oldest glacial deposits in the Wyoming Craton of the USA, with the oldest known glaciation there known as the Campbell Lake Formation of the Snowy Pass Supergroup. In addition, the 2442 ± 2 Ma Seidorechka Formation (Brasier et al. 2013) and the overlying 2435 ± 2 Ma Polisarka Formation (Amelin et al. 1995) of the Kola–Karelia Craton in Russia and Finland may tightly bracket the oldest Paleoproterozoic glacial event between 2442 Ma and 2435 Ma, respectively, implying that it lasted less than 7 Myr. Other glaciations may include the Meteorite Bore from the Pilbara Craton and the Padlei from the Hearne Craton.

Our results add to the growing evidence for large low-latitude supercontinent in the early Paleoproterozoic, including the Kaapvaal Craton and the clan of cratons that defines supercontinent Superior: Superior, Wyoming, Hearne, and Kola–Karelia (Bleeker 2003; Bleeker et al. 2016; Gumsley et al. 2017). These landmasses, at least in part contiguous, record a series of LIP events between 2510 Ma and 2440 Ma and include the Mistassini, Kaminak, Baltic, Baggot Rocks, and Matachewan LIPs before the ca. 2,426 Ma Ongeluk LIP of the Kaapvaal Craton. Cumulatively, these large juvenile volcanic provinces on extensive low-latitude continental landmasses are likely to have triggered near-equatorial glaciations via enhanced chemical weathering of aerially extensive, nutrient-rich continental flood basalts, and ultimately led to the first significant rise in atmospheric oxygen (Gumsley et al. 2017). Importantly, the dated near-equatorial Ongeluk LIP, conformably overlying and interfering with the uppermost Makganyene Formation glacial diamictites could illustrate the dual role of LIPs in these global events.

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References


From LIPs to gold in Rhyacian metawackes

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Abstract The Siderian-Rhyacian (2500-2050 Ma) was a period of: 1) extensive and frequent intrusive and extrusive intraplate magmatism (Large Igneous Provinces); 2) a sudden increase of oxygen in the atmosphere-hydrosphere system; 3) deposition of an increased variety of oxide mineral types; 4) intensive chemical and physical erosion; 5) formation of huge continental basins filled with clastic rocks affected by late deformation ca 2 Ga. Uplift of Archean continental blocks related to tectonism and LIP magmatism likely accelerated erosion and produced large volumes of clastic material. Oxidized and elemental metals were mixed in clastic debris from combined sources including: Archean crust, Rhyacian magmas and chemical sediments. The geodynamics of LIPs and basin formation played an important role in the distribution and abundance of metals such as gold before late tectonic processes determined their final location. Rhyacian clastic basins of the West Africa-Guiana land mass host large gold deposits. Rhyacian metawackes contain detrital gold. Rhyacian reconstructions could build on those of the Siderian and include specific tectonostratigraphic markers of the component land masses.

1 Introduction

Under nearly similar conditions to the Siderian Period (Gumsley et al. 2017) the Rhyacian was a period of widespread and persistent Large Igneous Province (LIP) activity (Bleeker and Ernst 2006; Ernst and Youbi 2017). One major pulse of LIP activity just preceded or was coeval to the formation of large clastic basins between 2.13 and 2.07 Ga.

Rhyacian lithospheric thinning and uplift of Archean masses likely took place on the continental margins of Superia as well as on the margins of pre-“SAMBA” land masses (Johansson 2014). LIP magmatism amplified intracontinental erosion and clastic sedimentation while LIP emplacement (decametric sills and dikes), gas release and erosion facilitated icehouse and greenhouse effects (Ernst and Youbi 2017). Barren highlands were battered by acid rains creating oxidized regolith and huge volumes of oxides of a variety of mineral types (Hazen et al. 2008). Consequently, an increased diversity of minerals (metal) oxides was available for clastic and/or chemical deposition in basins forming on locally sagging Archean lithosphere. Large et al. (2017) suggest that zinc, copper and gold were some of the key elements in Rhyacian shallow water environments.

Rhyacian clastic basins (Fig. 1; Bardoux 2012) compare in size and tectonic setting to the Archean Wits basin (Frimmel, 2005) which formed in a much smaller land mass. Rhyacian basins precede fluvial sediments called Tarkwaian which contain significant paleoplacer gold of undetermined sources (Cooper 1934, Sestini 1973). Vestiges of these diagnostic polymict conglomerates have been transposed near lithospheric structures. In French Guiana quartz boulder conglomerates are interlayered with Rhyacian metawackes (Bardoux 2012).

Figure 1. Rhyacian clastic basins superimposed on Ernst and Youbi’s (2017) Siderian-Rhyacian LIPs compilation map. Blue outlines refer to the South American and African Rhyacian land masses assembled by late Rhyacian (Eburnean-Transamazonian) orogenies. Rhyacian carbonate occurrences and Francevillian fauna are tectonostratigraphic markers that may serve as tie points to Rhyacian reconstructions.

Rhyacian clastic basins are unconformable onto and across multiple older Rhyacian arc sequences.
that had been deformed prior to clastic sedimentation. In certain cases gold in these clastic sediments was entrapped nearly 160Ma after the last arc magmatism and gold is related to late thermal events ca 2 Ga old (Daoust 2016). This thermal event is coeval to massive uplifting of the lower crust in western Suriname where very large and long-lived LIP events culminated (Kroonenberg et al 2016).

Uplifted Archean continents (Rosa-Costa et al. 2003) and Rhyacian magmatic arcs (some VMS bearing) are expected erosional sources of Rhyacian sediments and gold. These basins are underlain by lithospheric structures that tapped lithospheric and mantle magmas which locally represented additional potential metal sources (Hronsky et al. 2012) in part enhanced by the first significant hydration of the subcontinental mantle lithosphere ca 2160 Ma. Thus, Rhyacian metasedimentary basins contained magmatic and detrital metals in proportions that were related to proximity to magmatic and erosional sources and to lithospheric structures.

2 Paleoreconstruction of the Rhyacian

Prior to the assembly of supercontinent Nuna, Rhyacian land masses are considered to have been somewhat scattered over earth’s surface (Eglington 2013). The largest Rhyacian pre-“SAMBA” land mass formed of the assembly of Baltica, Sarmatia, West Africa, Guiana Shield, Sao Francisco, Congo Craton and possibly Kalahari is thought to have been positioned near one of Earth’s poles (Eglington 2013). This hypothesis may not reconcile with the formation of: 1) large clastic basins after limestone formation on cratonic margins of West Africa (Vic and Billa, 2015, Fig. 1); 2) manganiferous strata in Africa and the Guiana Shield; 3) different structural vergences between landmasses and; 4) the slope facies siltstones containing NeoRhyacian (2009 Ma) Francevillian Fauna in Gabon (El Albani et al. 2015).

Apparent polar wander path (APWP) data from French Guiana (Theveniaut et al. 2006) suggest that French Guiana was close to the equator during the Mesorhyacian (ca. 2130 Ma) at the time of initiation of the clastic basins.

3 The Leo-Guiana Shield land mass

Most reconstructions of the Leo and Guiana Shields are Pangean (Frimmel 2014). In many cases, lithostratigraphy and regional structural trends do not match. The reconstruction of Onstott et al. (1984), however, aligns structural patterns, Archean land masses, and key tectonostratigraphic sequences between the Leo Shield (Vic and Billa, 2015) and the Guiana Shield (Bardoux, 2012) and other Rhyacian land masses reasonably well. Some features suggest that the Leo shield drifted southeast of the Guiana Shield prior to Pan African orogeny.

4 Gold in Rhyacian metaclastic basins

Many Rhyacian lode vein gold deposits could define their own category. These metawacke hosted gold deposits were mostly affected by a single late phase of compression/transpression. Most metaclastic basins comprise thick beds of metawackes interbedded with geochemically distinctive black shales.

During deformation black shales facilitate strain partitioning and syn-metamorphic high strain. Rheological contrasts of clastic lithotypes enhanced permeability and fluid flow. Deformation created inversion style folding and faulting (Williams et al., 1989) around rigid Archean basement and Rhyacian granitoids. Numerous Archean blocks were converging towards the end of the Rhyacian period causing numerous and diverse tectonic inversions thru thick skinned tectonics with a final twist of wrench tectonics. Veining principally formed in
metawacke by rheological contrasts. Permeability is enhanced by switches from transpressive to transtensional strain that may relate to a transformation from far-field to body-force stresses (Lebrun et al. 2016). Alteration mineralogy with auriferous veins is primarily potassic and chloritic and reflects the bulk composition of the rock host.

Although the main source of Rhyacian quartz/carbonate vein-hosted gold in Rhyacian metawacke is likely to be the mantle, there is evidence that sedimentary gold may be a further source of metamorphic (orogenic) gold and a component of enrichment.

In the Guiana Shield, a clast of pre-metamorphic gold occurs in Rhyacian garnet-biotite-muscovite phyllite (Fig. 3a, b). The same sample exhibits detrital gold grains (Fig. 3c) as well as garnet porphyroblasts overgrowing pre-metamorphic quartz and pyrrhotite that contain micron-scale gold inclusions (Fig. 3d; Thompson and Bardoux 2015).

Figure 3. Cases of a metawackes in Guyana; b strained garnet porphyroblast growing on pyrrhotite containing gold; c detrital grains containing gold near garnet; d gold inclusions in pyrrhotitic garnet porphyroblast (Photos courtesy of P. Thompson).

Figure 4 also exhibits polyphased euhedral pyrite in a foliated metawacke from Suriname. The auriferous inclusion-rich core is overgrown by an inclusion-poor outer zone. This late pyrite phase grew prior to synkinematic pressure shadows while pyrite porphyroblasts were rotated. This timing relationship indicates that gold is pre-deformation. Very often altered selvedges outside auriferous quartz veins exhibit pyrite pseudomorphs variably replaced by chlorite (Thompson and Bardoux 2015). If such pyrites contained gold inclusions like in the upper part of Figure 4, chloritization could have mobilized gold and sulphur in metamorphic fluids that transferred these elements to host rock and ultimately to lode vein arrays.

Figure 4. Polyphased pre-kinematic automorph pyrite with pressure shadows in metawacke from Suriname. Gold inclusions are in the oldest pyrite phase. Pseudomorphs are locally chloritized (Photos courtesy of P. Thompson).

5 Endowment of Rhyacian metawakes

More than 30 percent of the Rhyacian gold endowment is from clastic metasedimentary rocks in the Leo and Guiana Shields (Bardoux 2012). The Siguiiri deposit (Guinea) is hosted in Birimian wackes of the Leo Shield (Lebrun et al. 2017). The Tier 1 Rosebel deposit (Suriname) is hosted in Armina wackes (~5 MozAu produced; Wasel and Donald 1997; Daoust 2016). Armina wackes contain Archean detrital zircons (Daoust 2016).

6 Discussion

As Rhyacian LIPs and clastic basins are nearly coeval, the formation of these basins, their size and provenance of sediments hosting Tier 1 gold deposits may link to LIPs activity and synchronous thermalism and hydrothermalism on lithospheric structures. Rhyacian paleo-reconstructions should be further tied with paleostratigraphic markers to better constrain these potentially related elements. An updated reconstruction of Rhyacian land masses will assist gold exploration in Rhyacian clastic basins by providing a global framework within which these basins were assembled prior to final tectonometamorphism. Technically most Rhyacian clastic basins should contain Archean detrital zircons and many may contain traces of gold invisible to the
naked eye. Between Wits and Tarkwaian paleosedimentary gold, all favorable conditions were assembled during Rhyacian sedimentation for some gold to be available in a detrital or biogenic mode. During deformation and local LIPs activity, minerals of Rhyacian metawacke, were transformed by dehydration and decarbonation reactions. Some metals were immobile during these processes, others, including gold, reached seisimogenic, chemical (redox) and P-T traps in locations of favorable ground preparation (eg. older Rhyacian Arc settings).

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The LIP record of the Siderian-Rhyacian (2500-2050 Ma)

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Abstract. The Siderian-Rhyacian time period 2500-2050 Ma, is associated with breakup of a Late Archean supercontinent (or supercratons), and also with a range of dramatic environmental changes, including the Great Oxidation event and glaciations, and major ore deposits of a various commodity types. It has been previously shown (particularly for the Phanerozoic) that Large Igneous Provinces (LIPs) can be linked with such dramatic tectonic, environmental and metallogenic events (e.g. Ernst and Jowitt 2013; Ernst, 2014; Ernst and Youbi 2017). The LIP record of Siderian-Rhyacian time is reviewed as a contribution to understanding the LIP influence on rifting, atmospheric-oceanic changes and formation of ore deposits during that period. This summary includes LIP s and interpreted LIP fragments (those diminished in size by erosion and continental breakup). LIPs can consist of basaltic volcanism, sill provinces, mafic-ultramafic layered intrusions, and associated silicic magmatism. However, LIPs are often dominated by regionally extensive mafic dyke swarms, with a radiating geometry whose focal point locates both a mantle plume centre and associated continental breakup (or attempted breakup). The events are organized in order of decreasing age.

1 The 2500-2050 Ma LIP record

1.1 2500-2510 Ma events

Multiple c. 2500 Ma LIP nodes are located along various margins of the Superior craton. The 2510 Ma Mistassini LIP (giant radiating dyke swarm) is on the SE side, the 2505 Ma Ptarmigan swarm on the NE side and the 2500 Ma Irsuaq swarm is on the N side; each is linked to a potential plume on the margins of the Superior craton. In the Karelia-Kola craton the 2440-2510 Ma Baltic LIP (dyke swarms, layered intrusions and volcanics) includes a c. 2500 Ma pulse (e.g. Kulikov et al. 2010) and the Hearne craton contains the 2500 Ma Kaminak LIP (dyke swarm) (Sandeman et al. 2014); both of these cratons have been reconstructed with the Superior craton (Bleeker and Ernst 2006; Gumsley et al. 2017). The 2500 Ma Kilarsaarfik dykes are present in the Greenland portion of the North Atlantic craton which is hypothesized to have been juxtaposed adjacent to NE Superior craton at this time (Nilsson et al. 2010), where it could be linked with the Ptarmigan swarm. The Zimbabwe craton contains the 2510 Ma Crystal Spring swarm whose age-match with the Mistassini LIP suggests reconstruction of Zimbabwe and the eastern Superior craton (Söderlund et al. 2010).

1.2 2480-2440 Ma events

The 2480-2450 Ma Matachewan LIP (giant radiating swarm, layered intrusions and bimodal volcanics) dominates the southern Superior craton and includes Ni-Cu-PGE mineralization (e.g. East Bull Lake Suite) (e.g. Ernst and Bleeker 2010; Ciborowski et al. 2015). Corresponding units in Karelia-Kola are also linked in the reconstruction (Bleeker and Ernst 2006). Typically, the 2500-2440 Ma units in Karelia-Kola (also important for Ni-Cu-PGE-Cr) are grouped as a single event (the Baltic LIP, or BLIP), but the BLIP should actually be parsed into two separate events that can be matched with the two distinct Superior craton plume centres, 2510 Ma Mistassini and 2480-2450 Ma Matachewan (e.g. Kulikov et al. 2010). The southern margin of the Pilbara craton is host to the 2450 Ma Wongarra-Weeli-Wolli LIP (mainly volcanics). The Zimbabwe craton hosts the 2.47 Ga Mtshingwe dyke whose match with the Matachewan LIP was additional support for the reconstruction of Zimbabwe near the eastern Superior craton (Söderlund et al. 2010).

1.3 2430-2410 Ma events

The newly dated 2426 Ma Onegluk LIP (dykes, sills and volcanics) is a key event in the Kaapvaal craton with links to the glaciations and the Great Oxidation event (e.g. Gumsley et al. 2017). The 2420-2410 Ma Widjemoooltha LIP (giant dyke swarm) of the Yilgarn craton (Smirnov et al. 2013; Pisarevsky et al. 2015) is notable for its association with the Ni-Cu-PGE economically important Jimberlana dyke-like layered intrusion. Additional LIP fragments of this age include the 2410 Ma Sebanga Poort dykes of the Zimbabwe craton (Soderlund et al. 2010), and the Ringvassoy dykes in the Norbotten terrane of the Karelian-Kola craton (Kullerud et al. 2006). The poorly dated Du Chef dykes of eastern Superior craton but may also be of this age (Ciborowski et al. 2014).

1.4 2380 (-2420) Ma events

The 2375 Ma Bangalore LIP (dykes, sills and volcanics) is distributed throughout the Dharwar craton (e.g. Kumar et al. 2012). Additional events of this age occur in the North Atlantic craton: Graedefjord dykes of west Greenland (Nilsson et al. 2013) and the Scourie dykes in the Lewisian complex of NW Scotland (Davies and Heaman 2014); note that the Scourie dykes range in age from 2375-2412 Ma, overlapping with events in section 1.3.
1.5 2330-2310 Ma events

The 2330 – 2310 Ma Kuito-Taivalkovski dyke swarm is present in Karelia (Salminen et al. 2014; Stepanova et al. 2015) but not currently recognized elsewhere (Ernst 2014).

1.6 2250-2240 Ma events

After a 60 Ma gap LIP magmatism resumes with the <2250-2240 Ma Hekpoort volcanics of the Kaapvaal (Gumsley et al. 2017), and 2240 Ma dykes in the Vestfold Hills (Lanyon et al. 1993). Additional magmatism of this age is known from other blocks (but the data are currently unpublished).

1.7 2230-2200 Ma events

Most prominent during this interval is the 2220-2210 Ma Ungava-Nipissing LIP (giant radiating dyke swarm and sill province) of the Superior craton (e.g. Ernst and Bleeker 2010) with Co-Ni-As-Ag ore (sills in Cobalt plate) and Ni-Cu-PGEs (Shakespeare intrusion) and which can be linked with coeval Karjalitic (Koli) sills in Karelia-Kola (e.g. Vuollo and Huhma 2005; Davey et al. 2016). In the Slave craton there are separate 2230 Ma Malley and 2210 Ma MacKay giant dyke swarms that each converge to the eastern margin of the Slave craton. The west Greenland portion of the North Atlantic craton hosts the 2210 BN1 (boninitic-noritic) dyke swarm (Ernst and Bleeker 2010). The 2221 and 2209 Ma Kandlamadugu and Somala giant dyke swarms, respectively, are present in the Dharwar craton (French and Heaman 2010). Also relevant to this time interval are the 2208 Ma Turee Creek mafic intrusives and volcanics and the possibly correlated Cheela Springs volcanics of the Pilbara craton (Martin and Morris 2010).

1.8 2190-2180 Ma events

The Southwestern Slave magmatic province of the Slave craton includes a major dyke swarm and also associated alkaline magmatic centres (such as the Blachford with the Thor Lake rare metal deposits) (e.g. Buchan et al. 2010). The Tulemalu (-MacQuoid) dyke swarm is present in the Rae craton (Ernst and Bleeker 2010).

1.9 2170-2150 Ma events

The Biscotasing LIP (giant dyke swarm) is widespread in the Superior craton and linked to Payne River dykes and Cycle-1 magmatism along the eastern margin of the craton (e.g. Ernst and Bleeker 2010). A younger magmatic pulse is marked by the 2150 Ma the Riviere du Gue swarm (Maurice et al. 2009). The Wyoming craton hosts the 2161-2152 Ma Rabbit Creek swarm and the slightly older 2171-2157 Ma Powder Creek-South Pass swarm (Kilian et al. 2016). The 2150 Ma Hengling swarm is present in the North China craton (Peng 2015). The Dharwar craton hosts the 2180 Ma Mahbubnagar-Dandeli LIP (giant radiating swarm) (French and Heaman 2010; Ernst and Srivastava 2008).

1.10 2125-2100 Ma events

The 2125-2100 Ma Marathon LIP (giant radiating swarm) (Halls et al. 2008) is regionally important in the southern Superior craton. Magmatism of this age is also present in Karelia-Kola (e.g. Vuollo and Huhma 2005; Davey et al. 2017), Wyoming craton (Kilian et al. 2016) and also in the Hearne, Slave, and North Atlantic cratons (Ernst and Bleeker 2010; Davey et al. 2017). This is also the time of extensive cratonic sedimentation on many land masses (Bardoux and Ernst, this volume).

1.11 2070-2050 Ma events

The Superior craton hosts the 2075 Ma Fort Frances LIP (giant radiating dyke swarm) associated with the breakup up along the southern margin of the craton (e.g. Bleeker and Ernst 2006) and also the Lac Espirit and Cauchon dykes potentially related to a separate mantle plume on the NW side of the craton in present day Hudson Bay (Ernst and Bleeker 2010). The 2058 Ma Bushveld LIP is dominated by economically important nine-km-thick Bushveld intrusion, but also includes other mafic and silicic units distributed around the Kaapvaal craton, and also including the associated Cu-rich Phalaborwa carbonatite (e.g. Rajesh et al. 2013). In Karelia-Kola there is the Kevitsa-Kuetsjarvi-Umba event, with Ni-Cu-PGE mineralization (Martin et al. 2013; Malehmir et al. 2014). The 2050-2030 Ma Kangamiut-MD3 radiating swarm of west Greenland can be linked with dykes in Nain province (after closure of the Labrador Sea) to define a plume centre on the western side of the North Atlantic craton (Nilsson et al. 2010).

Summary

This brief survey provides an overview of the important LIP and LIP-fragment events that contributed to rifting and breakup, environmental change, and major ore deposits during the Siberian-Rhyacian (2500-2050 Ma) period.

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S01 – Geology, geodynamics and metallogeny of the Rhyacian (2.35 – 2.05 Ga)


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The Rhyacian “Montagne d’Or” auriferous volcanogenic massive sulphide deposit, French Guiana, South America: stratigraphy and geochronology

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Abstract. In French Guiana, the “Montagne d’Or” gold deposit (5 Moz at 1.5 gpt Au) is located in the northern branch of the Rhyacian Paramaca Greenstone Belt. The sulphide deposit is hosted by a bimodal volcanic and volcaniclastic, south-facing sequence that is affected by a penetrative E-W striking and south-dipping regional foliation. The volcanic stratigraphy is dominated by calc-alkaline felsic lithologies to the west, interbedded and interdigitated with tholeiitic mafic rocks to the east. Pillowed mafic flows and graded-bedded felsic volcaniclastic rocks are found and indicate explosive volcanism activity in a submarine environment. U-Pb zircon geochronology suggests that most of “Montagne d’Or” volcanic and intrusive rocks have crystallized during an evolving magmatic event, from 2155 Ma to 2140 Ma. A porphyry intrusion crosscutting the ore yields a U-Pb zircon age of 2140±5.1 Ma, hence constraining a minimum age for the sulphides mineralization. This also indicates that the sulfide mineralization is coeval with magmatism, attesting for the volcanogenic nature of the “Montagne d’Or” gold deposit.

1 Introduction

The Guiana shield possesses a known potential for volcanogenic sulphide deposits (VMS; Gibbs and Barron 1993; Sidder et al. 1995; Channer and Anderson 2000), but only few occurrences have been discovered yet. The “Montagne d’Or” gold deposit is the first VMS discovered in the Guiana shield (Franklin et al. 2000). Its discovery has been followed by the finding of the Serra do Ipitinga Au-Ag(Zn-Cu) VMS deposit in Brazil (Faraco et al. 2006; Klein et al. 2009) and the Dorlin exhalative stratabound gold bearing tourmalinite deposit in French Guiana (Fig. 1; Lerouge et al. 1999; Milési et al. 2003). The Groete Creek and Aremu gold deposits in Guyana probably represent also a VMS-type mineralization (Sherlock and Michaud 2000).

Figure 1. Geology of Guiana shield and metallogeny with location of the “Montagne d’Or” deposit; Adapted from Voicu et al. (2001); Delor et al. (2003b); Daoust et al. (2011). NGT: North Guiana Through ; NSSZ: Northern Suriname Shear Zone ; CGSZ: Central Guiana Shear Zone.
The geological characteristics and genetic processes related to these VMS deposits are still poorly documented and need to be better constrained. This study proposed a revised stratigraphic model for the VMS deposit of the “Montagne d’Or”, a mining property of “Compagnie Minière Montagne d’Or” (CMO), and presents a series of U/Pb zircon dates that are consistent with the inferred volcanogenic origin.

2 Geological setting

2.1 Regional geology

The “Montagne d’Or” deposit is located in northwestern French Guiana of South America, at approximately 180 km southwest of Cayenne (Fig. 1). It is hosted by the northern branch of the Proterozoic Paramaca Greenstone Belt (PGB). The PGB is interpreted as the remnant of a volcanic arc sequence formed between 2.18 to 2.13 Ga, which has been accreted/deformed during the Transamazonian orogeny in order to form two regional-scale synformal branches located to the north and south of a Central TTG complex dated at 2.15 to 2.12 Ga in French Guiana (Vanderhaeghe et al. 1998; Delor et al. 2003a,b; Enjolvy 2008).

The PGB comprises a lower volcanic member known as the Paramaca Formation and an upper sedimentary member, the Armina Formation. The Armina Formation crops out along the northern margin of the northern branch of the PGB and is interpreted as a turbiditic flysch sequence (Bosma et al. 1983; Ledru et al. 1991; Gibbs and Barron 1993).

Three main tectonic and deformational events have been recognized. One of them, the D2a event, is responsible for east-west trending structures of the Guiana Shield, and is related to the formation of several pull-apart basins in the northern branch of the PGB, also known as the North Guiana Trough (Fig. 1; Ledru et al. 1991; Vanderhaeghe et al. 1998; Delor et al. 2003a).

Three types of gold deposits have been identified in the PGB, (1) gold-bearing conglomerates, (2) orogenic gold deposits, and (3) stratiform/stratabound deposits (Milesi et al. 2003), the latter includes the “Montagne d’Or” deposit.

2.2 Geology of “Montagne d’Or” deposit

The “Montagne d’Or” deposit is hosted by a bimodal volcanic sequence and related sedimentary rocks forming a narrow, 9 km-long by 1 km-wide, structural inlier of the PGB surrounded by gabbro, granite and diorite intrusions. This greenstone belt is located 5km to the north of the Central TTG complex and 15km south of the North Guiana Trough. A rhyolite rock of the “Montagne d’Or” belt have been dated by 207pb/206pb analyses on zircons and yielded an age of 2152±8Ma (Delor et al. 2003a).

The primary stratigraphy of the “Montagne d’Or” volcanic edifice has been transposed by a penetrative E-W trending, steeply south-dipping regional schistosity exhibiting down-dip stretching and mineral lineations. This schistosity is regionally developed, parallel and coeval with the formation of the steeply-dipping E-W trending Chauve-souris shear-zone to the south. Regional metamorphism is at upper greenschist – lower amphibolite facies.

Figure 2. a Geological map modified from CMO and b Stratigraphic model for the “Montagne d’Or” deposit; FWZ: Footwall zone; LFZ: Lower favorable zone; UFZ: Upper favorable zone; HWZ: Hanging-wall zone.
The “Montagne d’Or” volcanic sequence consists of three series 1) a lower mafic volcaniclastic unit overlain by 2) an upper mafic volcanic unit with tholeiitic affinity in the eastern part of the property, and interbedded/interdigitated with calc-alkaline felsic volcanic rocks to the west, all these rocks being overlain by 3) interbedded clastic and volcaniclastic rocks (Fig. 2a.). Based on the occurrence of pillowed mafic flows and graded-bedding structures in some felsic rocks, Franklin et al. (2000) suggested that the “Montagne d’Or” volcanic sequence is south-facing. The volcanic rocks are crosscut by syn-volcanic calc-alkaline intrusions and by «late» transitional diabase dykes.

The “Montagne d’Or” mineralization consists of two main sulphide horizons (LFZ and UFZ) and two subsidiary zones (FWZ and HWZ) occurring as (1) stratiform sulphide disseminations, (2) stockworks-veinlets, and (3) structurally-transposed layers of semi-massive sulphides. The gold-rich sulphide orebody consists mainly of pyrite, pyrrhotite and chalcopyrite with minor sphalerite, magnetite, galena and arsenopyrite, hosted inside chlorit-sericite-rich alteration zones (Franklin et al. 2000).

3 Stratigraphic model

On the basis of recent drill-holes provided by CMO, new lithological facies of the volcanic sequence have been identified, allowing us to refine the Franklin’s et al. (2000) stratigraphic model (Fig. 2b.).

The lower volcanoclastic unit reveals a variety of facies comprising massive theoleitic mafic flow and tuff alternating with very fine, well-layered mudstones and greywackes of mafic volcanic origin. Within the tuff facies, evidence for a south-facing sequence is preserved by graded-bedded horizons of juvenile felsic lapilli and pumices, that also indicate a mixed origin of clastic detritus as reworked volcanic clasts and primary felsic fragments. The uppermost part of this tuff unit is marked by the occurrence of thin layers of graphicite sediments.

The main lithological units, which include the upper mafic unit and the felsic unit, reveal that two bimodal eruptive sequences are present. A mafic tuffite horizon, with a calc-alkaline geochemical signature, occurs between the two sequences and seems to mark a pause in the volcanic activity. The Upper mafic unit is made up of predominantly massive volcanic flows at the base that grades upward into pillowed or sheeted volcanic flow with thin mafic tuff as interfloow material. The felsic unit consists of three type of lithologies, clearly showing the coexistence of intrusive and extrusive facies; 1) A slightly-altered, poorly-mineralized homogeneous quartz-feldspar granodioritic facies is abundant in the western part of the deposit. This granodiorite is interpreted as an interdigitated cryptodome with apophyseal sills, 2) Extrusive volcanic facies occur as well-bedded, locally graded-bedded horizons of felsic lapilli tuff showing granodioritic lapilli, pumices fragments and rare lithic clasts, and 3) Quartz-phyric and altered felsic cinder tuffs facies that is the principal lithology hosting the mineralization.

The first eruptive sequence starts by the deposition of felsic rocks related to the granodioritic cryptodome and overlain by tuffs generated during the emergence of the dome. Eastward, distal correlative facies are represented by felsic lapilli tuffs that are enriched in mafic lithic clasts, probably derived from the underlying mafic facies intruded by the granodiorite dome. Several horizons of mafic volcanic flows, including the uppermost mafic tuffite horizons, overly the felsic rocks towards the end of this eruptive sequence.

The second eruptive cycle starts with similar magmatic events with more abundant felsic lapilli tuffs at the summit of the reworked felsic cryptodome. This volcanic sequence suggests more vigorous rhyodacitic explosive activity and likely marks more viscous magmatism and/or shallower water depth towards the end of felsic volcanism.

The uppermost sequence consists of sedimentary and volcanic rocks that consist of mafic tuffs evolving into greywackes, and thick massive theoleitic mafic flows with amygdales overlain by a series of interbedded greywackes and mudstones with a marker horizon of south-facing graphicitic mudstone at the top.

Felsic porphyry intrusions, probably sills, cut across the whole sequence and are interpreted as a «late» magmatic phase of the felsic volcanism. The sulphide mineralization occurs through replacement processes and is mainly found within the felsic tuffs. Two intermediate porphyritic intrusions crosscut the mineralization and its alteration halos. Swarms of diabase dykes, crosscutting all lithologies, were emplaced during late increments of regional deformation.

4 U/Pb Geochronology

Using the LA-ICP-MS method, we acquired four new U-Pb zircon ages, two from the felsic unit and two other from porphyry intrusives of the “Montagne d’Or”. The felsic tuff

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Figure 3. U/Pb Zircon Geochronology of the Intermediate porphyric intrusive (I2P); LA-ICP-MS Spectrum results are standardized with 91500.
sample (T1) yielded an age of 2155.5 ± 4.6 Ma; the felsic porphyritic intrusion sample (I1P) yielded 2141.7 ± 5.3 Ma; the granodiorite sample (I1C) yielded 2140.7 ± 5.1 Ma; and the lowermost intermediate porphyritic intrusion (I2P) yielded an age of 2140 ± 5.1 Ma (Fig. 3). The last three facies, sample I1P, I1C, I2P, are intrusive into the felsic tuff, sample T1. Sample I2P corresponds to an intermediate porphyritic intrusion which cuts across the mineralization and its alteration halos, hence constraining a minimum age for the sulfide mineralization.

These U-Pb age data suggest that the “Montagne d’Or” volcanic and intrusive rocks were formed during a single and progressive magmatic event that lasted from ca. 2155 Ma to ca. 2140 Ma. Our geochronological data are consistent with age constraints presented by Delor et al. (2003a).

5 Discussion

The geological characteristics of the “Montagne d’Or” suggest that it is a bimodal mafic-felsic VMS deposit that probably formed in a tholeiitic back-arc environment (Franklin et al. 2000). Volcanic textures preserved by the volcanic rocks hosting the mineralization are consistent with explosive volcanism within a submarine environment. U/Pb geochronological dating reveals that the various types of extrusive and intrusive volcanic rocks have crystallized during the same magmatic event, most likely from ca. 2155 Ma to ca. 2140 Ma. The gold-rich sulphide mineralization is coeval with that magmatic event, as indicated by crosscutting relationships with late-stage intrusion, attesting for the VMS origin of the “Montagne d’Or” deposit which therefore is the first known occurrence of VMS gold deposit in the Guiana shield.

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Plume activity related to the Kaapvaal craton and implications for Rhyacian plate reconstructions and ore deposits

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Abstract. Refinements in the geochronology of the Kaapvaal provide new possibilities for correlations with other Archean crustal fragments. Paleomagnetic studies provide a number of possible positions for the position of the Kaapvaal in relation to the Superior supercontinent at the time of the emplacement of the Bushveld Complex. Previous workers position the Kaapvaal southwest of Superior based on migrating plume ages along that margin. This work considers an alternate position for the Kaapvaal, southeast of Superior and adjacent to Karelia, based on revised geochronology and an updated magmatic barcode.

1 Linking Bushveld Complex and Ventersdorp Supergroup plumes

Recent geochronological and paleomagnetism studies have done much to improve on the understanding of the paleogeographic location of the Kaapvaal craton in the Paleoproterozoic and the available information is reviewed here. Achieving precise and accurate ages for magmatic events, particularly for large igneous provinces (LIP) events, is critical in paleogeographical reconstructions, creating a barcode for different fragments of crust which can be matched against one another at the time of magmatic events. Dyke swarms provide additional information regarding possible plume locations; particularly where they intersect craton margins at high angles and form radiating patterns (Ernst et al, 2009).

The plume origin of the Bushveld Complex (Sharpe et al., 1981; Sawkins, 1984; Hatton 1995) is still debated and there exist a number of considerations. A number of radiating dyke sets are observed around the Bushveld Complex, however these have turned out to be older. The Rykoppies dyke swarm on the eastern margin of the Bushveld Complex have been demonstrated to be 2.70 - 2.66 Ga in age (Olsson et al, 2010; 2011), corresponding to the Ventersdorp flood basalt LIP of the same age. Olsson et al. (2010) postulated that the locus of magma flux represents a triple-junction related to the plume head. The event did not result in rifting and break-up, but rather only the thinning and subsidence of the crust from 2.66-2.06 Ga with the formation and development of the Transvaal Basin.

The Kaapvaal was considered to have been juxtaposed to the Pilbara fragment in a supercraton called Vaalbara (Cheney, 1996; Bleeker, 2003). Matching polar wander paths can be obtained for the two cratons as well strikingly similar geological features, including volcanic analogues (Maddina Basalt) to the Ventersdorp lavas mentioned previously, and suggest that the two cratons were joined as early as 2.78 Ga (de Kock et al, 2006) de Kock, 2009). It was thought that Vaalbara existed for about 500 My but the revised age for the Ongeluk lavas of 2426 ± 3 Ma (Gumsley et al, 2016) presents new scenarios for the history of Vaalbara, including linkages to the Great Oxidation Event (GOE). It is evident from the apparent polar wander paths that the two cratons follow very different paths after 2.44 Ga, the Kaapvaal being relatively stationary between 2.44 and 2.22 Ga and the Pilbara being at a much lower latitude; the stratigraphic correlation between the cratons also breaks down, suggesting cratonic breakup at ca. 2.44 Ga (Kampmann et al, 2015). Additional paleomagnetic information to be noted is provided by Letts et al (2011) which indicates sudden movement towards the pole at the time of the Bushveld LIP which becomes important below.
2 Paleo-reconstructions based on the magmatic barcode

Ernst & Bleeker (2006) and Söderlund et al, (2010) constructed magmatism barcodes for different Archean cratons (Figure 1). The addition of the 2.426 Ga Ongeluk age provides a cursory correlation to the Matachewan LIP event, recorded on the Superior Craton, and new estimates for the Machadodorp Fm put this event at around 2.1 Ga (Söderlund, pers comm), both of which assist in filling out the Kaapvaal barcode. Gumsley et al. (2016) and Bleeker et al. (2016) provided a reconstruction of the Superia Supercontinent based upon paleomagnetic poles, placing the Kaapvaal near the equator at Ongeluk times (Figure 2). Bleeker et al. (2016) consider the Bushveld LIP as a final stage of a hotspot track beginning with the Marthon LIP (2.100 - 2.125 Ga) and followed by the Fort Frances LIP (2.065 - 2.075 Ga); both of which correlate well with the Kaapvaal rock record. A concern regarding this is that there are no observable radiating dykes at 2.06 Ga, which suggests that the centre of plume was located more central to the position of the Bushveld Complex. The other consideration is the location of the only known Bushveld-aged intrusion anywhere, namely that of Kevitsa (2.058 Ga, Hanski et al, 2001), which was towards the south-eastern side of Superia at 2.4 Ga. What we propose is that the Kaapvaal and Pilbara were located east of Karelia-Kola at 2.4 Ga. It is postulated here that the 2.06 Ga LIP event resulted in partial continental breakup with the Kaapvaal breaking off and moving in a north-westerly direction, in-line with measurements by Letts et al. (2011), to come into strike-slip collision with the Zimbabwe craton, resulting in the Southern Marginal Zone of the Limpopo Mobile Belt. This consideration is demonstrated in the magmatic barcodes is that the Kaapvaal and the Zimbabwe cratons do not share a common magmatic history before ca. 2.0 Ga. For example, a prominent geological feature on the Zimbabwe craton is the 2.6 Ga Great Dyke which only extends into the Northern Marginal Zone of the Limpopo Mobile Belt, suggesting that it post-dates that tectonic event but pre-dates convergence with the Kaapvaal craton. It has been noted by numerous observers, beginning with Watkeys (1983) that the geology is not shared north and south of the Palala Shear Zone until about Waterberg times (ca. 1.9 Ga).

Figure 1. Barcode record of Archaean cratons. The width of individual bars corresponds to the 2σ error in radiometric ages (modified after Söderlund et al. 2010). Arrow depicts possible age match of mafic intrusions (radiating dyke swarms, sill provinces and other components of LIP) between cratons. The record reveals three post-2.0 Ga magmatic events common to both the Zimbabwe and Kaapvaal cratons, while no matches occur in pre-2.0 Ga times, in favour of formation of Kalahari at ca. 2.0 Ga. The new age for the Ongeluk lavas (2426 Ma, Gumsley et al. 2016) is represented in red on the Kaapvaal barcode. The position of Kevitsa (2058 Ma: Hanski et al. 2001) is indicated on the Kola-Karelia barcode and is coeval to the Bushveld Complex. The Pilbara barcode is not shown though it is thought to have been joined to the Kaapvaal craton between 2.78-2.44 Ga (de Kock et al. 2009; Kampmann et al. 2015).

More is work needed to understand the geodynamic history of the Kaapvaal in the period 2.0 – 2.7 Ga and older to correlate it with other Archean fragments and to better understand the setting under which the Bushveld Complex and the Venterdsorp Supergroup were emplaced. Correlations with magmatic events and other geological similarities between the Kaapvaal and the Karelia domain, such as the 2.65 – 2.80 Ga magmatic events found in the Ilomantsi and Kianta terranes, are important for delving this story.
Figure 2. Paleoreconstruction of Superia at ca. 2.4 Ga indicating proposed positions of various cratons, modified after Gumsley et al. (2016) and Bleeker and Ernst (2006), showing the relative positions of the Kaapvaal-Pilbara assembly with respect to Superia.

Figure 3. Schematic model for the origin of the Bushveld Complex with top Map views and Cross-section views at distinct stages of formation (Olsson et al. 2011). The initial plume-induced rifting and volcanism stage at 2.70 Ga erupted the Klipriviersberg group (komatiitic) basalts and injected voluminous magma at depth. Crustal doming associated with this resulted in at least 3 directions of radiating dykes. Cooling of the magmas led to negative-bouyancy-driven down-welling, eclogitisation of the SCLM, which facilitated the formation of the Transvaal Basin. Possible orogenic activity along the northern craton margin triggered decoupling and foundering of the dense mantle root allowing the rapid upwelling of asthenosphere, producing large volumes of magma and ultimately resulting in the emplacement of a large lopolith into the Transvaal sedimentary basin.
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Early, syn and late orogenic gold mineralization in the southern Ashanti greenstone belt, Ghana

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Abstract. The Ashanti Greenstone Belt, Ghana, hosts a variety of orogenic gold deposits and paleoplacers that contain a gold endowment over 150 million ounces. These deposits represent multiple episodes of gold mineralizations during the Eburnean Orogeny (~ 2.1 Ga). Investigating the relative timing between the deformation and the mineralization events provides new insight on the metallogenic evolution of the Ashanti Greenstone Belt during the Rhyacian, and may suggest new hypothesis for exploration. This communication highlights the different timing of the gold mineralization in the Ashanti Belt with an emphasis on the early orogenic Wassa gold deposit.

1 Introduction

The Rhyacian Ashanti greenstone belt, southwest Ghana, is the largest gold province of the West African Craton (Fig. 1). Main deposits include the giant Obuasi gold system (62 million ounces, Fougrouse et al. 2017), the world-class Tarkwa paleoplacer (40 Moz, Milési et al. 1991), the Prestea-Bogoso system (15 Moz, Allibone et al. 2002a) and the early orogenic poly-deformed Wassa system (over 5 Moz, Golden Star Resources 2014). These deposits developed during two distinct phases of the Eburnean Orogeny (~ 2.1 Ga). Wassa represents a new poly-deformed deposit-type in West Africa and highlights a potential for new discoveries in the Sefwi Group mafic meta-volcanic rocks.

2 Structural model

The structural evolution of the Ashanti Greenstone Belt was recently investigated by Allibone et al. (2002b), Feybesse et al. (2006) and Perrouty et al. (2012), who reported two major orogenic phases: Eoeburnean and Eburnean, 5 shortening events and a possible extensional event (D3).

Host rocks correspond to mafic volcanic rocks of the Sefwi Group (> 2.16 Ga), sedimentary rocks of the Kumasi Group (2.15-2.13 Ga) and clastic sedimentary rocks of the Tarkwa Group (2.11-2.10 Ga) that unconformably overlies the older lithologies. All these lithologies have undergone greenschist facies metamorphism. Tonalitic, granodioritic, granitic and leucogranitic intrusions formed during the two orogenic phases.

The first shortening event (D1) event is characterized by kilometer-scale tight to isoclinal folding of the Sefwi Group. The second shortening event (D3) is contemproaneous with the late stage of the Tarkwa Group sedimentation and developed or reactivated major NE-SW structures, such as the Ashanti Fault Zone, as well as kilometer-scale folds in the Sefwi, Kumasi and Tarkwa groups. D3 is related to the sinistral reactivation of syn-D1 faults, and is locally associated with macro-scale folding (e.g. at the Wassa deposit). D5 and D6 are late and minor events.

3 Mineralization

Four main episodes of gold mineralization can be distinguished in the southern Ashanti greenstone belt and range over a 100 Ma timespan, from 2164 ± 22 Ma (Le Mignot et al. 2017) for early orogenic gold mineralization at Wassa, to 2063 ± 9 Ma (Pigois et al. 2003) or 2030-1980 Ma (White et al. 2014) for late orogenic gold mineralization at Damang (Fig. 2). Most of the orogenic gold systems are located at the periphery of the Tarkwa Basin, on the west along the Ashanti Fault (e.g. Prestea-Bogoso) and on the east along the contact with the Sefwi group basement (e.g. Damang). Paleoplacers are limited to the vicinity of Tarkwa.

A few major deposits (e.g. Wassa) and several gold occurrences are hosted by the Sefwi Group rocks. They are spatially associated with tholeiitic meta-basalt units (Perrouty et al. 2014) and associated with district scale deformation zones.

3.1 Early orogenic gold

Early orogenic gold deposits are largely underexplored and the Wassa system (Fig. 2) is the first to be clearly documented in West Africa (Perrouty et al. 2015). These early gold systems have undergone multiple phase of deformation, metamorphism and gold remobilization during the Eburnean orogeny.

At Wassa, the first stage of gold mineralization is associated with quartz-carbonate veins that were folded and boudinaged during the D1 deformation event. Disseminated gold-bearing pyrites are aligned and stretched within the S1 ductile fabric, which suggests a pre- to early- D1 gold mineralization event. The Wassa area has been re-folded during the D5, D4 and D3 events. Recent Re-Os age dating of the stretched pyrites confirms the early orogenic timing of the first gold mineralization episode in the Ashanti greenstone belt, at 2164 ± 22 Ma (Le Mignot et al. 2017).
Figure 1. Location of Ashanti Greenstone Belt (red square) in the West African Craton (modified after Milési et al. 2004).

Figure 2. Location of major gold deposits in the southern Ashanti Belt 3D geological model (modified after Perrouty et al. 2014). The model displays the F1 folded mafic volcanic Sefwi Group, felsic-intermediate intrusions and dolerite dykes. The Kumasi and Tarkwa groups have been made transparent.
3.2 Gold paleoplacers

The Tarkwa pale placer is hosted by Tarkwa Group meta-sedimentary rocks, where gold is generally found along conglomerate layers (i.e. paleochannels). The bedding-parallel gold grade distribution in the Tarkwa deposit supports a sedimentary origin (Sestini 1973), but the source of the gold is still controversial.

3.3 Syn-orogenic gold

Syn-orogenic gold mineralization in the Prestea-Bogoso system (Fig. 2) corresponds to gold-bearing pyrite and arsenopyrite (disseminated and in veins) associated with carbonate alteration. The ore zones are distributed within a 10 m to 100 m large graphite-rich deformation zone (the Ashanti Fault Zone, Allibone et al. 2002a), which makes the contact between the Sefwi Group mafic meta-volcanic rocks and the Kumasi Group meta-sedimentary rocks. At Wassa, a second stage of gold mineralization is present and mainly consists of a syn-orogenic remobilization of gold, associated with euhedral pyrite aggregates in F1 and F4 fold hinges.

3.4 Late orogenic gold

The Damang deposit (Fig. 2) is the youngest gold mineralization episode to be documented in the Ashanti greenstone belt (White et al 2014). It is a typical late, post metamorphic peak, orogenic gold deposit where gold is mainly associated with sub-horizontal quartz-pyrite veins associated with reverse faulting. Locally, the late orogenic veins crosscut and possibly remobilized paleo placer-like gold mineralization (Tunks et al. 1994).

4 Summary

Rhyacian gold mineralization in the Ashanti greenstone belt occurred during multiple mineralization episodes. The Ashanti Fault Zone is the main exploration target and hosts the largest gold endowment of the district. Early orogenic deposits such as Wassa are largely underexplored in Rhyacian terranes and may be unrecognized in Archean terranes. The structural and metallogenic setting of these poly-deformed systems are critical parameters of the geological evolution of the belt as they may have contributed to an early gold enrichment, which was later remobilized along major structures. These early deposits may also be possible sources of gold for the paleoplacers.

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References


Earth's first continent: a Precambrian Pangaea?

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Abstract. A high-grade Paleoproterozoic metamorphic belt ties scattered Archean cratonic fragments into a global Precambrian continental reconstruction that provides linkage backward into Hadean Earth, and forward into Paleozoic Gondwana and Laurentia.

The proposed continent forms a hoop at mid-latitudes. It may have evolved on the rapidly spinning Hadean Earth as low-density, weak proto-continental lithospheric material thickened and gravitated pole-ward.

1 The reconstruction

Continental plate tectonic reconstructions are long-term goals of Precambrian research (e.g. Sears and Price, 1978; Williams et al. 1991; Bleeker, 2003; French and Heaman, 2010). Here I propose a new global reconstruction based on a belt of high-grade Paleoproterozoic metamorphic rock that ties together scattered Archean/Paleoproterozoic cratonic fragments into an ellipsoidal continent (Fig. 1). The continent appears to have evolved from >3.5 Ga to 550 Ma. Its outer rings were cratonized by 1.8 Ga, and its central region was cratonized by 550 Ma.

The high-grade Paleoproterozoic metamorphic belt records metamorphic temperatures of 800 to 1000 C, and pressures of 7 to 12 kbars. With exhumation equivalent to ~20 to 35 km, the belt commonly includes granulite facies anorthosite bodies. The belt is truncated at both ends of each Archean cratonic fragment but reconstructs into an ellipsoid that passes counterclockwise from Baltica to Greenland, North America, Siberia, North China, West Africa, South America, South Africa, India, Antarctica, Australia, and back to Baltica. The proposed continent has the essential geometry of Pangaea, with Laurentian and Gondwanan halves. It resembles Paleopangaea of Piper (2010) except that it closes the loop from Australia to Baltica.

The geologic map (Fig.1) shows the Late Precambrian crustal configuration of the proposed continent, while the inset map shows its corresponding lithospheric configuration. The high-grade Paleoproterozoic metamorphic belt divides Archean/Paleoproterozoic cratonic fragments into two concentric rings. The rings are highlighted by synclinal greenstone belts that are generally concentric to the ellipsoid.

The long axes of ~250 km thick, diamondiferous lithospheric keels define a continuous loop that is concentric with the cratonic rings (Fig. 1, inset). Where studied in detail, Slave Province kimberlite xenoliths define concentric domain boundaries within the North American lithospheric keel (Davis et al., 2003). The crystallization ages of peridotitic diamonds from the keels date to 3.5 Ga, while eclogitic diamonds date to younger than 2 Ga, suggesting that the lithospheric keels first thickened by some pre-subduction planetary process, and that eclogite-generating subduction began by 2 Ga (Gurney et al., 2010).

2 Hadean hoop

The proposed continent could provide linkage backward into the Hadean Earth. During the late heavy bombardment period of Hadean to Eo-Archean time (~4.1-3.8 Ga), impact processes may have differentiated the continental proto-lithosphere through repeated vaporization, condensation, and mixing of the Earth’s outer layers (Hamilton, 2003). The highly depleted continental proto-lithosphere gained compositional buoyancy relative to primitive mantle (Canil, 2008).

The proto-continent may have accreted into a hoop at mid-latitudes on the rapidly spinning Hadean Earth as low density continental differentiates migrated pole-ward over the peridotitic magma ocean. As the weak proto-lithosphere accreted and thickened, it would have risen isostatically. It would have been unable, however, to sustain steep slopes and high elevations due to its gravitational instability. As time progressed and the lithosphere slowly crystallized, gravitational spreading and thinning may have led to the formation of concentric greenstone belts and intervening granite gneiss terranes of Archean and early Paleoproterozoic ages.

Rather than conjugate proximity, detailed correlations among Archean stratigraphic sequences of widely scattered cratons (Bleeker, 2003) may record similar tectonostratigraphic
and petrochemical evolutions of segments of the hoop that had similar initial lithospheric thicknesses and that therefore experienced correspondingly similar subsidence histories.

3 Proterozoic subduction

Proterozoic miogeoclines and long-lived accretionary orogenic belts onlapped the edges of the continental hoop. Subduction was initiated in Paleoproterozoic time along its outer edge and continued intermittently through the Proterozoic and into the Paleozoic, and in some cases continued into the present. Subduction along its outer edge may have driven remobilization and uplift of deep Archean crust in the medial high grade metamorphic belt. Juvenile Paleoproterozoic to Neoproterozoic magmatic arcs filled the centroid of the hoop. The youngest orogen, the Arabian Shield, occupies the center, and was active until ~550 Ma.

4 Rhyacian dike swarms and rifts

Rhyacian dike swarms, including correlative 2.18-2.19, 2.21, and 2.23 Ga dike swarms in the Slave, Superior, and India cratons (French and Heaman, 2010), are generally radial or concentric to the ellipsoid, as are several Proterozoic rift basins and orogenic belts (Fig. 1 inset). In the proposed reconstruction, correlations among dike swarms and rift basins on various Archean cratonic fragments do not imply direct conjugate connections, but rather, correlative extensional hoop stresses around the ellipsoid.

5 Neoproterozoic remobilization

Neoproterozoic orogenic belts reactivated Paleoproterozoic belts between Antarctica and Australia, India, and Africa, as well as some within South America, West Africa, and North China. I suggest that, instead of recording independent continental collisional events among disparate, widely separated cratonic fragments, these belts could represent tectonic systems that alternately dilated and contracted in concert with overall extensional and compressive hoop stresses around the ellipsoidal continent. Those stresses may have reflected boundary conditions during episodes of peripheral subduction and quiescence. Expansion of the perimeter of the continent would open radial rift basins, while contraction would generate short-lived compressive orogenies in those basins.

6 Early Paleozoic breakup

In Early Paleozoic time, the continent split into Laurentia and Gondwana along a dextral transpressive transform that sheared out peri-Gondwana and peri-Laurentian terranes. Faunal evidence suggests Early Cambrian proximity between SE Siberia, SW Laurentia, and Morocco (Palmer and Repina, 1993).

7 Paleomagnetic implications

The model challenges interpretations of continental drift that assume a dipolar Precambrian Earth. Tests for the dipolar nature of the Precambrian geomagnetic field commonly assume randomly drifting cratons (Evans, 2013). The present model, however, proposes a Precambrian continent that was geographically fixed at mid-latitudes.

The complex drift patterns for individual cratons that are commonly proposed to explain Precambrian paleomagnetic results typically lack independent geologic evidence for corresponding tectonic plate motions, such as subduction zones and passive margins. Precambrian paleomagnetic results could also be explained by pulsations of a complex, tessellated magnetic field across a fixed continent. Geodynamo convection may be driven in part by latent heat of crystallization of the inner core, which grew slowly over time (Roberts and Glatzmaier, 2001). The proposed geological model of a long term, stable continental lithosphere for the early Earth may help constrain parameters for Precambrian evolution of the magnetic field.

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Lithospheric thickness contours. Min 100 km, Max 250 km. Adapted from ciei.colorado.edu. Anticline symbol traces lithospheric keel axis. Dots – Diamondiferous pipes. Short black lines – generalized dyke trends.
Geochronology and geodynamic setting of Rhyacian (2.25-2.03 Ga) orogenic zones in Sarmatia (SW Baltica)

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Abstract. A large set of recently acquired U-Pb zircon age and Nd isotope data is presented and discussed in terms of the geotectonic evolution of Sarmatia during the Rhyacian. It is shown that a large portion of continental crust within Sarmatia, including the East Sarmatian and Teteriv-Ingul orogens, was formed during the Rhyacian. Deposition of sedimentary rocks started at ca. 2.25-2.20 Ga and these rocks were metamorphosed and migmatized at 2115-2090 Ma. Extensive development of felsic and mafic igneous complexes at 2080-2030 Ma was likely related to the post-collisional extension with delamination of the lithospheric mantle. Metamorphic and magmatic events at ca. 2.1-2.0 Ga were linked to a collision between the Sarmatia and Volgo-Uralia segments of Baltica. Continued subduction along the northern margin of the assembled craton has eventually resulted in a collision with Fennoscandia at ca. 1.82 Ga.

1 Introduction

Sarmatia, one of the three crustal provinces that form Baltica (Bogdanova et al. 1996), is located in the SW part of the craton, bordered by Volga-Uralia to the east and Fennoscandia to the north. Sarmatia comprises the Ukrainian Shield (UkS) and the Voronezh Crystalline Massif (VCM), separated by the Paleozoic Pripyat-Dnieper-Donets Aulacogen, and is made of several Archean domains with ages ranging between 3.75 Ga and 2.7 Ga that are separated or surrounded by the Rhyacian (2.25 to 2.03 Ga) orogenic zones.

Recent geochronological and geochemical information collected for the Rhyacian rocks of Sarmatia allows for correlation of geological events in different parts of Sarmatia and identification of tectonic settings in which different rocks assemblages developed. This new information constrains the Rhyacian processes that were active during the assembly of Sarmatia and allows for correlation of geologic events on Sarmatia with those on other continents and may eventually allow placement of Sarmatia into Columbia/Nuna reconstructions. The Sarmatia tectonic evolution is discussed here in light of recently collected geochronological (U-Pb zircon) and geochemical (Nd isotope) data.

2 Geological setting

In the Ukrainian Shield, there is a Rhyacian orogenic zone (Teteriv-Ingul Orogen) comprised of the Ingul and Teteriv belts (Fig. 1). The Ingul Belt is located in the central part of the shield and includes amphibolite-facies metamorphic rocks of the Ingul-ingulets Series, and Rhyacian granites of the Ingul (formerly Kirovograd) and Novoukrainka complexes. The Ingul Belt separates the Mesoarchean Middle Dnieper Domain to the east from the Paleoarchean Podolian Domain to the west. Further to the northwest, the Ingul Belt continues into the Ros-Tikych Domain, which is comprised of amphibolite-facies metamorphic rocks of the Ros-Tikych Series and various Rhyacian granitoids. The Ros-Tikych Domain joins the Ingul Belt with the SW-NE striking Teteriv Belt, which is comprised of amphibolite-facies metamorphic rocks of the Rhyacian Teteriv Series and Rhyacian granites of the Zhitomir, Berdychiv and Bug complexes. Recent U-Pb zircon and monazite dating and results of Sm-Nd isotope investigations have proven the Rhyacian age of these rocks (Shecherbak et al. 2008; Stepanyuk et al. 2015; Zyultsle et al. 2016b).

The eastern part of the VCM is occupied by the ca. 2.1-2.0 Ga East Sarmatian Orogen (ESO), which consists of two segments extending in NW direction along the border between the Archean to Paleoproterozoic Volgo-Uralia and the Archean Azov-Kursk Domain. The eastern (external) segment is called the Vorontsova terrane and it is comprised of homogeneous metamorphosed sandy flyschoid rocks with varying proportion of carbonaceous material. These rocks belong to the ca. 2.2-2.1 Ga Vorontsova Series and they were metamorphosed in amphibolite facies. The Vorontsova terrane is intruded by the widely distributed ultramafic to felsic complexes (Terentiev et al. 2016c).

The western segment of the ESO is composed of the Losevo Series that is comprised of predominantly volcanic tuffs, basalts, and plagiorholites. These rocks are intruded by gabbros of the Rozhdestvensky Complex and calc-alkaline rocks of the Usman Complex that vary in composition from gabbro-diorites to trondhjemites and granodiorites (Terentiev et al., 2016b, c and references
The Rhyacian evolution of the VCM ended with deposition in two small superimposed volcano-terrigenous basins, the Kalach and Baygora grabens (Terentiev et al. 2016a).

**Figure 1.** Schematic map of Sarmatia, modified after Bogdanova et al. (2016).

### 3 U-Pb Geochronology

In the Teteriv belt, the oldest dated rocks (2150 to 2130 Ma) are fine- to medium-grained granodiorites that were intruded into the Teteriv Series. Zircons from gneisses of the Teteriv Series yielded ages of 2106 and 2115 Ma (Shumlyanskyy et al. 2015). Early plagiomigmatites crystallized at 2090-2080 Ma; these were followed by granites of the Zhytomyr, Berdychiv and Bug complexes that intruded between 2080 and 2000 Ma (Kostenko et al. 2011, 2012; Shcherbak et al. 2008; Stepanyuk et al. 2000; 2015; Zyultsle et al. 2016b) Inherited cores of zircon crystals are up to 2185 Ma old, suggesting a Rhyacian age for the protolith of these granites.

Small areas within the Ros-Tikych Domain are Late Archaean (ca. 2.7 Ga; Ponomarenko et al. 2010), but Rhyacian rocks prevail (Shcherbak et al. 2008; Zyultsle et al. 2016a). Granites and rocks of the diorite-tonalite-plagiogranite association yielded ages in the range of 2050-2030 Ma, whereas plagiogranites of the Zvenihorod Complex are somewhat older and crystallized at 2100 Ma. The age of the metamorphic rocks of the Ros-Tikych Series remains poorly constrained.

In the Ingul Belt, ages of granites of the Ingul Complex range between 2065 and 2020 Ma. These granites are often strongly deformed and contain numerous restites of their protoliths. The age of the Novoukrainka gabbro-monzonite-syenite-granite massif is indistinguishable from that of granites of the Ingul Complex and fall in the interval of 2040-2030 Ma (Stepanyuk et al. 2005). The age of the Ingul-Ingulets Series is unconstrained.

The oldest rocks in the ESO are metavolcanic and metaterrigenous rocks of the Losevo Series that were deposited between 2215 and 2155 Ma (Terentiev 2013). Sediments of the Vorontsovka Series were metamorphosed at ca. 2104 Ma (Bibikova et al. 2009). Terentiev (2015) has shown that zircons from this series range from ca. 2230 to 2090 Ma.

According to Terentiev et al. (2016c), melanorite–quartz meladiorite–melagranodiorite and quartz diorite–tonalite–granodiorites of the Elan Complex were formed at ca. 2090 Ma; ultramafic–mafic–diorite layered intrusions of the Mamon Complex crystallized at ca. 2070 Ma; quartz diorite–tonalite–granodiorite of the Novaya Melovatka massif intruded at 2058-2053 Ma; and norite–diorite of the Aprelevskoe body crystallized at ca. 2035 Ma.

Granitoids of the Losevo terrane belong to three age groups: (1) migmatite (ca. 2115 Ma); (2) tonalite-trondhjemite-granodiorite and trondhjemite-granodiorites of the Elan Complex that were crystallized between 2100 and 2075 Ma; and (3) high-K monzogranite and granodiorite of I-type that form small massifs of the Pavlovsk Complex (ca. 2080-2075 Ma) (Terentiev et al. 2016b). Bibikova et al. (2009) dated granite of the Bobrov Complex that intruded into the Vorontsovka Series at ca. 2020 Ma. U-Pb zircon ages for high-Mg basaltic andesite of the Baygora area and andesite and dacite porphyry of the Kalach Graben fall in the ca. 2050-2040 Ma range.

Hence, the Rhyacian orogenetic event(s) in Sarmatia lasted for about 100 m.y. from ca. 2140 to 2035 Ma, whereas supracrustal successions were deposited between ca. 2250-2200 and 2100 Ma.

### 4 Nd isotope systematics

The Rhyacian metamorphic rocks of the northern part of the Teteriv Belt have juvenile Nd isotope composition. εNd2100 values of 13 analyzed samples vary from 0.4 to 4.8, whereas their Nd(DM) model ages range from 2.2 to 2.4 Ga (Fig. 2). Two samples of gneisses revealed negative εNd2100 values (-0.5 and -3.0), and Nd(DM) model ages of these samples are 2.4 and 3.0 Ga, respectively. Granitoids of the northern part of the Teteriv Belt have εNd2100 values between 0.3 and 3.5, and Nd(DM) model ages between 2.2 and 2.4 Ga. In contrast, metamorphic rocks of the southern part of the Teteriv belt and granitoids of the Berdychiv Complex have predominantly negative εNd2100 Values (-0.9 to -4.3 and 0.5 to -5.2, respectively) and relatively old Nd(DM) model ages (2.5 to 2.7 and 2.4 to 2.8 Ga, respectively; Stepanyuk et al. 1998; Dovbush et al. 2000). The Rhyacian rocks of the Ros-Tikych Domain have quite
variable Nd isotope systematics: $\varepsilon_{\text{Nd}}^{2100}$ ranges from -1.6 to 3.0, and Nd$_{\text{(DM)}}$ from 2.2 to 2.5 Ga.

In the Ingul Belt, granites of the Novoukrainka and Ingul complexes were analyzed for Nd isotopes. For the Novoukrainka rocks, $\varepsilon_{\text{Nd}}^{2040}$ varies from -0.2 to -2.6, and Nd$_{\text{(DM)}}$ from 2.3 to 2.6 Ga, whereas for the Ingul granitoids $\varepsilon_{\text{Nd}}^{2060}$ varies from -0.2 to -2.8 with one outlier at -6.4, and Nd$_{\text{(DM)}}$ from 2.3 to 2.5 Ga with an outlier at 3.0 Ga.

Figure 2. $\varepsilon_{\text{Nd}}^{(T)}$ values and DM model ages for the Rhyacian rocks of Sarmatia.

In the Ukrainian shield, juvenile Rhyacian rocks are found within the Teteriv Belt and the Ros-Tikych Domain, along the northwestern margin of Sarmatia. These structures might be interpreted as an accretionary prism that developed during subduction of oceanic crust in the southeastern direction. Amphibolites in these structures are similar to ocean-floor basalts. Further south, Rhyacian rocks of the southern part of the Teteriv Belt and in the Ingul Belt have older DM model ages, which could be interpreted in terms of either presence of Archaean basement or significant input of old crustal detrital material. Time of peak metamorphism could be estimated at 2115-2090 Ma, i.e., the time of migmatite formation and crystallization of metamorphic zircon. Younger (2080-2030 Ma) granites, widely distributed on the UKS, might correspond to the post-collisional (post-orogenic) extension and abundant crustal melting. Granitoids on the UKS commonly reveal Nd isotope systematics close to that of their hosting metamorphic rocks. Mafic rocks on the Ukrainian Shield, although present, are not as widespread as on the VCM.

6 Mineral deposits

The Rhyacian in Sarmatia is not as well-endowed as other Rhyacian terranes. However, several mineral occurrences and deposits should be mentioned. In the Ukrainian Shield these include the Klynts and Yurivske gold deposits located in gneisses of the Ingul-Ingulets Series. Several Li-(Cs-Rb-Ta-Nb) deposits relate to pegmatites of the Rhyacian granite complexes, and some of the REE-U-Th metasomatic deposits are related to aplitic-pegmatite granites, which developed towards the end of the Rhyacian. In the VCM, PGE-Cu-Ni sulfide deposits that are related to
layered mafic to ultramafic intrusions of the Elan (ca. 2090 Ma) and Mamon (ca. 2070 Ma) complexes are known (Terentiev et al. 2016c).

7 Conclusions

1. A significant portion of the continental crust within Sarmatia was formed during the Rhyacian, comprising two orogenic belts: the East Sarmatian Orogen along the eastern margin of Sarmatia, and the Teteriv-Ingal Orogen, along the northwestern margin of Sarmatia and in the central part of the Ukrainian shield with the Archean Podolian Domain in the core.

2. Deposition of sedimentary rocks (now sandwiched in accretionary prisms in orogenic belts) started at ca. 2250-2200 Ma, whereas the peak of metamorphism accompanied by migmatite formation occurred at 2115-2090 Ma. Depending on their depositional setting either on the oceanic crust or in proximity to the Archean continental crust, sedimentary rocks have either juvenile or continental crust-dominated Nd isotope systematics.

3. Widespread emplacement of felsic and mafic igneous complexes at 2080-2030 Ma was likely related to postcollisional extension, delamination of lithospheric mantle and extensive crustal and mantle (in the case of mafic rocks) melting. In the VCM, post-orogenic extension also triggered subsidence and formation of small volcanogenic-terrigenous basins.

4. Metamorphism and melting in Sarmatia during the Rhyacian was related to collision between the Sarmatia and Volgo-Uralia segments leading to the assembly of Baltica. Continued subduction of oceanic crust along the northern margin of the assembled craton finally resulted in a collision with Fennoscandia at ca. 1.82 Ga.

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Rhyacian terranes in Brazil: crustal evolution and metallogeny

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Abstract. The Rhyacian period (2.3-2.05 Ga) witnessed the most voluminous crustal growth in Brazil, which is loosely termed as, and/or confused with, the Transamazonian cycle. The rock-formation events took place in major accretionary (±collisional) belts within the major cratons, and are also evident in more or less preserved cratonic fragments and as discontinuous and reworked blocks in the basement of Mesoproterozoic and Neoproterozoic mobile belts. TTG and arc-related magmatic suites, metasedimentary and metavolcano-sedimentary (greenstones?) sequences are the main rock associations. At the end of the period, widespread mantle input, probably following collision events (and often high-grade metamorphism), is recorded by the intrusion of several mafic-ultramafic complexes, alkaline rocks and mantle-derived granitoids. Rhyacian metallogeny is also expressive. About one third of the orogenic gold, and world-class sedimentary (with hydrothermal overprint/enrichment) iron deposits were deposited in Rhyacian metavolcano-sedimentary sequences, rivalling the Archean greenstone belts, whereas Sn-Ta deposits formed in association with S-type granites and chromite deposits occur in mafic-ultramafic complexes towards the end of the period. Gold-bearing placer deposits apparently formed in rift and/or foreland basins in both the beginning and at the end of the Rhyacian.

1 Rhyacian crustal evolution in Brazil

Almost half of the Pre-Cambrian terranes in the Brazilian Shield have formed during the Paleoproterozoic Era (2.5 to 1.6 Ga – Fig. 1) in response to a variety of rock-forming processes operating in accretionary and collisional orogenies and in taphrogenic events. Most of this crustal growth occurred in the Rhyacian period (Fig. 2, Sato and Siga Jr. 2000), which is usually ascribed to the Transamazonian cycle of orogenies. These events are present in the Amazonian and São Francisco cratons, in the São Luís and Luiz Alves cratonic fragments, and as discontinuous and more or less reworked blocks in the basement of Mesoproterozoic and Neoproterozoic orogens, such as the Goiás massif (Brasília Belt), Tróia, São José do Campestre and Rio Piranhas massifs (Borboerema Province), Curitiba microplate (Mantiqueira Province), etc. The Rhyacian terranes are composed mostly of juvenile calc-alkaline (± TTG) granitoid suites and associated metavolcano-sedimentary (greenstone and greenstone-like) sequences. Some of these started to be formed in the Siderian period (e.g., Bacajá domain), but were subsequently involved in Rhyacian orogenies. The end of the orogenic events is characterized by widespread collisional, S-type magmatism and high-grade metamorphism. Post-collisional magmatism is mostly represented by mantle-derived mafic-ultramafic complexes, voluminous alkaline rocks, syenites and granitoids.

Figure 1. Distribution of the Paleoproterozoic terranes in Brazil. Rhyacian terranes are in green (Siderian in orange, Orosirian in magenta, Statherian in blue).

Figure 2. Cumulative curve of crustal growth of South America (adapted from Sato and Siga Jr. 2000). Note the accelerated growth rate between ca. 2.2 and 1.9 Ga.
2 Rhyacian metallogeny in Brazil

In response to large crustal growth, metallogenic events were also expressive in the Brazilian Rhyacian (Fig. 3).

2.1 Orogenic and paleoplacer gold

About one third of the known orogenic gold resources and past production (ca. 1000 t) is contained in Rhyacian metavolcano-sedimentary sequences of the Amazonian (Vila Nova-Ipitinga and Três Palmeiras greenstone belts), São Francisco (Rio Itapicuru greenstone belt) and São Luís (Aurizona Group and Chega Tudo Formation) cratons (Klein 2014; Klein et al. 2014; Silva et al. 2014). The sequences record predominantly greenschist facies metamorphic conditions, and the deposits share quite similar geological and genetic characteristics and formed towards the end of the Rhyacian (Fig. 3), i.e., late in the tectonic evolution of the hosting orogens.

Paleoplacer gold (and locally diamond) deposits are hosted in quartz-pebble conglomerates deposited in different stratigraphic positions within metavolcano-sedimentary sequences. Rift and foreland basins, and cover of greenstone belts are possible settings for this type of deposits. Undeveloped deposits in the Gurupi Belt have been correlated with the giant Tarkwa of the West African Craton (Klein, 2014). It is under debate if the giant Jacobina deposit, in the São Francisco Craton, belongs to this class e to the Rhyacian period (Silva et al 2014; Teles et al. 2015).

2.2 Sedimentary iron and manganese

Although Cenozoic supergene processes were fundamental for the formation of world-class sedimentary (with hydrothermal overprint/enrichment) iron and manganese deposits, many were deposited in Rhyacian metavolcano-sedimentary sequences. Rift and foreland basins, and cover of greenstone belts are possible settings for this type of deposits. Undeveloped deposits in the Gurupi Belt have been correlated with the giant Tarkwa of the West African Craton (Klein, 2014). It is under debate if the giant Jacobina deposit, in the São Francisco Craton, belongs to this class e to the Rhyacian period (Silva et al 2014; Teles et al. 2015).

2.3 Sn-Ta, Au-PGE and U hosted in S-type granites

Sn-Ta and Au-PGE deposits, along with U mineralization, occur in the external zone (basement) of the Brasília Belt in the Goiás tin province and other regions of the Goiás and Tocantins states. The deposits are hosted in Rhyacian S-type granites of the syn-tectonic Aurumina Suite (Dardenne and Botelho 2014).

The Sn and Sn-Ta deposits are comparable to the LCT (Li-Cs-Ta) granite-pegmatite class of deposits. Some gold deposits are associated with unusual PGE concentrations, which Botelho et al. (2006) ascribe to influence of graphite-bearing schists that are the wall rocks for the mineralized granites.

2.4 Cr (± PGE, ± Cu) in mafic-ultramafic complexes

Chromium (± PGE, ± Cu) deposits are associated with Rhyacian mafic-ultramafic magmatic events (Fig. 3). In the São Francisco Craton, Cr (±Cu) is related to post-collisional magmatism in the Itabuna-Salvador-Curaçá collisional belt. The age is similar to that of the Bushveld Complex in South Africa (Silva et al. 2014). A similar context is interpreted for the PGE mineralization in the Tróia Massif of the Borborema Province (Costa et al., 2015). Chromite deposits of the SE-Guyana Shield are considered to be associated with an intracontinental stratiform complex (Klein et al. 2014 and references therein).

2.5 Other mineral deposits and occurrences

Minor Cu and Cu-Au (VMS?) deposits are associated with metavolcano-sedimentary sequences in the Amazonian and São Francisco cratons (Klein et al. 2014, Silva et al. 2014), whereas Pb-Zn occurrences appear to be associated with siliciclastic cratonic/platform cover in SE Amazonian Craton (Klein et al. 2017).

3 Summary

The Rhyacian period is the main period of continental crustal growth in Brazil and this is widely associated with mineral deposits hosted mainly in metavolcano-sedimentary sequences. The second half of the Period is especially important for mineralization, which is in line with ore formation in the orogenic peak and post-collisional stages.

Acknowledgements

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Figure 3. Distribution of Rhyacian mineral deposits/events in Brazilian cratons and provinces.

References


S01 – Geology, geodynamics and metallogeny of the Rhyacian (2.35 – 2.05 Ga)
Tectonic inversion of a Rhyacian rift basin hosting Cu-Au±Fe mineralization: the Vakko-Kovo greenstone belt north of Kiruna, Sweden

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Abstract. The Norrbotten Ore Province in the Fennoscandian Shield is best known as the type locality for ‘Kiruna-type’ iron oxide-apatite deposits. North of Kiruna in the Vakko-Kovo belt, however, Cu-Au±Fe mineralization hosted by Rhyacian greenstones represents an important exploration target. In this study the stratigraphy and structural setting of the Vakko-Kovo greenstone belt has been investigated by conducting geological mapping accompanied by geophysical ground and airborne surveying. Modelling of gravity and magnetic data was combined with strike-dip measurements to interpret the area in 3D. The resulting structural framework yields valuable insights about the deformation characteristics, revealing E-W directed tectonic inversion of a rift basin, as well as the spatial relationships between reactivation along the boundary shear zones and Cu-Au±Fe mineralization.

1 Introduction

The Vakko-Kovo greenstone belt (VKGB) represents one of several Rhyacian (c. 2.1 Ga) rift-related volcanic-sedimentary successions occurring in the Kiruna area of northernmost Sweden (Fig. 1). Exploration in the VKGB during the 1970’s and 1980’s delineated several prospects and showings consisting of hydrothermal replacement and vein-hosted Cu-Au±Fe mineralization (e.g. Godin et al. 1979). Mineral targeting historically focused on a stratigraphic sequence that is correlative with greenstone units hosting the Viscaria Cu deposit further to the south (i.e., Kiruna Greenstone group). In contrast, the underlying stratigraphy (Kovo group) and its contact relationship with the Archean basement were mostly overlooked. Moreover, detailed field constraints on deformation styles, the number of deformation events, relative movements, and structural controls on Cu-Au-Fe mineralization were not systematically assessed.

In this study, we aim to establish a tectonic-metallogenic framework for the VKGB by integrating structural mapping and microstructural analysis with new airborne and ground geophysical modelling. A 3D structural framework for the area is presented based on 2D gravity and magnetic data modelling along four E-W-trending transects. Our preliminary results provide new constraints on the deformation history and tectonic evolution of the Vakko-Kovo greenstone belt, and offer insights into the structural control of hydrothermal Cu-Au-Fe mineralization in Rhyacian successions in the northern Fennoscandian Shield.

2 Tectonic setting

In the northern Fennoscandian shield, Karelian greenstones and related plutonic rocks unconformably overlie and intrude a composite Archean basement terrane (Fig. 1). Compared to greenstone belts in Norway and Finland, greenstones in northern Sweden tend to form smaller, disconnected domains enclosed by younger Palaeoproterozoic rocks. Individual belts occur mainly as north–northeast and north–northwest-orientated 5 to 15-km-wide, curvilinear zones aligned to major shear zones.

In northern Sweden (Norrbotten), Rhyacian greenstones and other Palaeoproterozoic metasupracrustal rocks are underlain by the Norrbotten craton (Lahtinen et al. 2005), a Meso- to Neoarchean continental basement terrane extending roughly from Luleå in the south to Sweden’s northernmost border (e.g. Öhlander et al. 1987).

The stratigraphically lowest part of the greenstones in the Norrbotten craton is the Kovo group (c. 2.5-2.3 Ga). This
succession is represented by continental-derived flysch (metaconglomerate, meta-arenite) deposited during early continental rifting related to the dispersal of the Fennoscandian shield from the supercontinent Kenorland (Martinsson 1997; Bleeker & Ernst 2006; Reddy & Evans 2009). The Kovo group is in turn overlain by the Kiruna Greenstone Group (c. 2.3-2.0 Ga) (Martinsson 1997, Bergman et al. 2001). Lithologically, the greenstone sequences predominantly comprise metavolcanic rocks (tholeiitic basalt and komatiitic lavas), meta-intrusive rocks (doleritic to gabbroic dykes and sills) and metasedimentary rocks such as amphibolitic pelite to schist, marble, black schist and banded meta-ironstones. (e.g. Pharaoh & Pearce 1984, Martinsson 1997). The rocks of the Kiruna Greestone Group are interpreted to have formed during an advance stage of continental rifting at a triple junction above a rising mantle plume (Martinsson 1997). The greenstone successions are overlain and intruded by synorogenic rocks formed between c. 1.90 and 1.78 Ga during the composite Svecokarelian orogeny. The effects of the syn- to late-orogenic (Svecokarelian) tectono-thermal events are recorded by the greestones. These include polyphase ductile deformation, peak metamorphism reaching upper greenschist to upper amphibolites facies, metasomatic-hydrothermal alteration and late-stage retrogression and brittle faulting. Locally, these overprinting processes formed metamorphic graphite, skarn-related Fe and hydrothermal Cu-Au±Fe mineralization.

3 Results from the Vakko-Kovo belt

The VKGB comprises two narrow N-S-striking zones of early Palaeoproterozoic sedimentary and volcanic rocks of low to medium metamorphic grade (Fig. 2). Archean basement separates and bounds the belts to the west, whereas the eastern border is formed by a younger (c. 1.88 Ga) granitoid pluton.

The deformation pattern is shown by the new structural geological map (Fig. 2). The mean structural features are represented by N-S striking folds, shear zones and stratigraphic contacts. Axial planes dip steeply towards the east. Locally, fold axis have been recognized with gentle dips towards the south. Form lines were primarily derived from the airborne magnetic and electromagnetic anomaly maps and represents continuous lithological boundaries or shear zones.

The map traces of the shear zones are derived from interpretations of geophysical data and geological observations. Deformation-style and shear kinematics along the zones are deduced from strain indicators in outcrop or thin-section. The constructed profiles based on gravity-magnetic modelling provide further constraints on the structural features in terms of dip direction and sometimes kinematics.

The mapped shear zones are typically 3 to 5 metres in width and are localized along lithological boundaries. Most shear zones dip steeply to moderately to the east and have accommodated dip-slip reverse movements in combination with a minor component of dextral strike-slip (Fig. 3). Normal shearing has been recorded along the boundary shear zone between the Kovo group and the Archean basement, as well as along the western contact between the Kovo group and the Hauki quartzite. Mineralizations of Cu-Au±Fe, in particular along the Kovo belt’s western boundary, are associated with calcite-quartz veins (Kovo gruvan) or K-feldspar altered breccia along a mylonitic shear zone near Kruuvivaara (2.8 ppm Au) (Figs. 2-4) (Luth et al. 2014). The age of the deposits is not known, but they should at least post-date the host rock (i.e., < c. 2.1 Ga) since a structural control is evident.

Figure 2. Geological map of the Vakko-Kovo greenstone belt with Cu-Au-Fe mineralizations. 1: Kruuvivaara, 2: Kovo gruvan.
The eastern borders of both the VKGB are marked by major shear zones with a reverse (top-to-the-west) component and upright isoclinal folds striking parallel to the shear zones. In the adjacent pluton, deformation is weak, whereas the Archean basement is locally folded and clearly fragmented along NW–SE-striking dextral faults or shear zones. A southward deepening of the Archean basement (compare profiles CC’ and DD’) may partly have been accommodated by these NW-SE deformation zones as well.

4 Discussion and conclusion

The deformation patterns in the VKGB record an early phase of E–W extension, followed by NE–SW- to E–W-directed shortening. Early extension led to thinning and fragmentation of the Archean basement into separate fault blocks and basins, providing depocentres for rift-related sediments (cf. Kumpulainen 2000). Normal shearing observed along the major shear zones bounding the Vakko and Kovo belts to the east may correlate with this early phase of extension. Subsequently, crustal shortening inverted the basins and was accommodated by folding and reverse movements along moderately to steeply southeast-dipping shear zones. Some of these shear zones represent reactivated normal faults. The resulting crustal stack mainly comprises supracrustal units, but also includes fragments of Archean basement. Contact between the supracrustal units and the Archean basement are therefore mostly tectonic.

The absolute timing of compressive deformation in the VKGB is not well constrained but most likely occurred during the Svecokarelian orogeny at c. 1.9-1.8 Ga (Bergman et al. 2001). The weakly deformed intrusion east of the Kovo belt is part of the PMS-suite which formed around 1.88-1.86 Ga (Fig. 2). Tight, upright folds within the Kiruna greenstone group which appear to wrap around the intrusion must have formed later as they likely result from shortening in front of a rigid and more competent intrusion. Likewise, the large syncline marking the eastern border of the Vakko belt developed adjacent to competent Archean rocks. In the central and northern part of the Kovo belt shortening caused E–W flattening, as well as reverse and dextral shearing along N to NE-striking shear zones. The latter may be the result of lateral extrusion towards the north.

Deformation by NE–SW to E–W shortening is largely consistent with the results from earlier geological studies in the Kiruna area (e.g. Wright 1988, Vollmer et al. 1984), and regional studies (Bergman et al. 2001, Weihe et al. 2002). Wright (1988), however, argues that all structural features were formed before the intrusion of the granitoid batholith to the east and that the surrounding supracrustal rocks were not affected by the intrusion. Conversely, Vollmer et al. (1984) concludes that diapirism is a likely explanation for the observed deformation patterns in the area. However, some other features favouring an
emplacement model, such as a high-temperature shear aureole with pluton-side-up kinematic indicators do not accord with our observations (e.g. He et al. 2009).

Despite the ongoing debate about the tectonic processes at work, the spatial relationship between deformation and Cu-Au-Fe mineralization in the VKGB is demonstrated by the 3D structural framework (Fig. 3). In particular shear zones along the boundary between the Archean basement and the overlying Kovo group seem to have played a key role in controlling the occurrence of several Cu-Au-Fe deposits. As such, Rhyacian basin inversion during the Svecokarelian orogeny (c. 1.9–1.8 Ga) likely caused reactivation of the boundary shear zones creating paths for fluids and remobilizing metals from the Archean basement and Karelian greenstones. Hence, depending on the structural configuration, all the stratigraphic levels of the Karelian greenstones in northern Sweden should be considered as prospective for hydrothermal Cu-Au-Fe mineralization.

Figure 4. Cu-Au±Fe mineralization associated with deformation along the western boundary fault of the Kovo greenstone belt. a carbonate-quartz vein with Cu-Au in Kovo gruvan. b K-feldspar altered and mineralized protomylonite with C-S fabric indicating western-side-up (Archean basement) sense of shear. c Breccia from the same outcrop with matrix containing 2.8 ppm Au.

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Re-Os arsenopyrite geochronology at the massive sulphide ore from Mina III, Crixás, central Brazil: Rhyacian as an important gold metallogenetic epoch

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Anglo Gold Ashanti

Abstract. Gold mineralization from Mina III is structurally controlled by low-angle, thin-skinned thrust-faults and occurs in massive sulfide lenses, disseminated in high-strain zones and in quartz veins within carbonaceous schist of the stratigraphically upper sedimentary section or at their contact with metabasalts. The age of mineralization was interpreted as either Archean or Neoproterozoic. More recently it was constrained to the Rhyacian (2.2-2.1 Ga). To resolve this problem, a direct age determination of sulfide ore using Re-Os was undertaken. Two samples with large grains of arsenopyrite were carefully chosen from high grade sulfide ore (12 g/t). One sample, M3-1, represents a more pristine ore while the other sample, M3-2, is affected by late deformation and metamorphism. The Re-Os systematics yield a 2126 ± 16 Ma age for the M3-1 sample. The M3-2 sample did not produce an isochron. The robust result supports the Rhyacian as an important gold metallogenetic epoch.

1 Introduction

The Crixás greenstone belt, located in the Archean-Paleoproterozoic Goiás-Crixás terrain, hosts the largest gold-only deposit of Central Brazil and the country’s sixth gold reserve (~25 mt in the average 6g/t Au). Gold occurs in massive sulfide lenses, disseminated in high-strain zones and quartz veins, associated with arsenopyrite and pyrrhotite and/or pyrite. The main host is a carbonaceous schist of the stratigraphically upper sedimentary section of the greenstone belt, or at their contact with metabasalts, structurally controlled by low-angle, thin-skinned thrust-faults.

The age of the mineralization has been debate and was interpreted either as Archean (Thomson 1987) or Neoproterozoic (Thomson and Fyfe 1990; Fortes et al. 2003). In order to better constrain the age-span of the source area for the siliciclastic rocks of the upper stratigraphic sequence, Jost et al. (2010) performed U-Pb SHRIMP and LA-ICP-MS of detrital zircons obtaining ages ranging from 3.3 Ga to 2.2 Ga. Jost et al. (2010) has also performed U-Pb LA-ICP-MS for zircons from a mafic dyke that cuts across the mineralized interval obtaining an upper intercept age of 2170 ± 16 Ma. However, the zircon grains show significative corrosion and could represent inherited minerals. Consequently, the age must be considered with discretion. Considering the significance of a direct age of the ore for the gold exploration on the Crixás greenstone belt, we applied the Re-Os isotopic method to sulfide samples from the massive ore of the Superior Zone, Mina III area. The massive ore is currently exhausted, but hosted half of the gold reserve averaging 12 g/t. Other prospects are still under exploration by Mineração Serra Grande S.A/Anglo Gold Ashanti.

2 Geological background

The Crixás greenstone belt is one of the five greenstolith grade supracrustal sequences of the allochthonous Archean-Paleoproterozoic Goiás-Crixás terrain. It lies in the central portion of the Tocantins Province, a Neoproterozoic orogen formed by the collision between the northwestern Amazon and the southwestern Parapanema cratons against the easterly São Francisco/Congo cratons during the Brasilian/Pan-African cycle (Pimentel et al. 2000). Located in the northwestern part of the terrain, the greenstone belt comprises, from bottom to top, the Côrrego Alagadinho (100 to 500 m thick metakomatiites), Rio Vermelho (300 m thick metabasalts) and Ribeirão das Antas (500 m thick metasedimentary sequence) formations (Fig. 1a,b).

The Ribeirão das Antas Formation hosts the massive ore of the Superior Zone, Mina III area, and is composed of nearly 100 m of carbonaceous phyllite in the base containing dolomite lenses, and is laterally interfingered with and, towards the top, replaced by more than 400 m thick rhythmic metagraywackes (Jost et al. 2010). The metasedimentary sequence and the gold orebodies are intruded by NW-trending mafic dykes that vary from 1 to 20 m wide.

The massive sulfide ore of Mina III consisted of several lenses oriented along regional foliation from the surface to up to 450 m deep. The lenses were usually 0.5 to 2.5 m wide and 50 to 200 m long and sulfides were commonly constituted of as much as 95% pyrrhotite and/or arsenopyrite (see Jost et al. 2010 and references therein).
3 Materials and methods

3.1 Sampling

Two samples (M3-1 and M3-2) from arsenopyrite-rich massive lenses of the Mina III area were selected for Re-Os systematics. The arsenopyrite occurs as large grains and represents more than 80% of total sulfides (Fig. 2). Each sample was split in several different fractions and the arsenopyrite was separated using conventional isolation methods.

Sample M3-1 is coarse-grained inequigranular with disseminated up to 2 cm long, subhedral and lozenge-shaped arsenopyrite crystals in a dark gray gangue with quartz (~15%), white mica (~10%), K-feldspar (~7%), carbonate (~7%), and minor plagioclase (~3%), biotite (~1%) and traces of apatite (Fig. 3a). Arsenopyrite is the main sulfide phase (~70%), whereas pyrrhotite + chalcopyrite (~10%) and magnetite (~1%) are subordinate. Arsenopyrite occurs as lozenge-shaped and subhedral crystals up to 10 mm long and contains millimetric disseminated inclusions of biotite, carbonate, chalcopyrite, pyrrhotite, magnetite and gold. Pyrrhotite and chalcopyrite occur either as isolated inclusions or filling fractures that crosscut the arsenopyrite. Magnetite occurs as subhedral disseminated inclusions in arsenopyrite, rarely in pyrrhotite. Visible Au, up to 45 µm, occurs as isolated irregular to rounded inclusions in arsenopyrite (Fig. 3b).

Figure 1. a Simplified geology from Crixás greenstone belt. b Idealized stratigraphic column of Crixás Group (Mkmt-metakomatiites; Mb-metabasalts; CP-carbonaceous phyllite; Dol-dolomite lenses; Mg-metagraywakes). Modified from Jost et al. (2010).

Figure 2. Photograph from the underground section showing the approximate sampling position (Aspy-arsenopyrite).

Figure 3. Sample M3-1. a Shot from a magnifier showing mega crystals of arsenopyrite (Aspy) in a dark gray gangue phase composed by quartz, mica, feldspar and carbonate. b disseminated visible gold (Au) inclusions in arsenopyrite. Reflected light.

Sample M3-2 is medium- to fine-grained, inequigranular and with a foliation given by oriented arsenopyrite, and carbonate, in a subordinate gangue of garnet, carbonate, ilmenite and biotite. Arsenopyrite is the dominant sulfide (80%) and occurs as disseminated, flattened, subhedral and lozenge-shaped to subhedral whitish gray crystals up to 15 mm (Fig. 4a). It contains very fine-grained inclusions of carbonate, chalcopyrite, pyrrhotite, magnetite and gold. Pyrrhotite represents ~13% of the sulfides and occurs as aggregates either surrounding or as fracture fillings of arsenopyrite. Chalcopyrite represents ~5% of the sulfides, is commonly associated to pyrrhotite and occurs mainly around arsenopyrite crystals. Magnetite occurs mainly as inclusions in arsenopyrite. The
gangue is very fine-grained, and consists mainly of pinkish dark brown, subhedral, fractured and locally zoned garnet (~20%), fine-grained aggregates of twinned carbonate (10%) and subhedral, brownish to dark-green biotite (~10%). Ilmenite occurs as tabular disseminated crystals. Visible Au, up to 100 µm, occurs either as irregular, rounded or flake inclusions, or as fracture fillings in arsenopyrite, pyrrhotite and chalcopyrite (Fig. 4b).

Figure 4. Sample M3-2. a Shot from a magnifier showing disseminated arsenopyrite (Aspy) mega crystals in a gangue composed by pinkish dark brown garnet (Grt) and a dark gray mass of carbonate and biotite. b disseminated visible gold (Au) and chalcopyrite as inclusions in arsenopyrite and gold in veinlets. Reflected light.

3.2 Re-Os procedures

Each sample was split in several different fractions avoiding metal contact and the arsenopyrite was separated using conventional isolation methods and purified by handpicking. The Re-Os analyses were performed in the Department of Earth & Atmospheric Sciences, University of Alberta. Samples were digested following the Carius tube procedure (Shirey and Walker 1995) using an inverse aqua regia solution (10N HCl and 16N HNO₃). After dissolution, osmium was separated using solvent extraction (Cohen and Waters 1996) followed by microdistillation (Birck et al. 1997) for purification. Rhenium extraction was made by common anion exchange chromatography (Morgan et al. 1991). The Os samples were loaded onto Pt filament and Re samples onto Ni filaments covered, respectively, by Ba(OH)₂ and Ba(NO₃)₂ activator solutions and then loaded into the ThermoFisher Triton thermal ionization mass spectrometer (see Morelli et al. 2010 for procedures details). All Re analyses were performed using static faraday collectors and Os analyses were carried out in an electron multiplier in peak hopping mode. The $^{187}\text{Re}$ decay constant used for age calculation was $\lambda = 1.666 \times 10^{-11}$ a⁻¹ from Smoliar et al. (1996). Isochron regression were made using Isoplot (v.3.0, Ludwig 2003).

4 Results

The Re-Os arsenopyrite systematics applied for the M3-1 sample produced five analyses from different fractions. The total Re content ranges from 0.5 to 4 ppb and can be considered low when compared to arsenopyrite from Homestake gold deposit (Morelli et al. 2010) but similar to those obtained at Meliadine gold district (Lawley et al. 2015). The $^{187}\text{Re}/^{188}\text{Os}$ ratio is not very high and total Os ranges from 20 to 100 ppt. A Model 1 isochron yields a $2126 \pm 16$ Ma age with a 0.38 initial $^{187}\text{Os}/^{188}\text{Os}$ (Fig. 5). Sample M3-2 presented very low Re content (< 0.5 ppb) in all fractions analyzed and also very low total Os being unsuitable for dating.

Figure 5. Re-Os isochron showing a Rhyacian age for sample M3-1.

5 Discussion

The timing of gold mineralization from the Crixás greenstone belt has been subject of a wide debate and Archean to Neoproterozoic age have been suggested. Recently, Jost et al. (2010) addressed the subject based on the provenance U-Pb ages of graywackes from the upper part of the greenstone belt and on the crystallization age of mafic dykes that crosscut the orebodies. The study constrained the age of the mineralization to be younger than 2.2 Ga and older than 2170 ± 16 Ma.

The M3-1 sample was collected from an interval where the ore was not affected by late deformation and mineralogical transformation. The petrography revealed gold inclusions isolated inside of arsenopyrite megacrystals with low degree of gold remobilization. The
M3-2 sample was collected from an interval with relatively strong deformation and enriched in pinkish dark brown garnet. Gold occurs as isolated inclusions but is frequent in veinlets that crosscut the flattened arsenopyrite grains indicating some degree of remobilization. The M3-2 sample revealed very low Re and also very low Os being unsuitable for dating. The deformation and metamorphism possibly have played some role in the Re-poor composition of the arsenopyrite. The more preserved interval produced a Model 1 isochron with a 0.38 initial $^{187}$Os/$^{188}$Os for the gold-bearing massive sulfide lens. The initial ratio suggests some degree of Os crustal contribution, perhaps from the carbonate schists, normally enriched in Re and Os. A 2126 ± 16 Ma age obtained for the M3-1 sample is younger than the age found by Jost et al. (2010) for the post-mineralization mafic dyke. However, the age of the mafic dyke was produced by discordant U-Pb zircon analyses. Despite any possible uncertainty in this age, our direct ore dating confirms the Rhyacian as an important gold metallogenic epoch for the Crixás greenstone belt as previously stated by Jost et al. (2010).

The Rhyacian is an important period in other large gold systems. One example is the gold events related to the Eburnean Orogeny in the West Africa Craton where recent Re-Os dating were applied to early and late orogenic gold deposits providing direct dating of the polyphase mineralization (Le Mignot et al. 2017). In South America, at the Guiana shield, significant Au reserves are associated to major structures in granite-greenstone belts related to the Rhyacian orogenesis, possibly syn- to late orogenic gold style (Voicu et al. 2001; Daoust et al. 2011). In Brazil, other gold mineralization hosted in greenstone belts has been constrained to the Rhyacian, the Rio Itapicuru at the São Francisco Craton (Pimentel and Silva 2003), although lacking a more detailed work.

After our findings, it is possible to consider the Rhyacian as an important metallogenic epoch for gold-bearing greenstone belts in central Brazil, extending the importance of this period for gold in South America. Further dating work in other occurrences in the Crixás-Goiás terrain is encouraged to refine the age of different phases and better understand its gold endowment.

6 Conclusions

The direct dating of the gold-bearing arsenopyrite from the Mina III yields a Model 1 isochron age of 2126 ± 16 Ma for the massive ore. This age corroborates the previous findings of Jost et al. (2010) and supports the Rhyacian as an important gold metallogenic epoch for the greenstone belts in central Brazil expanding the significance of this period of time for gold mineralization in South America.

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Southern Mali crustal evolution, a geochemical and isotopic study and its implications for the petrogenesis and metallogensis of the Rhyacian Baoulé-Mossi domain, southern West African Craton

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Abstract. The Rhyacian Baoulé-Mossi domain is endowed in a variety of minerals. Because of the extremes riches of the region, its geodynamic evolution is the subject of much debate. Having a renewed understanding of how this region evolved through time will provide the required tools to recognize the source of the mineral endowment and provide new tests to locate additional resources. Sixteen samples extending from The Banfora Belt and into the eastern portion of the Siguiri Basin were analysed for elemental composition as well as U-Pb, O and Lu-Hf isotopes. The new data collected indicate that the intrusions occurred mainly between ca. 2140 and 2080 Ma and it is clear that the older intrusions occurred in the easternmost portion of the study area. Geochemically, elements such us Nb, Ta, and Ti are depleted whereas Th, Nd, Sm and Gd are slightly enriched and REE are highly fractionated. O and Hf isotopes signatures indicate that the intrusions are the result of predominately juvenile magmas that interacted with an older crust. Overall the data presented here appear to support an arc-type evolution in which Cu-rich regions evolved in the easternmost portion while the west is predominately Au-rich.

2 Geology overview

The southern WAC is composed by the Leo-Man rise (Fig. 1). It extends over Burkina Faso, Ghana, Mali, Niger, Côte d’Ivoire, Liberia, Guinea, Sierra Leone, Togo and Senegal (Abouchami et al. 1990). It is divided into a Rhyacian domain (east) and an Archean domain (west). The Archean, known as the Kénéma-Man domain, is predominately composed of highly metamorphosed TTG gneisses emplaced between ca. 3600 and 2600 Ma (Milési et al. 1992).

The Rhyacian counterpart or Baoulé-Mossi domain, is composed by narrow sedimentary basins and correspondent linear to arcuate volcanic belts, all intruded by several generations of granitic intrusions. Regionally, the rocks show signs of metamorphism up to greenschist and granulite facies (Baratoux et al. 2011).

The stratigraphy of the Baoulé-Mossi domain defined by Béziat et al. (2000), is broadly summarised as: thick mafic package, locally pillowed basalts, dolerites and gabbros, of tholeitic affinity; a detrital volcano-sedimentary sequence of turbidites, mudstones and carbonates; and a coarse, clastic sedimentary package. Volcanic activity occurred between ca. 2300 to 2100 Ma, while emplacement of felsic volcanics is bracketed between ca. 2250 and 2000 Ma (de Kock et al. 2012).

Granitic intrusions across the domain have been described as TTG-like (Vidal et al. 2009), and classified into three major groups: potassic alkaline plutons, two-mica intrusions with or without amphibole, and one-mica intrusions usually amphibole rich (Tapsoba et al. 2013).

The current published geochronological record shows continuous magmatism between ca. 2200 and 2050 Ma. Some authors report peaks of magmatism at ca. 2210 - 2190, 2180 - 2150, 2110 - 2100 and 2090 - 2070 Ma (de Kock et al. 2012).

Isotopically, the domain reflects the formation of juvenile crust during the period between ca. 2200 and 2000 Ma (Abouchami et al. 1990). Recent studies also recognised its juvenile character and had identified a greater amount of crustal contamination and reworking of a component potentially as old as ca. 2800 Ma (Pettersson et al. 2016; Abati et al. 2012).
3 Samples and methodology

For the purpose of this study 16 samples representing igneous felsic intrusions were collected from an area that stretches from the Banfora Belt (Burkina Faso) to the Siguiri Basin (Guinea). Sample processing included documentation of hand specimen appearance, petrographic characterisation, and whole-rock geochemical analysis. Additionally, samples were crushed to obtain zircon concentrates suitable for in-situ U-Pb, O- and Lu-Hf isotope measurements.

3.1 Whole-rock geochemistry

Major elements and Cu and Ni were measured by X-Ray Fluorescence Spectrometry (XRF). Trace elements were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), or by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The loss on ignition (LOI) was determined between 105 and 1000 degrees Celsius, and the results are reported on a dry sample basis, with the LOI1000 determined gravimetrically.

3.2 Isotope measurements

Samples were prepared for U-Pb geochronology, Lu-Hf and O isotopic measurements by sample crushing and subsequent preparation of epoxy discs after Claoué-Long et al. (1995). Zircon grains imaging was done using Back Scattered Electron (BSE) and Cathodoluminescence (CL) detectors. U-Pb geochronology was determined using Sensitive High Resolution Ion MicroProbe (SHRIMP) at the John De Laeter Centre for Isotope Research (JDL), Curtin University. General procedures and analytical conditions are described in and Claoué-Long et al. (1995).

Subsequently, O isotopes measurements were performed in situ using a CAMECA IMS 1280 HR2 ion microprobe, at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Vandoeuvre-lès-Nancy) after Martin et al. (2006). Lu-Hf measurements were performed in a New Wave/Merchantek UP-213 laser-ablation microprobe, attached to a Nu Plasma multi-collector ICP-MS at the GEMOC/CCFS Centre, Macquarie University, after Belousova et al. (2006).

4 Results

4.1 Rock description and petrology overview

Rock classification was established based on modal composition after microscopic examination. Samples are largely by granites (~50%) and by granodiorites, monzodiorites, diorites, syenites. All the studied samples show some degree of alteration.

Mineralogically, two groups of intrusions were identified: 1) amphibole rich intrusions, dominated by plagioclase, alkali feldspar, quartz, biotite, titanite, apatite, zircon and some sulfides and oxides; and 2) biotite and muscovite rich intrusions that are predominately amphibole free, associated with plagioclase, alkali feldspar, quartz, and zircon.

4.2 Geochemical characterisation

Using the Frost et al. (2001) classification for felsic intrusions, samples are magnesian, alkali-calcic to calc-alkalic and peraluminous. Exceptions are rocks with SiO$_2$ < 62% that tend to be metaluminous.

Harker diagrams of major elements vs. SiO$_2$ show negative correlations while the more mobile elements (Na and K) show a more scattered pattern. Trace element
binary plots show some linear trends, and in some cases, less methodical variations. In the case of Au (+Cu) indicators such as Nb/Y and Th/Yb plotted against SiO₂, values predominately fall within the ore forming reference suites (Loucks 2014). Cu metallogenic fertility indicators (SiO₂ vs. Sr/Y) fall within the barren reference suite west of the Morila Belt, but within the ore fertile range across the Banfora Belt. Elements such as Nb, Ta, and Ti are strongly depleted while Th, Nd, Sm and Gd are moderately enriched. Sr shows an evolution from enriched to depleted from east to west. REE patterns show depletion of heavy lanthanides.

4.3 Geochronological and isotope changes

Overall, ages across the study area range from ca. 2150 to 2080 Ma, while the O isotope signatures show supracrustal contamination (6 to 11‰) and Lu-Hf varies with εHf between 0 and +8, calculated from interpreted crystallisation ages, showing a superchondritic signature and TDM ages between ca. 2800 and 2300 Ma.

5 Discussion

Although the geodynamic environment in which the WAC evolved is still subject of debate, the new data presented here provide some insights into the evolution of the Rhyacian Baoulé-Mossi domain for the period between ca. 2150 and 2050 Ma and clues on the reasons behind the significant metal endowment of this region.

Traditionally the felsic intrusions described across the Baoulé-Mossi domain and the WAC have been described as TTG-like or TTG equivalents. The samples studied here do not fully satisfy TTG characteristics as defined by Moyen and Martin (2012). The Samples are more akin to modern granitic intrusions.

Recent studies e.g. Petersson et al. (2016), suggests the region evolved under an arc-type environment. This hypothesis has been based on geochemical elemental and isotopic constraints. In their studies they describe the calc-alkaline and metaluminous samples as having strong depletions of Ta and Nb, whereas the peraluminous samples have negative Eu, Ti and P anomalies. The samples studied here are alkali-calcic to calc-alkalic, peraluminous (Bt-Ms bearing) to metaluminous and display depletions in Ta, Nb, and Ti.

In addition to the described geochemical indicators the ages of the studied samples display a systematic westward younging. The Banfora samples in the easternmost portion of the study area are as old as ca. 2150 Ma while in the Siguiri Basin the felsic intrusions are around 2080 Ma. This pattern of magmatic front migration is also observed in Phanerozoic arc systems (Li and Li 2007).

Besides the geochemical and geochronological evidence that points towards an accretionary-arc-type model for the evolution of the WAC and, in particular, of the Baoulé-Mossi domain for the period between ca. 2150 and 2050 Ma, the isotopic evidence also seems to point towards a juvenile origin also consistent with an arc-type evolution. Recent studies presenting isotopic data, such as Lu-Hf and Sr–Nd e.g. Abati et al. (2012) and Petersson et al. (2016) show the juvenile character of the region. The new data presented here show εHf values between 0 and +8, suggesting that the intrusions were the result of juvenile magmas interacting with some crustal material. An important step to further constrain the type and source of the crustal contamination is to study O isotopes. In our study, δ¹⁸O values vary between 6 and 11‰ suggesting that the reworked crustal material incorporated by the juvenile magmas was exposed to near surface processes, most likely as part of the sedimentary cycle. The presence of peraluminous muscovite-rich intrusions is usually associated with crustal thickening which provides a means for crustal contaminations as juvenile magmas in their ascent interact with the thickened crust.

Overall the data presented here appear to suggest that a retreating arc system associated with an accretionary front gave way to a collisional type environment after the accretion between the Baoulé-Mossi and the Archean Kénema-Man domains, providing a fertile environment for the metallogenic system found in West Africa. Metallogenic systems such as porphyry Cu are associated with convergent environments, hydrous melts within arc-type regions and emplacement of felsic intrusive complexes (Cooke and Wilkinson 2014), while orogenic Au is related to lithospheric delamination following the collision stage in post-collisional environment (Richards 2009; Eglinger et al. 2017).

Craton margins are considered important to mineral deposit distribution. Understanding the changes in the elemental and isotopic compositions helps to identify areas that behave as regional margins. In the case of the study area, the Hf signature is significantly less radiogenic towards the Banfora Belt. This less radiogenic region also displays some geochemical indicators that point towards a Cu-fertile portion of the domain. The mentioned characteristics are consistent with the known identified porphyry systems just east of the Banfora Belt. Positive Cu-rich geochemical indicators change into more Au-rich fertility indicators and more radiogenic Hf signatures in the direction of the arc front migration.

We argue that the fundamental changes in elemental and isotopic compositions between the far eastern portion of the study area and the western part of the region strongly control the Au and Cu endowment across the Baoulé-Mossi domain. The arc evolution triggered suitable environments to potentially develop Cu-rich systems in the eastern most portion of the study area pre- ca. 2100 Ma. Conversely, the collision between Archean and Paleoarchean Rhyacian roterozoic domains post ca. 2100 Ma triggered the appropriate transient geodynamics that explain the widespread occurrences of Au rich systems across southern Mali and into Guinea towards the Archean-Rhyacian boundary.

6 Conclusion
The geodynamic evolution of the Baoulé-Mossi domain between the Banfora Belt and the eastern portion of the Siguiri Basin shows characteristics that resemble Phanerozoic arc-type systems. During the period between ca. 2140 and 2080 Ma, the main geochemical characteristics of felsic intrusions include: calc-alkaline nature associated with strong depletions of Ta and Nb and also with negative Eu, Ti and P anomalies; an evolution from metaluminous (<65% SiO$_2$) to peraluminous signature with increasing SiO$_2$ content.

The geochemical characteristics are associated with a clear pattern of ages getting younger towards the west. In the eastern most portion, the Banfora Belt U-Pb ages range predominately between ca. 2150 and 2115 Ma, while across southern Mali and into eastern Guinea the U-Pb age range is between ca. 2105 and 2080 Ma.

The combination of geochemical and geochronological characteristics favours the idea that this portion of the Baoulé-Mossi domain evolved from an arc-type system and into a collisional orogen. This evolution provided the appropriate architecture to Cu and Au rich systems. This renewed understanding provide explorers with clear predictive tools to further identify mineralised camps.

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Lithostratigraphic, structural and hydrothermal evolution of the Rhyacian Karouni orogenic Au deposit, Guyana South America

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Abstract. The Karouni orogenic gold deposits are located in north-central Guyana 35 km to the W of the 3 Moz Omai gold deposit. They are hosted within the ~2145 Ma volcano-sedimentary rocks of the Barama-Mazaruni Supergroup, part of the Paleoproterozoic to Neoproterozoic Guiana Shield. Karouni consists of two deposits, Smarts and Hicks, located 2 km apart along the NW striking Smarts-Hicks Shear Zone (SHSZ). Both deposits are hosted within a sequence of immature sandstone, basalt flows, ultramafic rocks and granodiorite intrusions. Regional scale deformation during the Trans-Amazonian Orogeny led to tectonic inversion, greenschist facies metamorphism and the development Smarts-Hicks shear zone. Gold mineralisation relates to late dextral movement on the SHSZ. Ore bodies are controlled by dilatational jogs formed at changes in strike during the D3 deformation event. Mineralized NW-striking V3a veins are preferentially hosted in high MgO basalt whereas mineralised N-S V3b veins are hosted in adjacent high Ti dolerite and granodiorite dikes. Hydrothermal alteration selvages are narrow (4 to <1 m) and show progression from chlorite/epidote to carbonate to albite dominated mineralogy with proximity to the vein. Gold is located within pyrite in the proximal alteration zones and as free Au within the veins.

1 Introduction

The Karouni gold deposit is located in north-central Guyana, approximately 160 km SW of the capital of Georgetown and 35 km to the W of the 3 Moz Omai gold deposit. They represent one of the few active gold mines in the Rhyacian greenstone belts of the Guiana Shield. Karouni consists of two deposits, Smarts and Hicks, containing 330,200oz. gold in Proven & Probable Reserves, and Resources of 1,130,100oz gold, including an Measured & Indicated Resource of 626,200oz gold and an Inferred Resource of 503,900oz gold (Troy Resources, press release September 2, 2016). More than 200 years of placer mining has taken place in the region. (Gibbs and Barron 1993), however, relatively few modern ‘hard rock’ mines have been discovered or developed. Exploration in the region has been challenged by dense tropical forest, Quaternary sedimentary cover over the greenstone belts (up to +50 m thick), lack of infrastructure and overall poor understanding of geological controls for Au mineralization.

This study provides a unique opportunity to investigate an exposed and accessible gold deposit in the Guiana Shield utilizing diamond drill core and open pit mapping to illustrate key lithological, structural and hydrothermal alteration features including the extensive vein system that controls gold mineralization. Geological characteristics of the Karouni deposits include sulfide and base metal poor, structurally controlled quartz-carbonate veins and associated hydrothermal alteration zones hosted within greenschist facies volcano-sedimentary rocks, often characteristic of orogenic Au deposits (Groves et al. 1998, McCuaig and Kerrich 1998; Goldfarb and Groves 2015).

2 Regional geology

The Karouni deposit is hosted in the volcano sedimentary rocks of the Barama-Mazaruni Supergroup, part of the Paleoproterozoic to Neoproterozoic Guiana Shield of north-eastern South America. Equivalent rocks in Venezuela, Suriname, French Guiana and Brazil form a 2000 km long belt along the NE margin of South America (Gibbs and Barron 1993). The age of these rocks is constrained by U/Pb zircon ages of 2120±2 Ma and 2131±10 Ma obtained from intermediate-felsic metavolcanic rocks at Omai (Norcross et al. 2000) and from felsic volcanic rocks of the Yurauri Formation of eastern Venezuela, respectively (Day et al. 1995). The greenstone belts have been multiply intruded by several phases of magmatism, including early TTG complexes dated between 2180 and 2130 Ma (U/Pb zircon) (Delor et al. 2003 a, b; Vanderhaeghe et al. 1998) and younger granodiorite to granitic plutonic rocks dated between 2096 and 2080 Ma (U/Pb zircon) (Norcross et al. 2000; Delor et al 2003a, b; Hildebrand et al. 2014).
The Trans-Amazonian Orogeny was the main protracting deformation event to affect the Rhyacian rocks of the Guiana Shield due to collisions with the Archean Leo Shield of West Africa (Vanderhaeghe et al. 1998). In the Karouni area, regional scale deformation (D2reg) during the Trans-Amazonian Orogeny led to the inversion of stratigraphy, metamorphism to greenschist facies and development of regional scale shear zones including the Makapa-Kuribrong shear zone in central Guyana (Fig. 1).

Figure 1. Simplified geological map of northern Guyana with major Au deposits compiled by the authors from the national geological maps of Guyana, Brazil, Venezuela and Suriname. The location of the MKSZ-Makapa-Kuribrong shear zone was taken from Walrond (1980).

3 Lithostratigraphy

The camp scale lithostratigraphic sequence at Karouni is divided into three units: (1) a lower volcanic unit consisting of ultramafic to high MgO basalts and tholeiitic porphyritic/amygdaloidal basalts, and high Ti dolerite (2) an immature sedimentary sequence of volcanoclastic conglomerates and coarse-grained sandstones, and (3) an upper sequence of laminated, carbonaceous siltstone and fine-grained sandstone. The Karouni camp is extensively intruded by several suites of calc-alkaline, intermediate to felsic plutonic rocks. These include the large Karouni Batholith which borders the deposits to the SW and a syntectonic granodiorite which is prominently exposed in the Hicks deposit where it constitutes an important host rock for Au mineralization. Several phases of more localized dike suites have also been documented. These include early, foliated, andesite porphyry dikes, syntectonic rhyolite porphyry dikes and late, post mineralization mafic dikes.

Figure 2. Geological map of the Karouni camp compiled from mapping and aeromagnetic interpretation by the author and Troy Resources.

4 Structural setting

The structural setting of the Karouni deposit is complex and multiphase. The following deformation events are recorded: an early phase of calc-silicate veins associated with an early thermal event (D1), compressive ductile deformation associated with regional and local scale shallowly NW F1 folds and the development of the dominant NW-SE S1 foliation, (D2a), transpressive ductile deformation linked with E-W steeply dipping ductile shear zones and development of a weak E-W S2 foliation and near vertical E and W plunging F2 folds (D2b), transpressive brittle deformation associated dextral strike-slip faulting and Au bearing veins (D3), and brittle extension associated with late normal faulting (D4). The quartz monzonite plutons exert an important first order control on the camp scale structures as supracrustal rocks deform around these intrusions and ductile-brittle shear zones develop in close proximity to their margins. This includes the primary structural feature at Karouni, the Smarts-Hicks shear zone (Figs. 2, 3). The Smarts-Hicks shear zone initiated as a reverse fault during D2a before reactivation via sinistral strike-slip movement, during D2b. Later reactivation of the shear zone during D3 caused dextral strike slip movement and development of NW trending, sub-vertical, gold bearing shear veins (V3a) and N-S trending, sub-vertical extensional (V3b) quartz-carbonate-chlorite veins. The dip and orientation of the horizontal sigmoidal wings of the (V3b) veins indicate dextral strike-slip movement.

The Smarts and Hicks deposits are localized at a change in strike of the Smarts-Hicks shear zone from 120° to 130°, forming dilatational jogs during the D3 dextral strike-slip event (Fig. 3). At the mine scale, mineralized shear zones with V3a veins are preferentially hosted in the ultramafic/high MgO basalt unit, which was commonly carbonated/hydrated early in the deformation history.
resulting in a rheologically weak unit relative to the surrounding rocks. Competent rocks including the high Ti dolerites, rhyolite porphyry, andesite porphyry and granodiorite dikes adjacent to the shear zones are preferred sites for extensional \( V_{3b} \) vein development.

![Image](image.png)

**Figure 3.** Interpreted geological map and cross section of the Smarts open pit, interpretations based on 1:100 scale geological mapping and DDH logs by the first author. Orebodies interpreted from ore control assay data.

### 5 Gold mineralization and hydrothermal alteration

Gold mineralization, both in the Smarts and Hicks deposits, is associated with the \( V_{3a} \) and \( V_{3b} \) veins. The \( V_{3a} \) veins are shear zone hosted and composed of qtz-cal-chl±tour±py±sch±au commonly with vein margin parallel laminae of chl and chl-cal altered wall rock. They contain variable grades which range from unmineralized (<0.2 ppm) to greater than 10 ppm Au. Higher grades (>100 ppm) in these veins correlate to the presence of free gold and minor Au associated with disseminated pyrite. Hydrothermal alteration around the \( V_{3a} \) shear veins is 1-5m thick associated with distal chlorite, talc and calcite alteration ultramafic rocks and moderate silicification and abundant quartz-calcite stingers within the proximal zone.

The typically higher grade (5-100 ppm Au) \( V_{3b} \) veins are hosted within the high Ti dolerite at Smarts and granodiorite and rhyolite porphyry dikes at Hicks. They are composed of qtz-cal-chl±tour±py±sch±au, but are dominated by white, massive quartz. Detailed diamond core logging and petrography of the least altered to strongly altered high Ti dolerites associated with the \( V_{3b} \) veins has shown a zonation pattern of distal chl-epi-rt alteration transitioning to an intermediate cal-chl-alb-rt and proximal qtz-alb-rt-cal alteration in a 3-4 m wide halo around these veins. Locally, \( V_{3b} \) veins also contain an additional innermost hydrothermal alteration zone, 1-5 cm wide, consisting of a bleached halo of alb-qtz-ttn, which completely obliterates the original textures of the host rocks. A halo of disseminated pyrite, 1m wide, develops in the proximal alteration zones replacing abundant primary magnetite. The pyrites consist of coarse (up to 1 cm), euhedral pyrite crystals and contain significant Au as inclusions, fracture fills and rims. Au inclusions are observed in equilibrium with inclusions of telluride minerals including calavarite and petzite. Gold with proximity to both sets of veins (\( V_{3a} \) and \( V_{3b} \)) strongly correlates with Bi, Ag and W.

Hydrothermal alteration in the granodiorite and rhyolite porphyry dikes is 3-5m thick and is characterized by distal chl-ser alteration with chlorite replacement of mafic minerals such as hornblende and sericite replacement of K-feldspar. Intermediate alteration is characterized by qtz-chl-cal-musc which transitions to proximal qtz-alb-cal. Pyrite is located in the proximal assemblage replacing chlorite.

### 6 Conclusions and future work

Changes in strike of the Smarts-Hicks shear zone and resultant dilatational jogs are important controls on Au mineralization at the Karouni camp scale. This strike change maybe be the result of a corresponding variation in the strike of the host rocks, especially the rheologically weak high MgO basalt unit, folded during E-W oriented strike-slip shearing (D\(_2\)b). Rheologically competent rocks such as the high Ti dolerite and granodiorite deformed in a brittle style and thus constitute a preferential host for mineralized \( V_{3b} \) extensional veins during D\(_3\) deformation. The high Ti dolerites were also a favourable chemical trap due to their high magnetite content. Magnetite is replaced by Au-bearing pyrite in the proximal alteration zone suggesting a redox reaction as a possible mechanism of Au deposition. Coarse, native gold within both \( V_{3a} \) and \( V_{3b} \) quartz veins suggests phase separation during active movement on the shear zone as another possible Au precipitation mechanism. Narrow alteration zones around veins indicate a relatively low fluid flux resulting in a low fluid to rock ratio.

The Karouni gold deposits have many geological similarities to the nearby Omai gold deposit (Voicu et al. 1999) such as: 1) similar sulfide poor, qtz-cal-
chalcopyrite-tellurides-Au veins with similar textural styles (crack seal laminated, open space filling); 2) similar concentric hydrothermal alteration zones and minerals (cal-alb-chl-tt-epi-py); and 3) similar late orogenic timing, with mineralization controlled by the last brittle-ductile deformation event. There are also some significant differences including: 1) dominance of mafic/ultramafic host rocks at Karouni vs granitoid host rocks at Omai; 2) flat lying Au bearing veins at Omai vs near vertical vein sets at Karouni; 3) presence of shear zone hosted mineralized veins at Karouni vs lack of those at Omai; and 4) much smaller mineralized area and smaller overall gold endowment at Karouni.

Future work will include dating of granitoids and porphyry stocks via SHRIMP U/Pb on zircon, which potentially provide absolute ages that can constrain the deformation history. Lu-Hf, trace element and O isotopes analysis will be applied to the same zircons in order to constrain the chemistry and source/contamination of the magmas.

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References


S02 – Ore forming magmatic-hydrothermal processes along active margins

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Metallogenic potential of Argentina

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The geotectonic evolution of Argentina provides an appropriate frame of reference to understand the processes that are responsible for the formation and distribution of major mineral deposits and districts. It is, as well, an adequate foundation to define metallogenic belts, outlining prospective areas for the localization of mineralized systems that share common large-scale ore-forming processes.

1 Geotectonic setting

The Argentine territory consists of a cratonic nucleus (the Rio de la Plata craton) in the eastern part of the country and that is largely covered by Phanerozoic sedimentary rocks, an Upper Precambrian-Lower Cambrian belt (Pampia), in the central part of Argentina, consisting of metamorphic rocks affected by mostly Paleozoic intrusions. The Andean Orogen is developed to the west. The basement of the Andean Orogen as well as the southern part of the country consists of a mosaic of parauthocotous and allochtonous terranes, including Patagonia, Cuyania, Chilenia and Antofalla main blocks (figure 1). These main geotectonic features are at the origin of the metallogenetic characteristics of Argentina.

2 Deposit models and total resources

In the northwest, there are two main environments of metallogenic importance: the Ordovician basin deposits developed in the margins of the Pampean region, partially covering the Arequipa-Antofalla terrane, and the Andean Cenozoic magmatic arc. The first environment includes saddle reef Au-Sb veins that are part of a belt that extends to the north up to Peru and polymetallic Pb-Zn SEDEX deposits (Aguilar, La Colorada). The second environment includes some world-class clusters of porphyry Cu and porphyry Cu-Au deposits, such as Taca Taca and Lindero that were formed in an arc environment, and Bajo de la Alumbrera and Agua Rica that sit in a back arc setting. Epithermal polymetallic deposits are related to calderas and domes, including the southern extension of the Bolivian Tin Belt (Pirquitas and Chinchillas). In this region, identified resources reach 46 Moz Au, 875 Moz Ag and 58 Blbs Cu.

The south-central Andean region contains some of the richest metallogenic belts in the world related to the Cenozoic magmatic arc (figure 2). Some of the most prominent metallogenic models include: high-sulfidation Au-Ag deposits (Pascua-Lama, Veladero), at least four porphyry Cu clusters (Los Helados-Josemaria; Pachón-
Negro, Cerro Moro, El Pingüino) and epithermal polymetallic deposits (Navidad). Identified resources reach 19 Moz Au and 1150 Moz Ag.

Figure 2. Arc, back-arc and extensional magmatism in Argentina. Terrane abbreviations. MJ: Mejillonia; AN: Antofalla; PP: Pampa; CY: Cuyania; CH: Chilenia; PT-MNP: Patagonia-North Patagonian Massif; PT-MD: Patagonia-Deseado Massif; MD: Madre de Dios. CRP: Rio de la Plata craton

Other than the already described base and precious metals resources, Argentina hosts U deposits containing 32,000 t U in total resources. They are related to three main models: volcanicogenic, stratabound and surficial deposit types. In addition, there are REE deposits related to Mesozoic alkaline magmatism and carbonatite intrusions, as well as weathered crust elution REE ores in the NW of Argentina. The early mining activity in Argentina, mainly developed during the first half of the twentieth century, involved the exploitation of numerous W-Sn vein and greisen deposits and Be-Li-Nb pegmatites in the Pampean region. The area has not been the target of further exploration and it deserves a re-evaluation.

Sedimentary basins are rich in industrial minerals. They involve one of the most important concentrations in the world of Li in salt lakes (Salar del Hombre Muerto, Rincón, Olaroz, Cauchari) with measured resources reaching 40.4 Mt LiCO₃ and 134 Mt K as a by-product. Argentina also hosts the fifth world largest borates province with 127 Mt B₂O₅ resources included in salt lakes as well as in Tertiary continental sediments. Both Li and B are genetically related to the volcanic activity that surrounds the salt lakes. In the Mesozoic back-arc Neuquén basin, the sedimentary sequence contains one of the richest potash deposits in the world, containing 2.5 Bt KCl.

Figure 3. Distribution of main commodities in Argentina. Abbreviations: see figure 2

3 Metallogenic potential

Quantitative assessment of undiscovered porphyry Cu deposits of the Andes and similar evaluations for other deposit models, allowed to define a geologic potential for the Argentinian territory of up to 300 Mt of Cu, 6 Mt Mo, 10,000 t (321 Boz) Au, 300,000 t (9,700 Boz) Ag, 10 Mt Zn, 10 Mt Pb, 100 Mt LiCO₃ and 250 Mt B₂O₅.
The comparison of mineral resources of Argentina in terms of economic weight by commodity, deposit models and deposit ages (figure 4), allows highlighting interesting features of the metallogenic potential of Argentina. Almost 50% of resources are present in porphyry type deposits and 40% in sediment-hosted deposits. Copper represents 40% of the total economic resources value, KCl 20%, LiCO3 16% and Au 11%. Finally, of the considered resources, 20% constitute mineral deposits of Mesozoic age, 50% Neogene age and 20% of Quaternary age.

Finally, it should be noted that the analysis of the evolution of total mineral resources in Argentina shows that they are related to the successful exploration programs developed by mining companies since the 90’ thanks to a favourable legal framework that promotes the mining investment.

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Fluid evolution of mixed base-metal gold mineralization in the Tethys belt: Koru deposit, Turkey

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Abstract. Koru is one of a number of base-metal gold deposits hosted by Oligo-Miocene volcano-sedimentary rocks of deposits in the Biga peninsula. Barite, quartz and galena are main minerals and are accompanied by minor amounts of sphalerite, pyrite, chalcopyrite, covellite and marcasite. Th of fluid inclusions indicates two distinct fluid pulses, one at high temperature (340ºC) commensurate with epithermal mineralization and boiling/near boiling conditions and the second approximately 150ºC lower. Salinity in both instances was from 11–0.2 wt. % NaCl. The range of temperatures within individual samples is consistent with variations from near lithostatic to hydrostatic pressure during vein and fracture opening. There are two different ranges of δ³⁴S values of H₂S in equilibrium with barite (+5.5 to +7.9 ‰) and sulfide minerals (-2.1 to -0.5 ‰), indicating that the sulfur in sulfide minerals and barite derived from different sources; magmatic and seawater respectively.

1 Introduction

The Turkish segment of the Tethyan Eurasian Metallogenic Belt, which extends from Western Europe through Anatolia to Iran, is currently being intensively prospected and contains a number of active mines. Western Anatolia and the Biga Peninsula in particular, contain a number of gold dominated deposits (Kısladag, Efemcukuru, Ovacık, Kartaldag, Muratdag, TV Tower) or base-metal deposits with lesser amounts of gold. There are a number of polymetallic deposits with different metal associations and ages in the Biga Peninsula such as epithermal Au-Ag, porphyry Au-Cu-Mo and epithermal Pb-Zn-Cu-Au deposits. The main deposits in this area are Koru (0.5 Mt at 8% Pb, 2% Zn, 300 g/t Ag), Tesbihdere (2.8 Mt at 5.76 g/t Au), Arapucandere (4.0 Mt at 16.4% Pb, 12.1% Zn, 2.23% Cu, Au av. 4 g/t and Ag av. 260 g/t) Tepeoba (4.86 Mt at 0.32 % Cu, 0.046 % Mo), Kartaldag (153 Mt at 1.12 g/t Au), Haliliaga (4.1 Mt, 11.01 g/t Au), Kirazlı (4.2 Mt, 7.6 g/t Au), Kucukdag (4.30 g/t Au, 15.0 g/t Ag, and 0.68% Cu, Smith, 2014), (Madendag (8 Mt at 1.25 g/t Au) (MTA, 1993). The majority of the deposits, in northwest Turkey, are high to low sulphidation Au + Ag deposits and associated copper-gold porphyry but there are a much smaller number that are exploited for Pb and Zn as galena and sphalerite, the Koru deposit being one of these. The Koru deposit, is a typical example of the volcanic-volcanoclastic hosted deposits in the Biga Peninsula, is located 50 km NE of Çanakkale. The deposit is one of a number of spatially close mineralized locations such as Eskikisla, Tahtalıkuyu, İkinci viraj, Bakır kuyusu, Derin Dere, Kuyutaşı Tepe, Saroluk and the Tesbihdere, deposit which shares many features, not only within this area, but with similar styles of mineralization in the Biga Peninsula and western Turkey (Figure 1). All mineralization in the Koru region is tectonically controlled, predominantly in the pyroclastic rocks as vein-type and stockwork-type. In the ore veins sphalerite, galena, pyrite, chalcopyrite, quartz barite and calcite are the main minerals and they are accompanied by small amounts of fahlore (tennantite), marcasite, covellite and bornite. The volcanogenic rocks hosting the deposits consist of agglomerate, lapilli stone...
and tuff with andesite intercalations in the lower parts, silicified rhyolitic breccia at middle parts and silicified rhyolitic tuffs in the upper parts. Hydrothermal alterations are observed associated with mineralization in the pyroclastic rocks manifested as zeolitization, chloritization and silicification (quartz + kaolinite and/or illite and/or I-S associations with small amounts of alunite).

2 Fluid inclusion petrography

There were two distinct phases of mineral deposition from hydrothermal fluids, each at different temperatures. However, associated with each phase there were several pulses of mineralization. Early quartz shows textures that are consistent with many epithermal deposits (Bodnar, 1985). The crystals are euhedral, with several phases of euhedral overgrowths and L-V and V-L inclusions aligned at 90° to the crystal face.

The earliest inclusions in the centre of the quartz are predominantly V-L or V-only with some L-V. Homogenization is either to the liquid or vapour phase at similar temperatures and hence are indicative of boiling. The inclusions in the overgrowths are predominantly L-V, with variable L/V ratios, and there are some V-L inclusions.

The second phase of mineralization has quartz that is texturally distinct from the early euhedral crystals and can be seen in places to replace the earlier euhedral quartz or more commonly abut against these crystals. This quartz has smaller anhedral crystals and is cleaner in appearance with fewer inclusions. All the inclusions are L-V with larger, but more consistent L/V ratios. There is also an associated second generation of lighter coloured sphalerite with fluid inclusions that are consistent with those of the second generation of quartz.

There are also two generations of baryte, the earliest of which is distinguished by small irregular crystals that are cut by larger elongate crystals. Both generations of baryte have also been observed cutting the second generation of quartz (Fig. 2). The first generation of baryte contains very few inclusions and it is nearly impossible to tell if those present are primary or secondary. The inclusions are mainly L-only but there are some L-V inclusions that look to be primary and with small bubbles that appear not to be from leakage. Their homogenisation temperatures are generally lower than the second generation of quartz inclusion. The last stages of mineralization are the large elongate baryte crystals that cut most of the earlier minerals. In theses the inclusions are L-only and where there are L-V inclusions these are the product of leakage. Earlier generations of quartz have secondary trails of these L-only inclusions cutting the euhedral crystals. Therefore it is possible to document a series of pulses of fluids each with distinct mineralization that records fluid events from high temperature boiling fluids through to an influx of low temperature < 50°C fluids.

3 Composition of the fluids

Microthermometric measurements of fluid inclusions in quartz, sphalerite and baryte were obtained using a Linkam heating-freezing stage (THMS600) mounted on an Olympus microscope in Pamukkale University. The chemical analysis of individual inclusions, or groups of small related inclusions, was made by Laser-ablation inductively-coupled mass-spectrometry (LA-ICPMS) using an Agilent 7500c mass spectrometer, combined with a Geolas ablation system in Leeds University.

In quartz and sphalerite the eutectic melting was observed between -40°C and -50°C. The majority of inclusions homogenize (Thliq) to liquid comprise the majority of the measurements and these are given as the average with the minimum and maximum recorded temperatures. The Thliq values are shown graphically (Fig. 3) as box and whisker plots where the shaded box represents the 25th to 75th percentile range, the horizontal
lines are the 5th and 95th percentile values and individual points are outliers. The mean and median values (black and white horizontal lines in the shaded box) are in most cases identical and the data is normally distributed. This approach allows a clearer visual appreciation of the data. In Qz-1 Th\text{liq} values are between 249° C and 354° C, in Qz-2 between 166° C and 251° C and Th\text{vap} homogenization for vapour-rich inclusions in Qz-1 are between 315° C and 354° C. In Sph-1 Th\text{liq} values are between 248° C and 341° C, although there are some V-rich inclusions in which homogenization could not be observed due to the darkness of the sphalerite. In Sph-2 Th\text{liq} was between 134° C and 228° C. Th\text{liq} values for baryte-1 inclusions were between 70° C and 217° C, but the large range and the somewhat uncertain petrography of the L-V inclusions makes us treat these values with caution (inclusions may have leaked).

Figure 3. Homogenization temperatures for the different generations of quartz (Q), sphalerite (S) and baryte (B). Two distinct temperature ranges are evident.

The majority of the inclusions in baryte-2 are L-only and therefore trapped below c.50° C. Tm\text{ice} values for L-V inclusions in Qz-1 are between -0.9° C and -5.1° C (1.6 to 8 equiv wt% NaCl), Qz-2 between -0.6° C and -5.6° C (1.1 to 8.7 equiv wt% NaCl) but could not be observed in V-rich inclusions. In Sph-1 Tm\text{ice} are between -1.8° C and -5.5° C (3.1 to 8.7 equiv. wt% NaCl) and in Sph-2 between -0.1° C and -7.5° C (0.2 to 11.1 equiv. wt% NaCl). In baryte-1+2 Tm\text{ice} are between -0.3° C and -3.4° C (0.5 to 5.5 equiv. wt% NaCl). The salinities of the inclusions in the different minerals essentially covers the same range, however the highest salinities are in sphalerite hosted inclusions (Fig.4).

The element/Na weight ratios obtained for L-V or V-rich fluid inclusions, ablated in early quartz and sphalerite, are shown in Fig. 5. There is no statistical difference in the element ratios of inclusions in either mineral and confirm that sphalerite was precipitated from the same high temperature fluid as quartz. The fluids are dominated by the alkali’s and alkaline earth elements and it is noteworthy that the K/Na ratio is bimodal. K/Na ratios of >1 are not frequently found in acid-sulphate alteration zones.

Figure 5. LA-ICP-MS data as wt/wt ratios relative to Na (value 1) from inclusions in the first generation of quartz and sphalerite. K/Na has a bimodal distribution but overall the other element ratios are the same in both minerals.

4 Discussion and conclusions

Fluid inclusions in minerals and ores from the Koru deposit are characterized by high to moderate temperatures and low to intermediate salinities. The higher temperature inclusions are clearly primary occurring in, and terminating at the boundaries of the growth zones. There is evidence that the ore fluid boiled from the presence, in both quartz and sphalerite, of L-V and V-rich inclusions in close association and which homogenise over the same temperature range. There are also variable L/V ratios commonly observed in individual fluid inclusion arrays. There are bands of chalcedony associated with normal euhedral quartz growth and the morphology of the Qz1 overgrowths is indicative of near equilibrium quartz deposition by a fluid saturated with respect to silica which is consistent with saturation caused by adiabatic cooling due to decrease in pressure during deposition. The evidence of fluid boiling in the earliest quartz is crucial as it allows the pressure and depth of mineralization to be
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constrained by the boiling assemblages of L/V and V-rich inclusions that homogenize over the same narrow temperature range ~310°C to 350°C, which for a lithostatic or near lithostatic pressured system equates to between ~600m to 700m depth. If we were to infer the fluid system was hydrostatically pressured the depth would be around 1700m which does not fit with the geological evidence (as the veins are near surface) or the model for this style of epithermal mineralization. The pressure at the temperature of boiling can be constrained (Fig. 6) at ~140 bars corresponding to the highest Th values for the primary L-V and V-L inclusions in both quartz and sphalerite. The pressure at the lower values of primary L-V inclusions in Qz1 and sphalerite is ~50 bars. As we previously stated the high temperature and pressure must imply a near lithostatic pressured system at a depth of ~600 – 700m (Fig. 6b). However for significant fluid flow to occur the pressure has to decrease to closer to hydrostatic pressure. If this occurs at the depth mentioned then the pressure will decrease to ~50 bars which corresponds to the minimum temperatures recorded in the Qz1 and sphalerite L-V inclusions.

Boiling and associated cooling was episodic with clusters of such inclusions observed on the growth surfaces of Qz1 and the several growth bands observed in Qz1 (Fig. 2). The majority of inclusions do not indicate extensive boiling, rather the variable L/V ratios represent trapping of fluids as the hydrothermal fluid cooled as the pressure decreased from near lithostatic to hydrostatic. The lack of extensive boiling during the transition between the two pressure regimes indicates that the decrease in P-T would have been close to the L-V curve. Thus we suggest that the growth of Qz1 and sphalerite occurred during periods when the pressure varied between close to lithostatic to close to hydrostatic with the maximum quartz growth at the lower pressures when there was open space in the vein systems. Sulphide minerals and quartz precipitated in the open spaces between the first baryte crystals along with the second generation of smaller baryte crystals.

The $^{34}$S V-CDT values of sphalerite, galena and baryte from Koru deposit change in the range of ~1.9 to ~0.1 (average ~1.2) ‰, -5.2 to -3.0 (average ~ -3.9) ‰ and +14.9 to +17.3 (average +16.5) ‰ respectively. The heaviest $^{34}$S values of the second generation baryte are consistent with $^{34}$S derived from Eocene sea water. The first generation of baryte has $^{34}$S values which are lower than seawater at the surface such as at White Island, New Zealand (Hedenquist 2013).

The $^{34}$S V-CDT values of baryte has $^{34}$S values which are lower than seawater at the time of mineralization and we suggest this was caused by micron sized sulphides (observed in this baryte) whose very negative $^{34}$S values lowered the $^{34}$S values of the baryte. Despite the difference in sulphur isotopes both generations of barite derived $^{34}$S from the same seawater source. The distinctly negative $^{34}$S values of galena are lower than those of magmatic sulfur, but would be comparable with sulphide originating from bacterial reduction of seawater $^{34}$SO$_4$. However, two distinct surface reservoirs of reduced and oxidised surface seem improbable. Pre-existing sulphides, with negative $^{34}$S values, in the country rocks could have been leached by the hydrothermal fluids but there is no evidence of any such sulphides. Therefore, we suggest that the negative $^{34}$S values of the sulphides are due to boiling of the magmatic fluid at depth. Such a process has been shown to produce very negative $^{34}$S at the surface such as at White Island, New Zealand (Hedenquist 2013).

**Figure 6.** Pressure-Temperature-Depth plot (drawn from data in Haas, 1971)

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Habit and chemistry of apatite at Chuquicamata, Chile

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Abstract. Apatite is well suited to the study of porphyry systems. It occurs in both the magmatic and hydrothermal domains and the large range in possible trace element substitutions can reveal crystallisation conditions that reflect key events during porphyry formation. This project aims to use the trace element chemistry of apatite as a probe of porphyry development. A global study of apatite composition will aim to identify fingerprints which may be indicative of a fertile porphyry environment. Initial results from the Chuquicamata Cu-Mo porphyry complex, Chile reveal limited compositional differences in major and trace element compositions (Ca, P, Cl, Na, Mn, S, Se, Fe, Mg, Al, Si, La, Ce, Nd) between apatites of different habits that are interpreted to be of igneous origin. However, vein-hosted and hydrothermally-altered apatite are compositionally distinct, probably controlled by strong fractionation of elements during separation of magmatic-hydrothermal fluids. This suggests potential for the future study of potassic alteration in porphyry systems using apatite.

1 Introduction

The majority of the world’s Cu and Mo is sourced from porphyry deposits associated with arc magmatism. These magmas release metal-rich, hydrous fluids during crystallisation. However the majority of arc-related magmas do not form mineralised systems and the controls of this dichotomy are not well understood.

As new porphyry deposits become harder to find there is the need to develop more advanced, but lower cost and less invasive methods of porphyry exploration. As a result, the use of igneous mineral chemistry to fingerprint fertile porphyry systems has become an area of significant interest (e.g. Bouzari et al. 2016; Williamson et al. 2016). These characteristics make apatite an ideal indicator mineral for porphyry exploration. This research aims to develop apatite as a tool for exploration by means of a global study comparing apatite chemistry from porphyry deposits and barren arc segments. Igneous apatite can be developed as a probe of fertile arc magma evolution, with hydrothermal apatite providing insights into the role and character of the exsolved fluids.

We present preliminary apatite analyses from the Chuquicamata Cu-Mo porphyry deposit, Chile. The compositions of both magmatic and hydrothermal apatite have been determined by scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) and electron microprobe analysis (EMPA). Intra-crystal compositions together with a range of texturally distinct hydrothermal and magmatic apatites have been identified, some with markedly different compositions.

2 Geological Setting

The Chuquicamata Cu-Mo porphyry deposit sits at the southern end of the 12 km-long Chuquicamata Intrusive complex in northern Chile. Three distinct porphyries dominate the complex: the Este (granodiorite to monzogranite), Banco (monzodiorite) and Oueste (monzogranite to granodiorite) porphyries, which were intruded between 35 and 33.5 Ma. The host rock comprises mostly metasedimentary and meta-plutonic rocks including the Elena granodiorite which, although compositionally similar, predates the main mineralising porphyries. The deposit is cut by the West Fissure fault so that the mineralised complex to the east is in contact with the barren Fortuna Complex to the west (Ballard et al. 2001; Ossandón et al. 2001).

3 Methods

Polished thin sections of samples from three main porphyries were examined using scanning electron microscopy (SEM) to determine the textures, mineralogy
and paragenetic associations of apatite. The major element (Ca, P, F, Cl, Na, S, Mn) chemistry of selected apatites was determined by SEM-energy dispersive spectroscopy (SEM-EDS). Trace elements (Sr, Fe, Mg, Al, Si, La, Ce) were subsequently determined by electron microprobe (EPMA). EMPA analyses were conducted using a 20-kV, 20 nA beam current and 5 µm beam diameter. Fluorine values in apatite are notoriously difficult to obtain accurately due to its migration during microprobe analysis (Stormer et al. 1993). Stoichiometric constraints limit the F content of apatite to <3.76 wt.% (Pyle et al. 2002); however higher values are often reported. To minimise the overestimation of F and the effects of migration on the rest of the crystal, F was measured on the first cycle, and unnecessary beam exposure was avoided.

4 Sample petrology

4.1 Mineralogy of porphyry samples

The Este porphyry is predominantly composed of medium-grained euhedral plagioclase (2 mm) and smaller K-feldspar phenocrysts. Primary amphibole (2 mm) has been completely replaced by biotite. The phenocrysts are surrounded by a groundmass of equigranular K-feldspar and fine biotite laths. The Oueste porphyry is of a similar composition but plagioclase phenocrysts have been substantially altered and anhedral quartz and feldspar are dominant. The Banco porphyry is finer grained; plagioclase phenocrysts are <2 mm. The finer groundmass is dominated by amorphous K-feldspar with quartz, biotite and titanite. The Elena Granodiorite contains phenocrysts of plagioclase and biotite, and pseudomorphs of magmatic amphibole in a quartz-dominated groundmass with K-feldspar and biotite laths. Within the samples analysed, potassic alteration is the dominant form of hydrothermal alteration. Some chlorite-sericite alteration is also visible, particularly as chlorite replacing biotite along cleavage planes.

4.2 Apatite occurrence and habit

A wide variety of apatite textures are observed; these are classified as either magmatic or hydrothermal in origin based on coeval mineral assemblages (Fig. 1). Magmatic apatite most commonly occurs as inclusions within plagioclase, K-feldspar, quartz and biotite (Fig. 1A). These are on average the finest apatite crystals (<50 µm) and are euhedral to subhedral. Magmatic apatite is also observed as euhedral crystals comprising part of the groundmass (Fig. 1C). Hydrothermal apatite is associated with secondary hydrothermal minerals and is subhedral to anhedral in shape. The majority of the hydrothermal apatite is replacement style (Fig. 1B), although some is observed within distinct veins (Figs. 1D and 1E). Vein-hosted apatite is typically intergrown with other vein minerals, including chalcopyrite and bornite. All of the hydrothermal assemblages associated with apatite in this study are typical of potassic type and the earliest stage of magmatic-hydrothermal activity at Chuquicamata (Ossandón et al. 2001).

In this study altered apatite has been defined as a separate apatite type and is distinguished texturally from unaltered crystals by the occurrence of worn and uneven edges and by multiple mineral inclusions including titanite, oxides and monazite (Fig. 1F) that are often concentrated in discrete zones. Inclusions within unaltered apatite are rare.

5 Apatite chemistry

5.1 Magmatic vs. hydrothermal apatite

The average composition for magmatic apatite is 9.8 Ca apfu and 6.1 P apfu, fluorine dominant with low Cl contents (0-0.2 apfu). Hydrothermal apatite has a similar major element composition with an average of 10.1 Ca apfu, 6.1 P apfu, and 0.05-0.17 Cl apfu (Fig 2). F concentrations were not considered further in this study due to the difficulties associated with their measurement. Concentrations of Al, Si, Na, S, and REEs (La, Ce, Nd) show positive correlations with each other as a result of their substitution behaviour (Pan and Fleet, 2002).

5.2 Variations between apatite types

There is no significant difference in major and minor element chemistry between phenocryst-hosted and matrix-hosted apatites. The majority of the hydrothermal apatite (replacement style) are of comparable compositions. However, there is a compositional difference for hydrothermal apatites hosted within distinct veins and altered apatite (Fig. 2). Two groups can be defined: Group 1 consists of vein assemblages of apatite + K-feldspar + bornite (+anhydrite) (Fig. 1d); Group 2 is within an apatite + biotite ± chalcopyrite ± rutile (+anhydrite) vein assemblage (Fig. 1e). Group 1 is Mn-rich, whereas Group 2 is Na-, S-rich and P-poor. Altered apatite (Fig. 1F) can also have elevated Mn and Sr contents and lower Na, S, La, Cl, Ca and Si contents, similar to Group 1.

5.3 Compositional variations within single crystals

Zoning of apatite in backscattered electron SEM images is rare, suggesting, as is confirmed from chemical analysis, that there is little intra-crystal variation of the major and minor components in any of the apatite types. EMPA profiles were acquired for Este porphyry apatite that was predominantly in contact with biotite, either as inclusions or within the potassic hydrothermal matrix. These analyses show a sharp decrease in Fe and Si and less pronounced increases in La and Ce towards the centre of the apatite.
6 Discussion

Magmatic apatite is abundant within porphyry deposits as inclusions within phenocrysts, or within the groundmass. Its typical subhedral habit indicates growth from a low apatite-saturated melt and near equilibrium conditions (Webster and Piccoli, 2015). Hydrothermal apatite is typically more anhedral in shape and likely represents early magmatic-hydrothermal activity within the porphyry system. The vein-hosted apatite likely represents a later hydrothermal event than the replacement hydrothermal apatite. At Chuquicamata, there is little major element variation between texturally distinct magmatic apatite types, possibly related to the limited bulk compositional range of the host porphries. The majority of the early magmatic-hydrothermal apatite at Chuquicamata, at least in major and minor element terms, is indistinguishable. However, vein-hosted hydrothermal apatite is compositionally different. This could be related to prior phase separation in the exsolved magmatic-hydrothermal fluids which can cause significant fractionation of major and trace elements (e.g. Heinrich et

Figure 1 Apatite occurrences and habits observed within the Chuquicamata porphyry complex. a Magmatic apatite as (sub)-euhedral inclusions often within phenocrysts, in this case coexisting with ilmenite, a common mineral association. b Hydrothermal apatite is typically irregular in habit within a matrix of secondary hydrothermal minerals. c Magmatic apatite forming part of the igneous groundmass along with quartz, feldspars and biotite. d Hydrothermal apatite in a vuggy vein of bornite and K-feldspar within potassically-altered host rock. Its shape is irregular and typically contains inclusions of other minerals from the vein assemblage. e Apatite within a biotite and chalcopyrite vein. f Here, magmatic apatite has been partially altered, as has the biotite host. These apatites typically contain small inclusions of monazite.
*Figure 2* Plot of SEM-EDS and EMPA analysis (A) Mn vs. Na apfu, (B) S vs. Na apfu. Apatite type is also distinguished andapatites of magmatic and hydrothermal origin are coloured orange and purple respectively.

al. 1999). *Group 1* and *Group 2* vein apatite is associated with different vein assemblages suggesting that two distinct fluid types were involved. Although comparable compositions are reported for fluorapatite (Chang et al. 1996), the S content of *Group 2* may be a result of very fine sulphide inclusions.

Hydrothermal alteration does not appear to have affected the composition of primary igneous apatite crystals unless they are visually altered (Fig. 1F). The low Na and Si of the altered apatite match the effects of metasomatic alteration on apatite chemistry described by Harlov (2015). Compositions are also similar to the *Group 1* vein apatite which is within the same sample, suggesting the same type of fluid could have been responsible for both.

Variations in intra-granular composition may result from diffusion of minor elements between the host mineral and the apatite crystal. Alternatively the changing composition between across the grain may reflect the evolving composition of the magmatic-hydrothermal fluid.

Future work will utilise the lower detection limits of LA-ICP-MS for further analyses to determine the full spectrum of the REE and other trace elements. This study will also be extended to more deposits in order to identify common chemical signatures that can discriminate between igneous and hydrothermal apatites and potentially between fertile and barren porphyry systems. Ultimately, these differences will be used to develop an exploration methodology and to contribute to a deeper understanding of the controls on the formation of economic porphyry ore deposits.

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Lithocaps – characteristics, origins and significance for porphyry and epithermal exploration

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Abstract. Lithocaps are subsurface, broadly stratabound alteration domains that are laterally and vertically extensive. They form when acidic magmatic-hydrothermal fluids react with wallrocks during ascent towards the paleosurface. Although lithocaps typically have steeply-dipping structural roots, there is a significant component of lateral fluid flow involved in lithocap formation, either through permeable aquifers and/or a well-developed fracture mesh. Lithocaps can have lateral dimensions greater than 10 km and thicknesses of more than 1 km. In ancient settings, partially eroded lithocaps are typically exposed as silicified ridges and cliffs. These features do not mark the original paleosurface – instead they are erosional remnants of what was once an extensive subsurface alteration domain that may have been capped by low temperature argillic- and/or propylitic-altered rocks. High sulfidation state mineralisation typically occurs in silicic-altered rocks within lithocaps, either as stratabound replacements, veins and/or breccia cement. The quartz-rich mineralized domains can produce a resistivity high. Pyrite is ubiquitous in lithocaps prior to weathering, and can yield complicated chargeability responses, some of which may be associated with mineralization. The alteration assemblages are invariably magnetite-destructive, and can obscure the magnetic signature of an underlying porphyry deposit. Combining SWIR and whole rock geochemistry can provide effective vectoring tools within lithocaps.

1 Introduction

Lithocaps are volumetrically significant domains of hypogene silicic, advanced argillic and argillic-altered rocks that can form above and to the side of shallow-crustal hydrous intrusive complexes. A spectrum of mineralisation styles associated with the intrusive complexes can be obscured and/or at least partially hosted by a lithocap (e.g., Sillitoe 1995, 2010; Chang et al. 2011; Fig. 1). Lithocaps may host high-sulfidation state mineralisation. Some overlie and partially overprint porphyry deposits. Lithocaps can also overlie intermediate sulfidation veins, which can exceed 1 km thick, and may exceed 10 km in lateral dimensions (e.g., Yanacocha, Peru, Shuteen, Mongolia). They can be particularly challenging for exploration due to their lack of easily mappable alteration zonation patterns.

2 Genesis

When magmatic-hydrothermal fluids exsolve from a hydrous intrusive complex in the shallow crust, the fluids may spontaneously split into large volumes of vapour and comparatively small quantities of brine (Henley and McNabb 1978; Burnham 1979; Bodnar et al. 1985). The brines can produce potassic alteration and porphyry-style mineralisation in and around the apex of the intrusive complex. The vapour, which is the dominant fluid phase volumetrically (e.g., Heinrich et al. 2004), ascends towards the surface, carrying acidic species such as HCl(g) and SO2(g).

During the vapour’s ascent, it may condense into groundwater (e.g., Hedenquist and Taran, 2013). It could also partially contract back to liquid, provided that confining pressures increase through closure of the fracture mesh. In either scenario, the acidic fluid will be cooling gradually, causing acidic species that remain associated at high temperatures, such as HCl(aq), to dissociate, thereby increasing the acidity markedly due to the liberation of H+. Another important acid-forming process involves the spontaneous disproportionation of SO2(g) around 400 to 350°C. This chemical reaction liberates three moles of sulfuric acid and one mole of hydrogen sulfide for every four moles of SO2 (Rye et al. 1992; Rye 1993). Acid-forming processes during vapour ascent transform the fluids into some of the most chemically aggressive hydrothermal solutions that nature can create. They have the capacity to alter most rock types into massive domains of quartz and/or quartz-alunite through extensive water-rock interaction.

3 Alteration zonation

Two main components of hydrothermal fluid flow are required to form a lithocap – structurally controlled upflow from the deeper-seated magmatic fluid source, and lateral outflow, which can occur when the ascending magmatic-hydrothermal fluids reach their neutral buoyancy level and encounter a permeable stratigraphic or structural aquifer. Broad vertical and narrow lateral alteration zonation patterns characterise the upflow
Figure 1. Schematic illustration of alteration zoning and overprinting relationships in a porphyry system (modified after Holliday and Cooke 2007; Cooke et al. 2014). Lithocaps can overlie and partially overprint porphyry-style mineralisation associated with shallow-crustal hydrous intrusive complexes. They may host high sulfidation-state mineralisation and can cover intermediate sulfidation state epithermal veins. The lithocaps will overprint and be surrounded by propylitic alteration assemblages that vary from high to low temperature alteration subfacies (i.e., actinolite, epidote and chlorite subfacies) as a function of proximity to the intrusive source. The roots of the lithocap lie within the pyrite halo of the porphyry system. The degree of superposition of the lithocap into the porphyry system is contingent on uplift and erosion rates at the time of mineralization, and will vary from province to province, and from district to district. Abbreviations: ab – albite; act – actinolite; anh – anhydrite; Au – gold; bi – biotite; bn – bornite; cb – carbonate; chl – chlorite; cp – chalcopyrite; epi – epidote; gt – garnet; hm – hematite; Kf – K-feldspar; mt – magnetite; py – pyrite; qz – quartz.

3.1 Alteration in the feeder system

Faults typically provide the focus for fluids to migrate upwards from magmatic fluid sources towards the lithocaps environment (Fig. 1). These structural roots are the sites where acidity increases gradually during fluid ascent, either due to HCl dissociation and/or SO2 disproportionation. The combination of acidification and gradual cooling produces a broad vertical alteration zonation pattern along the faults, potentially over the scale of a kilometre or more. Assemblages are zoned vertically from deep-level quartz–muscovite upwards through quartz–pyrophyllite–dickite, to quartz–aluminate and (at shallow levels) quartz–kaolinite and quartz–halloysite. The core of the upflow zone is generally composed of massive or vuggy quartz, forming as veins and/or replacements. Pyrite is ubiquitous throughout all of the hypogene alteration assemblages in lithocaps.

The broad vertical alteration zonation contrasts markedly with the narrow (metres or less) alteration halos that develop laterally around feeder faults in response to water-rock interaction. At any given depth, the central silicic domains within the fault system will pass outwards with sharp contacts through tight alteration halos (on the scale of centimetres to meters) to advanced argillic and/or argillic alteration assemblages. At deeper levels, massive quartz–pyrite veins may have narrow quartz–pyrophyllite–dickite halos. Similar veins at shallower levels may have quartz–aluminate halos. In both cases, these narrow advanced argillic alteration halos will typically pass outwards to background argillic and propylitic assemblages over the scale of meters or less.

High-sulfidation state mineralisation may be hosted in the structural roots to a lithocap. In deeper parts of the...
fault array, mineralisation may produce massive sulfide veins rich in bornite, chalcocite and/or chalcopyrite (e.g., Collahuasi, Chile; Masterman et al. 2005). At shallower levels, the quartz–pyrite–rich structures may be mineralised with tennantite–tetrahedrite and/or enargite, with gold occurring as a refractory phase in pyrite and enargite. Shallow quartz – pyrite veins may only contain traces of enargite, but can still be endowed with significant gold—silver mineralisation. Reactivation of faults can result in several stages of tectonic-hydrothermal brecciation which can disrupt mineralization.

3.2 Alteration in the lithocap

Huge volumes of lateral fluid flow are required to generate the large, stratabound alteration domains that compose a lithocap. The local environment needs to have significant topographic relief combined with an appropriate permeability architecture at the time of alteration, in order to facilitate lateral flow. This agrees well with the geomorphologic evolution of the El Indio belt and other deposits in the Andes (Bissig et al. 2002, 2015). Once neutral buoyancy has been achieved, lateral migration of acidic solutions may occur along a permeable aquifer, such as unconformity surface or poorly consolidated volcanioclastic breccias. In the case of rocks that typically have low permeability such as granitoids, fluids can follow laterally through a well-developed fracture mesh.

Lateral fluid flow facilitates fluid migration from the structural roots of the lithocap towards the paleosurface. The surface discharge sites may be more than 10 km away from the main upflow zone, and will be at a low point in the local topography. Although the main fluid flow direction is lateral, there is also a vertical component as the fluids continue to migrate upwards towards areas of low topography. The topographic controls on fluid flow imply that the alteration domains that define lithocaps may be distributed asymmetrically around the causative intrusion, with outflow dictated more by topography than by proximity to the fluid source.

In contrast to the structural conduits beneath lithocaps, the lithocap itself is characterised by very broad lateral zonation of alteration assemblages, transitioning outwards from central silicic cores composed of residual quartz (massive and/or vuggy textures), through advanced argillic alteration (typically quartz–alunite) to argillic (quartz–kaolinite ± illite) and lower temperature intermediate argillic (illite–chlorite) and propylitic (chlorite–calcite ± epidote) assemblages. High sulfidation state mineralization, if present, is typically hosted as replacements or breccia infill in the residual quartz domains. The same zonation patterns can occur vertically around lithocaps, although it is important to realise that propylitic assemblages can occur both below and above stratabound domains of silicic and advanced argillic alteration, particularly where several of these alteration domains have formed in what we call a ‘stacked’ lithocap (e.g., Quimsacocha, Ecuador; McDonald et al., 2011).

When uplift rates are extreme, lithocaps may be superimposed onto the top of early-formed alteration and mineralisation features in any underlying porphyry deposit (e.g., Lepanto – Far Southeast, Philippines; Chang et al. 2011). The degree of juxtaposition of the lithocaps and porphyry environments will vary from district to district, depending on local uplift and exhumation rates, the local history of mass wasting and the duration of magmatic-hydrothermal activity.

3.3 Surface features

What are the surface expressions of modern-day lithocaps? Wherever mountainous terrain overlies a magmatic-hydrothermal fluid source, there is likely to be a significant spatial separation between the surface discharge sites for gases and boiling waters, with only intermittent fumarolic discharges of magmatic gases likely to occur at high topographic levels directly above the intrusive complex. Significant lateral flow of acidic waters facilitates their discharge at lower topographic levels, away from the main upflow zone. This means that the surficial boiling acid springs could be located kilometres away from the area of fluid upflow. The upflow zone is most likely to be overlain directly by the sites of fumarolic discharges (e.g., Palinpinon, Philippines; Rae et al. 2003). Such surface manifestations may be trivial compared to the huge volume of alteration forming beneath the surface, and their significance could be easily missed.

4 Landform modification by erosion

Ancient lithocaps may be partially exposed at surface, cropping out as silicified ridges, ledges or cliffs. These silicic outcrops are typically the erosional remnants of far more extensive subsurface alteration systems that formed at the time of mineralisation. Today, they create degraded landforms that some explorers refer to as ‘silica caps’. Silica caps are erosional remnants of what were once more extensive lithocaps. They typically contain high-temperature alteration mineral assemblages (e.g., quartz – alunite – pyrophyllite) and are therefore unlikely to have formed at the paleosurface. As they are recently formed topographic anomalies, they typically do not directly overlie porphyry-style mineralisation. Instead, the porphyry deposit may be located several kilometres away from the silica cap, beneath areas of more subdued topography. This is because alteration assemblages that form directly above a porphyry deposit (e.g., phyllic, intermediate argillic and/or propylitic alteration assemblages) are likely to be less resistant to erosion than the silicic and advanced argillic alteration assemblages that characterise lithocaps, which tend to form on the shoulders of porphyry deposits, rather than silica caps, when searching for porphyry mineralisation.

Misunderstanding the origin and significance of ‘silica caps’ could prove costly during lithocap exploration. These domains are better described as massive and/or
vuggy quartz alteration zones, and should not be treated as the top of the hydrothermal system, unless there is supporting evidence that minimal landscape degradation has occurred after lithocap formation.

5 Exploration tools

Although lithocaps are sites of profound mineralogical, textural and geochemical changes to the protoliths, exploration for mineralisation within and beneath them can be challenging. Fine grained clay minerals are abundant, and textural destruction is common. Short-wave infra-red (SWIR) spectroscopy is an essential tool to aid in mineral identification in these environments. Without technological augmentation through the use of portable field-based SWIR detectors, field geologists will struggle to map alteration zonation in lithocaps effectively.

If high-sulfidation state mineralisation is associated with domains of silicic alteration, then resistivity surveys may help to identify prospective domains. As gold typically occurs as a refractory phase in pyrite, chargeability anomalies may be associated with high-sulfidation state mineralization. But pyrite is ubiquitous throughout lithocaps, and only some of the pyritic rocks may be gold-mineralized, making the identification of pyritic mineralized zones challenging. Furthermore, weathering can result in complicated chargeability anomalies, where pyrite is partially or completely replaced by limonites. Lithocaps are characterised by broad and thick domains of magnetite-destructive alteration, and so any positive magnetic anomaly associated with underlying magnetite-bearing porphyry copper-style mineralisation can be completely obscured.

Chang et al. (2011) demonstrated that a combination of SWIR analyses, focussing on spatial changes in the alunite 1480 nm peak positions, coupled with whole rock geochemistry (filtered based on the presence of alunite and absence of Cu, Au or Ag mineralisation), and augmented where required by LA-ICP-MS analyses of alunite, can provide effective tools for vectoring towards the heat and fluid source responsible for lithocap formation. The intrusive complex responsible for the lithocap is the most likely site to discover any associated porphyry-style mineralisation. But it is not guaranteed that an intrusive complex that produces a lithocap will always form high-grade mineralisation, either of porphyry and/or epithermal character. More characterisation of mineralised and barren lithocaps is therefore required to resolve whether tools can be developed to assess the potential fertility of lithocaps with respect to mineralization.

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Zircon composition: indicator of fertile igneous rocks related to porphyry copper deposits

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**Abstract.** Zircon from granitic intrusions associated with porphyry Cu mineralization contains high concentrations of Ce with Ce⁴⁺/Ce³⁺ greater than 100, reflecting oxidized conditions of the parental magmas. High Ce in zircon produces a prominent peak at Ce in the normalized REE patterns. This is in contrast to the REE patterns of zircon from barren and Sn-W bearing intrusions. The Ce⁴⁺/Ce³⁺ ratios of zircon vary across metallogenic belts and in districts hosting porphyry deposits. Within individual areas, zircon shows the highest Ce⁴⁺/Ce³⁺ from mineralized intrusions, and low values of barren or weakly mineralized intrusions, suggesting that the mineralized intrusions are intrinsically oxidized. Good examples include the Duobaoshan deposit in the northern Central Asian Orogenic belt, and the area around the Cerro Corona deposit in the Peruvian Cordillera.

Although high values of Ce⁴⁺/Ce³⁺, over 100, in zircon occur in intrusions associated with significant porphyry Cu mineralization, there is no global correlation between Ce⁴⁺/Ce³⁺ values and Cu tonnage. The values associated with fertile intrusions vary among different belts.

The Ce⁴⁺/Ce³⁺ values and Ce/Nd wt ratios show a broad positive correlation, suggesting that Ce/Nd of detrital zircon in sediments may be used for regional and district-scale exploration.

1 Introduction

Porphyry copper deposits are associated with granitic intrusions crystallized from oxidized parental magmas. The intrinsically oxidized nature is reflected by primary magnetite and titanite (e.g., Ishihara, 1977), but intense alteration of host rocks to deposits commonly obliterates the primary minerals. Zircon is ideal to study the compositions of parental magmas of granitoids because it is a typical accessory mineral in felsic igneous rocks. In addition, it is physically and chemically sturdy, retaining its original composition during intense hydrothermal and weathering-related alteration long after its crystallization.

Zircon, formulae ZrSiO₄, easily incorporates tetravalent cations such as Ti⁴⁺, U⁴⁺, Th⁴⁺, and Ce⁴⁺. The content of Ti in zircon is useful as a geothermometer (e.g., Watson et al., 2006), and the amount of Ce can be used as an oxygeobarometer. Rare earth elements (REEs) are mostly +³ in magmatic conditions except for Eu⁵⁺ in reduced conditions and Ce⁴⁺ under oxidized conditions. Preferential incorporation of tetravalent cations, such as Ce⁴⁺, into zircon structure gives high Ce in chondrite-normalized REE patterns (Fig. 1). Earlier, we reported high Ce⁴⁺/Ce³⁺, > 140, from large porphyry Cu deposits and lower values from smaller deposits in the Central Asian Orogenic Belt (Shen et al., 2015). We expanded the study of zircon composition to evaluate whether the results from the Central Asian Orogenic Belt are applicable to other terranes of different ages, and whether other geochemical features are present in zircon from fertile intrusions.

2 Study areas

2.1 Duobaoshan deposit in the Central Asian Orogenic Belt

The Duobaoshan deposit (reserves of 4.4 Mt Cu) is located in the Hinggan range on the northern perimeter of the Central Asian Orogenic Belt (Fig. 1). Mineralization took place at ~485 Ma (Liu et al., 2012), during the early metallogenic epoch of the belt, when several other Cu deposits formed in the belt, including the Bozhokol deposit (4.1 Mt Cu; Yakubchuk et al. 2012). The porphyry Cu-Mo deposit at Duobaoshan is hosted by diorite-granodiorite porphyry that was intruded by basaltic dykes and cut by barren quartz monzonites. Zircon grains from the mineralized and hydrothermally altered granodiorite show a chondrite-normalized REE pattern with high HREE and a peak at Ce (Fig. 2). The pattern is distinctly different from that for the bulk rock (grey lines in Fig. 2).

Zircon Ce⁴⁺/Ce³⁺ ratios of altered, mineralized granodiorite porphyry are high, ranging from 101 (low quartile) to 278 (high quartile value) and from 143 to 272, respectively. On
the other hand, zircon from barren quartz monzonite in the proximity of the deposit have low Ce\(^{4+}/\text{Ce}^{3+}\) values, 21 to 48 quartile values with median of 37.

Figure 1. The locations of Duobaoshan and Bozshakol deposits (485 Ma) in the Central Asian Orogenic Belt (CAOB, lime green area). Red solid squares are the locations of porphyry Cu deposits from which zircon data presented in Shen et al (2015) and the Duobaoshan deposit (this study). Other major porphyry Cu deposits are shown in red open squares. The tectonic map is revised after Jahn (2004).

2.2 Cerro Corona deposit in the Hualgayoc mining camp, northern Peruvian Cordillera

The Cerro Corona porphyry Cu-Mo mine (0.9 Mt Cu and high Au, 0.5 g/t) is hosted by at least seven phases of quartz diorite porphyry of the Cerro Corona intrusive complex (0.75 x 0.8 km in size). Our U-Pb zircon dating using a SHRIMP for five different phases indicates intrusive activity at 14.4-14.5 Ma.

Zircon grains from the Cerro Corona intrusive complex have a REE pattern similar to that for zircon from fertile intrusions that host large deposits in the Central Asian Orogenic belt (Fig. 2). The values of Ce\(^{4+}/\text{Ce}^{3+}\) for zircon are high, ranging from 354 to 570 in quartile values (median value of 483). Eu anomalies are between 0.59 and 0.64 for quartile values.

Numerous Miocene igneous rocks are present less than 10 km from the Cerro Corona deposit. Zircon composition from six intrusions outside the deposit have lower Ce\(^{4+}/\text{Ce}^{3+}\), with median values below 300.

Figure 2. Chondrite-normalized REE patterns for bulk rock (grey lines) and zircon (black lines) from mineralized and altered granodiorite porphyry. The abundances of REEs in zircon grains are determined in grain mounts in epoxy resin using a LA ICP-MS at the University of Ottawa.

2.3. Other deposits

The Canadian Cordillera hosts numerous porphyry Cu-Mo deposits in the Quesnellia terrane. The Highland Valley Copper deposit (1.82 Mt Cu) is hosted by the Guichon batholith (~ 210 Ma). Zircon grains show high Ce\(^{4+}/\text{Ce}^{3+}\) values, ranging from 61 (lower quartile) to 175 (upper quartile; Ward 2008). The Gibraltar deposit (1.74 Mt Cu) is hosted by the Granite Mountain batholith, ~ 210 Ma. Zircon grains from the batholith show a similar normalized REE pattern as many other fertile intrusions, with a prominent high at Ce with Ce\(^{4+}/\text{Ce}^{3+}\) ratios up to 170.

Figure 3. Chondrite-normalized REE patterns for zircon from different phases of the Cerro Corona intrusive complex 14.5 Ma in the Peruvian Cordillera.

Figure 4. Eu/Eu* vs Ce\(^{4+}/\text{Ce}^{3+}\) of zircon grains from mineralized and unmineralized granitoids. Note that lower and upper quartile values are shown as squares. Data sources: the Baogutu, Borly, Nurkazhan, Koksai, Aktogai, Kounrad deposits in the Central Asian Orogenic belt (Shen et al., 2015), Chuquicamata-Radomiro Tomic deposits (126 Mt Cu, 33-35 Ma; Ballard et al, 2002), El Salvador (17 Mt Cu, 42 Ma; Lee, 2008), HVC (1.82 MtCu, Ward, 2008), Sn-W deposit (Nardi et al. 2012), barren intrusions (Belousova et al., 2006). Gibraltar and HVC data include zircons from the entire...
batholiths. The amount of Ce$^{3+}$ in zircon is calculated based on partition coefficient between Ce$^{3+}$ in zircon and bulk rocks using the concentrations of Nd, Sm, Gd, Tb, Dy, Yb, Lu and Y in zircon and bulk rocks. The calculation method is similar to that described by Ballard et al. (2002) and Shen et al. (2015).

Granitic intrusions hosting Sn-W deposits are known to have reduced oxidation states based on their mineralogy (e.g., Lehmann 1982). The composition of zircon grains from such Sn-W deposits reported by Nardi et al. (2012) confirm that the parental magmas were indeed reduced. Zircon essentially lacks Ce anomalies with Ce$^{4+}$/Ce$^{3+}$ less than 5 and very low Eu anomalies (Eu/Eu* <0.25).

### 3 Discussion

New data from the Duobaoshan mine in the Central Asian Orogenic belt, the Cerro Corona mine in the Peruvian Cordillera and the Gibraltar mine in the Canadian Cordillera confirm our earlier conclusion; zircon in intrusions associated with mineralization have high values of Ce$^{4+}$/Ce$^{3+}$ and moderate Eu anomalies (Fig. 4).

The data from the areas of the Duobaoshan and Cerro Corona deposits shows a spatial variation of Ce$^{4+}$/Ce$^{3+}$ values. The highest value is in the mineralized intrusion and lower values in weakly mineralized and barren intrusions (Fig. 5).

Comparison of contemporaneous deposits from one metallogenic belt shows similar zircon chemistry for fertile intrusions. For example, porphyry Cu mineralization at Duobaoshan and Bozshakol are contemporaneous, 485 Ma, and their tonnages are similar (4.4 Mt vs 4.1 Mt; Yakubchuk et al., 2012). Although the two deposits are geographically separated by ~4000 km (Fig. 1), the compositions of zircon have very similar Ce$^{4+}$/Ce$^{3+}$ and Eu/Eu* values (Fig. 4).

The Gibraltar deposit and Highland Valley Copper deposit are similar in age, ~210 Ma, and are hosted by large batholiths in the Quesnellia terrane. Zircon composition from these two batholiths are also similar (Fig. 4).

This variation in Ce$^{4+}$/Ce$^{3+}$ among different metallogenic belts makes it difficult to put an absolute value to separate fertile from not-fertile intrusions. The compilation of data suggest that fertile intrusions contain zircon grains with Ce$^{4+}$/Ce$^{3+}$ values greater than 100 (less than 1 % Ce$^{3+}$), indicating relatively oxidized conditions compared to other intrusions in a district.

Weight ratios of Ce/Nd in zircon are positively correlated with Ce$^{4+}$/Ce$^{3+}$ (Fig. 5). The broad positive correlation suggests that the Ce$^{4+}$/Ce$^{3+}$ value of 100 is equivalent to Ce/Nd ratio of 10. Such information can be used in regional and district-scale exploration for porphyry Cu deposits without calculating Ce$^{4+}$/Ce$^{3+}$. The precise calculation of Ce$^{4+}$/Ce$^{3+}$ in zircon requires the bulk rock compositions as a proxy for the melt composition, since the La content in zircon is usually very low, close to several ppb. Zircon is a physically and chemically robust mineral that retains its original composition during subsolidus alteration, metamorphism, weathering and sedimentary processes. The information obtained this study shows that trace elements in zircon grains in stream and glacial sediments may be useful to target favourable areas for further exploration.

![Figure 5. Compilation of zircon REE data including non-mineralized intrusions. Data from the Cerro Corona complex and the area (this study), values from the mineralized granodiorite, contemporaneous mafic dykes, and late barren quartz monzonite from the Duobaoshan deposit (this study), and those from other deposits in the Central Asian Orogenic Belt (Shen et al., 2015).](image)

### 4 Summary

Zircon grains from granitoids associated with porphyry Cu deposits from three different terranes, Paleozoic Central Asian Orogenic Belt, Mesozoic Canadian Cordillera and Miocene Peruvian Cordillera, show a similar chondrite-normalized REE pattern with prominently high Ce and moderate Eu anomalies. The data confirm that the parental magmas associated with porphyry Cu mineralization were oxidized, resulting in high Ce$^{4+}$ values.
Zircon Ce⁴⁺/Ce³⁺ ratios for mineralized intrusions are relatively high compared to barren or weakly mineralized intrusions in a given area.

Since the ratios of Ce/Nd are positively correlated with Ce⁴⁺/Ce³⁺, trace element chemistry of zircon grains in stream and glacial sediments can be used to evaluate the fertility of igneous rocks. The information may be useful to identify areas with fertile igneous rocks that are buried by young sediments, and also in targeting favourable areas during regional exploration.

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Geochemistry of the porphyry-related intrusions of the Wasatch Mountains, Utah: implications for porphyry mineralization

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Abstract. The central Wasatch Mountains of Utah are host to a number of mineralized intrusions including the White Pine Fork and Park Premier porphyry deposits. The older intrusions to the west have been interpreted to have been emplaced at greater depths than those to the east. Recent advances in geochronology and new geochemical data show that the western stocks evolved to more felsic compositions with higher degrees of crustal contamination over time, whereas the eastern stocks show no significant variations. The greater contamination in the western stocks is consistent with magma ponding at greater depths, whereas the shallower emplacement depths of the eastern porphyries can account for the reduced contamination. The lack of pronounced geochemical evolution trends seen in other well-endowed porphyry districts, where they are explained by tectonic perturbations, may account for the small size of the deposits in the Wasatch Mountains.

1 Introduction

The central Wasatch Mountains of Utah are composed of Proterozoic and Mesozoic sedimentary and metamorphic rocks with younger Eocene to Oligocene igneous rocks (John, 1997). The deformed and metamorphosed Paleoproterozoic basement (~1700-1800 Ma) is overlain by Neoproterozoic metamorphosed and unmetamorphosed clastic sedimentary rocks of the Little Willow and Big Cottonwood Formations (Spencer et al. 2012). This sequence is topped by the Keetley volcanic suite, which comprises intermediate lava flows and flow breccias as well as associated volcanioclastic and pyroclastic rocks.

There are two generations of intrusive rocks exposed in the Central Wasatch Mountains which were emplaced from ~40 to 30 Ma. The Little Cottonwood, Alta and Clayton Peak stocks, are located in the western portion of the Wasatch Mountains range and have been interpreted to have deeper paleodepths of emplacement (~10 to 5 km; Fig. 1). The Eastern Stocks include the Flagstaff, Valeo, Pine Creek, Mayflower and Park Premier stocks and have shallower calculated depths of emplacement (Fig. 1; John 1989). The intrusions host a number of porphyry-style hydrothermal centres that have been mineralized to varying degrees (e.g., White Pine porphyry Mo; Park Premier porphyry Cu).

Figure 1. Generalised geologic map of the central Wasatch Mountains igneous rocks (after John 1989 and 1997). Geochronology sample locations are indicated. AT, Alta-Grizzly thrust; M, Mayflower mine; O, Ontario mine; PP, Park Premier mine; WP, White Pine Fork porphyry-Mo deposit.
We use new geochemical and geochronological data for the intrusions of the White Pine area to better understand their tectonic setting and link to mineralization.

2 District geology and geochronology

2.1 Western stocks

The western stocks of the central Wasatch Mountains igneous belt include the Clayton Peak, Alta and Little Cottonwood stocks. The Clayton Peak stock is a compositionally zoned diorite to quartz monzonite.

The Alta stock ranges from diorite through to quartz diorite compositions with fine- to medium-grained textures, whereas the Little Cottonwood stock is a coarse-grained granodiorite with large K-feldspar megacrysts up to 6 cm long, local pegmatoidal patches of quartz+K-feldspar+biotite=muscovite, and abundant mafic, intermediate and metamorphic xenoliths. The Little Cottonwood stock also hosts the White Pine Fork porphyry Mo deposit. The deposit is associated with the White Pine intrusion: a younger, finer grained and more leucocratic phase that has gradational contacts with the Little Cottonwood stock. The deposit has been interpreted to have an age of 26-23.5 Ma (John 1997) but Re-Os ages of molybdenite suggest an age of ~30 Ma (Smyk 2015). There has been no production at the deposit but it is estimated to contain a resource of 16 Mt at 0.1% Mo (John 1997).

2.2 Eastern stocks

The eastern stocks of the central Wasatch Mountains igneous belt include the Flagstaff, Mayflower, Ontario, Glencoe, Valeo, Pine Creek and Park Premier stocks. Compositionally, the eastern stocks are similar to each other and to the Alta stock and range from generally porphyritic and dioritic (Flagstaff and Mayflower stocks) to generally quartz dioritic to granodioritic (Valeo and Ontario stocks; Vogel et al. 2001).

Mineral deposits associated with the eastern stocks, include the Daly, Daly West and Judge polymetallic vein deposits. The composite Park Premier stock is host to the Park Premier deposit, a composite porphyry Cu-Au, Cu skarn and polymetallic vein deposit with an age of 33.5 Ma (John 1997).

2.3 Keetley Volcanics

The Keetley Volcanic field is a sequence of lahars, debris avalanche deposits, volcanic conglomerates, air-fall tuffs, ash-flow tuffs, and minor lava flows that are interpreted to represent the eroded remnants of a stratovolcano (Leveinen 1994; Vogel et al. 2001). The volcanic field extends over ~330 km² area between the eastern stocks of the central Wasatch Mountains and the western end of the Unita Mountains (Leveinen 1994). The Park Premier stock intruded the Keetley volcanic field and may be its intrusive equivalent (Vogel et al. 2001).

2.4 Geochronology

Calc-alkaline igneous rocks of the central Wasatch Mountains were emplaced in at least two separate events between 36-29 Ma (Thompson et al. 2015). The oldest phase is associated with the easternmost intrusions, including the Valeo, Flagstaff and Pine Creek stocks (ca. 35 Ma). Ignimbritic flows that form part of the Keetley Volcanic sequence and igneous clasts found within the Keetley Volcanics are also coeval with this phase. The Clayton Peak stock, which is generally associated with the westernmost stocks of the district, has a similar crystallisation age to the eastern stocks (ca. 35 Ma). The Alta stock, which is located next to the Clayton Peak stock in the central-west part of the district, has a slightly younger crystallisation age (ca. 33 Ma). The westernmost intrusion, the Little Cottonwood stock, has the youngest crystallisation age (ca. 29-30 Ma).

3 Geochemistry

3.1 Whole rock geochemistry

A total of 46 whole rock geochemical analyses were obtained from samples of both the western and eastern stocks of the central Wasatch Mountains igneous belt (Fig. 2). The western stocks (Little Cottonwood, Alta and Clayton Peak) range in composition from diorite through to granite (53 – 74 wt % SiO₂; Fig. 2a). However, the eastern stocks (Flagstaff, Mayflower, Ontario, Park Premier, Pine Creek and Valeo) and Keetley volcanics have a narrower compositional range (59 – 65 wt % SiO₂; Fig. 2a). Both the western and eastern stocks as well as the Keetley Volcanic rocks are calc-alkaline in composition (Fig. 2b).

The western stocks show a general trend of increasing compositional maturity with decreasing age. The oldest and easternmost of the western stocks, the Clayton Peak stock (34.64 ± 0.51 Ma; Thompson et al. 2015) has the most primitive composition (Fig. 2a), whereas the youngest of the western stocks, the Little Cottonwood stock (29.63 ± 0.27 Ma; Thompson et al. 2015) has the most felsic composition (Fig. 2a).

3.2 Sm-Nd isotope geochemistry

Samples of the Little Cottonwood, White Pine, Alta, Flagstaff, Valeo, Mayflower and Park Premier stocks were analysed for their Sm-Nd isotopic compositions (Fig. 3). Initial isotopic compositions for individual samples were calculated using ages obtained by ICP-MS U-Pb zircon geochronology on each of the samples (Thompson et al. 2015), and the chondritic uniform
reservoir (CHUR) to have a present-day $^{147}\text{Sm}/^{144}\text{Nd}$ value of 0.1967 and a $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.512638 (Wasserburg et al. 1981).

The igneous stocks have $\varepsilon_{\text{Nd}}$ compositions, particularly for the western stocks that range from -12.8 (Alta stock; Vogel et al. 2001) to -18.5 (White Pine intrusion; this study). In particular, the westernmost Little Cottonwood and White Pine intrusions have the lowest $\varepsilon_{\text{Nd}}$ values (-17.7 and -18.5, respectively) along with a sample of the Keetley Volcanics (-18.4; Vogel et al. 2001). In addition, these samples also display the most enriched compositions, with $f_{\text{Sm}/\text{Nd}}(t)$ values of -0.58 to -0.56, compared to the rest of the igneous stocks that range from -0.53 to -0.49 (Fig. 3). This would suggest that the westernmost stocks enjoyed a prolonged period of enrichment relative to the rest of the central Wasatch igneous suite. The new Sm-Nd data presented in this study are broadly consistent with data reported by Vogel et al. (2001), and support the model that the stocks were derived via partial melting of crustal rocks as early as ca. 1650 Ma (Vogel et al. 2001).

4 Discussion

The geochemical data presented here suggests a more complex evolution for the porphyry related intrusions of the Wasatch Mountains than has been previously recognised. Our data show that whereas the Western stocks evolve to more felsic compositions over time with a greater role for crustal contamination there is no such variation in the Eastern stocks. The increased contamination in the western stocks over time suggests that the magmas were ponding at depth and assimilating older crust, consistent with their greater depth of emplacement. The shallower emplacement depths of the eastern intrusions (John 1989) may explain the lack of geochemical variation as the intrusions would have probably been more rapidly emplaced and cooled allowing less time for assimilation. Studies of the evolution of intrusions related to porphyry mineralization in other well-endowed districts has shown that the magma evolves prior to mineralization (e.g., Central Chile, Hollings et al. 2005, Piquer et al. 2016; the Philippines, Hollings et al. 2011; and Panama, Baker et al. 2016) likely as a result of responses to ridge subduction and slab flattening. The absence of similar results in the Wasatch Mountains may account for the relatively small size of the know porphyry systems.

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References


Abstract. The Cenozoic evolution of the central segment of the Tethyan metallogenic belt is dominated by the oblique convergence and final collision of Gondwana-derived terranes and the Arabian plate with Eurasia, which created a favorable setting for the formation of the highly mineralized Meghri-Ordubad pluton in the southernmost Lesser Caucasus, in the Zangezur-Ordubad mining district. Paleostress reconstructions indicate anti-clockwise rotation from NE-oriented compression during the early and middle Eocene to NNW-oriented compression during the Pliocene. During the Eocene the N-S oriented faults are consistent with dextral strike-slip tectonics, correspond to synthetic faults and control the main porphyry Cu-Mo and epithermal deposits and prospects. The sinistral E-W oriented en-échelon faults correspond to antithetic faults. This strike-slip kinematics is consistent with the regional NE-oriented compression in the Zangezur-Ordubad district and concomitant with final subduction of the Neotethys along the Eurasian margin. Sinistral strike-slip kinematics along the E-W oriented faults resulted in clockwise rotation of the individual blocks of the Zangezur-Ordubad district. During the Oligocene and Miocene anti-clockwise rotation of the main paleostress compressional orientation resulted in reactivation of existing ore-controlling structures in a sinistral strike-slip tectonic regime, which is consistent with the re-orientation of the tectonic plate kinematics and re-organization of the Arabia-Eurasia collision.

2 Major regional district-scale structures

The Zangezur-Ordubad region consists of the Nakhtchevan and Zangezur tectonic blocks (Fig. 1), which behaved as two separate entities since the middle Eocene (Tayan et al. 1976), when uplifting of the Zangezur block started with respect to the Nakhtchevan block. The two tectonic blocks are separated by the NNW-oriented, dextral strike-slip Khustup-Giratagh fault zone (Fig. 1; Tayan et al. 1976). To the east, the major regional NNW-oriented, dextral strike-slip Khustup-Giratagh fault zone separates the Zangezur block from the Kapan block, in other words the Mesozoic Eurasian margin (Fig. 1).

The Zangezur-Ordubad mining district consists of the Meghri-Ordubad pluton in the southernmost Lesser Caucasus, Central Tethyan belt (Moritz et al. 2016a). It was formed by repeated intrusive activity from the mid-Eocene subduction to the Miocene post-collisional evolution of the southernmost Lesser Caucasus, with pulsed ore formation (Karamyan 1978; Melkonyan et al. 2008; Moritz et al. 2016a, b; Rezeau et al. 2016). It is a very fertile area and contains sixteen porphyry Cu-Mo, twenty epithermal Au and base metal and three skarn W-Cu-Mo, Fe deposits and prospects.

Regional strike-slip faults played an important role in the control of the porphyry Cu-Mo, epithermal and skarn systems hosted by the Meghri-Ordubad pluton.

The aim of this study is to understand how ore deposit and prospect location, ore body geometry in the Zangezur-Ordubad mining district are linked to the long-lasting Eocene to Mio-Pliocene regional strike-slip tectonics, and far-field plate tectonic evolution from Eocene subduction to Miocene post-collision.

We discuss the paleostress and the kinematic environment of the major strike-slip and oblique-slip ore-controlling faults throughout the Cenozoic tectonic evolution of the Meghri-Ordubad pluton based on detailed structural field mapping of the ore districts, stereonet compilation of ore-bearing fractures and vein orientations in the major porphyry and epithermal deposits, and the paleostress reconstructions.
Eocene tectonic and ore control regime

Paleostress reconstructions reveal a NE-SW-oriented compressional setting during the early and middle Eocene, which was favorable for dextral displacements along the two major, regional NNW-oriented Khustup-Giratak and Salvard-Ordubad strike-slip faults (Fig.1). This resulted in the formation of a N-S oriented transrotational basin, known as the Central magma and ore-controlling zone (Tayan 1998).

Since the Eocene the N-S oriented faults are consistent with subparallel dextral strike-slip tectonics and correspond to synthetic faults (Fig. 1; Tashtun, Meghriget, Spetry, Tey, Terertasar, Dastakert and Nshanakar faults) and the sinistral E-W oriented en-échelon faults correspond to antithetic faults (Fig. 1; Aramazd, Voghji, Meghrasar, Meghriget-Cav, Bughakyar and Agarak faults).

This strike-slip kinematics is consistent with the regional NE-oriented compression in the Zangezur-Ordubad mining district revealed by the paleostress indicators and corresponding to Eocene SW- to NE-oriented plate convergence and Neotethys subduction beneath Eurasia along the Lesser Caucasus-Zagros segment of the Tethyan belt (Barrier and Vrielynck 2008). Sinistral strike-slip kinematics along the E-W oriented faults resulted in clockwise rotation of the individual blocks of the Zangezur-Ordubad district (Figs. 1 and 2). Such block rotation is typical for strike-slip fault systems, with the blocks rotating synthetically with respect to the main master faults (Kim et al. 2014).

During the Eocene, dextral displacement along the major N-S oriented strike-slip faults were favorable for creating of NE-oriented en-échelon normal faults or extension fractures. These faults can be observed from the regional scale down to the ore body scale in the porphyry and epithermal systems. The N-S oriented faults, in particular at their intersection with E-W and NE-oriented faults, were important ore-controlling structures for the emplacement of major porphyry Cu-Mo (e.g., Dastakert, Hanqasar, Aygedzor and Agarak) and epithermal Au, base
metal (e.g., Tey-Lichkvaz and Terterasar) deposits and prospects.

The NE- to NNE-oriented structures were important controls of the skarn deposits and prospects. They occur mainly in the northern and southern Bargushat blocks (Fig. 1). The Svaranc Fe skarn deposit related with the regional NNW-oriented Khustup-Giratagh dextral strike-slip fault and the Kefashen Cu-Mo and W prospects occur at the contact of the Geghi intrusion and Middle Devonian to Late Permian carbonate rock and shale along a NW-oriented thrust zone (Fig. 1; Harutyunyan 1995).

Figure 2. Clockwise block rotation in the Zangezur-Ordubad mining district.

4 Oligocene tectonic regime: structural control of the world class Kadjaran porphyry deposit

The paleostress data indicate a progressive anti-clockwise rotation of the main stress axes from regional NE-oriented compression (Fig. 3a) to NNE-oriented compression during the Oligocene (Fig. 3b) and to N-S compression during the Miocene. Therefore, since the Oligocene, magmatic intrusions and ore deposits were progressively emplaced under a different regional tectonic regime than their Eocene counterparts.

The Oligocene giant Kadjaran porphyry deposit formed in the immediate vicinity of the NNW oriented Tashtun and E-W oriented Voghji fault intersection (Fig. 1). The E-W-, NE- and N-S oriented ore and dike controls reveal that structures inherited from the Eocene dextral strike-slip tectonics were reactivated during the Oligocene. However, the reverse motion along the E-W and NE-oriented faults controlling the 26-27 Ma-old ore-bearing veins at the Kadjaran porphyry deposit is not compatible with dextral strike-slip tectonics under a NE-oriented compression. These reverse fault geometries indicate that ore formation at Kadjaran occurred under a different tectonic regime, more consistent with progressive NNE- to N-S oriented compression compatible with the paleostress rotation from the late Oligocene to Miocene (Fig. 3b).

In the Kadjaran deposit, the early porphyry veins are predominantly NE- to NNE-oriented and late chalcedony and carbonate veins crosscutting 22 Ma-old granodiorite porphyry dikes are mainly steeply-dipping E-W oriented, which is consistent with N-S oriented compression during the Miocene.

Figure 3. Characteristics of the major N-S oriented ore-controlling faults. a from the early and middle Eocene to early Oligocene. b during the late Miocene with the formation of the Meghri – Tey graben.

5 Miocene to Pliocene tectonic regime: structural control of the Lichk porphyry-epithermal system

Paleostress reconstructions in the Zangezur-Ordubad region indicate a progressive rotation of the major compression from NNE-oriented during the Oligocene to N-S-oriented during the Miocene and finally to NNW-oriented during the Pliocene, which is consistent with the re-orientation of the tectonic plate kinematics and re-organization of the Arabia-Eurasia collision since at least the late Miocene (Allen et al. 2004; Austermann and Iaffladano 2013).

The early Miocene E-W oriented extensional setting was favorable for intruding the early Miocene porphyritic granite-granodiorite of the Voghji massif along the footwall of the Tashtun fault (Fig. 1). This reveals that the Tashtun fault had an essentially oblique, normal fault behavior and controlled the western boundary of the Meghri-Tey graben since the early Miocene (Figs. 1 and 3b; Tayan et al. 1998). The eastern boundary of the graben was controlled by the N-S oriented Meghriget fault (Figs. 1 and 3b). The geometry and N-S orientation of the Meghri-Tey graben is consistent with E-W and NE-orientation of the main extensional stress axes during the Miocene and Pliocene, respectively (Fig. 1).

The Miocene Lichk prospect is hosted by a 22.2 Ma-old porphyritic granodiorite emplaced within a release bend between the western and eastern segments of the Tashtun fault (Fig. 1). The geometry of the release bend is inconsistent with dextral kinematics along the Tashtun fault. However, it could have formed during sinistral kinematics. Dextral kinematics is recorded along the eastern segment of the Tashtun fault during the Oligocene.
with displacement of the early Oligocene diorite porphyry dike. During the Miocene mineralization event, the Tashtun fault had a sinistral oblique-slip kinematics, which is recorded by sinistral displacement of segments of the epithermal system controlled by the NE-oriented Lichk fault. Thus, we conclude that the Lichk deposit and its host granodiorite porphyry were emplaced during Miocene sinistral reactivation of the Tashtun fault, which was behaving as a dextral tectonic system until the early Oligocene. The switch of the Tashtun fault behavior resulted in the development of a pull-apart basin and the formation of the Lichk porphyry - epithermal system. It coincides with the progressive rotation of the main compressional orientation from the early Oligocene to the Miocene, and then the Pliocene (Fig. 3).

6 Discussion and conclusions

The proposed tectonic model explains the structural control of porphyry Cu-Mo, epithermal and skarn deposits and prospects of the Zangezur-Ordubad mining during the early Eocene to Mio-Pliocene tectonic evolution of the district in the context of regional strike-slip tectonics.

The progressive change of the main compressional paleostress orientation recorded in the Zangezur-Ordubad region, rotating from NE during the early and middle Eocene to NNE during the early Oligocene to N-S during the Miocene and finally to NNW- during the Pliocene, is consistent with the re-orientation of the tectonic plate kinematics from Eocene subduction to Mio-Pliocene post-collision.

During the Eocene NE-oriented compression created the essentially dextral strike-slip tectonic regime along the major N-S oriented strike-slip fault. The structures formed during Eocene dextral strike-slip faulting, concomitant with final subduction of the Neotethys, were repeatedly reactivated during the subsequent Neogene tectonic evolution of the Zangezur-Ordubad region, as one evolved from a subduction to a post-subduction geodynamic setting.

The Oligocene and Miocene deposits and prospects were formed essentially in a sinistral strike-slip tectonic regime, which created the favorable geometry and adequate conditions for the emplacement of vein and stockwork-type porphyry Cu-Mo deposits, including the giant Oligocene Kadjaran deposit and the Miocene Lichk prospect.

This underlines the importance of regional strike-slip tectonics as a fundamental control on the formation of Cenozoic porphyry-epithermal systems and associated magmatism within the Lesser Caucasus, which is comparable to many other metallogenic belts.

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Fluid-involved processes at the magmatic-hydrothermal transition in Torres del Paine, Chile, studied through fluid inclusions in miarolitic quartz

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Abstract. Quartz crystals from miarolitic cavities in the Torres del Paine igneous complex, Chile, contain inclusions that document the fluid-related processes during the complete late-stage magmatic-hydrothermal evolution of the pluton. We are able to distinguish seven inclusion types based on phase composition at room temperature. Among those are dominantly aqueous fluid inclusions ranging from vapor-rich inclusions (Type I) over 2-phase vapor-liquid (Type II) to simple and complex brines (Type IV+V), as well as CO$_2$-bearing 3-phase-fluid inclusions (Type III), crystallized silicate melt (Type VI), and hydrous salt inclusions (Type VII). Inclusion petrography combined with growth textures identified by variable pressure, secondary electron imaging and preliminary microthermometric measurements is used to construct a first concept of the processes during the magmatic-hydrothermal history of the pluton. This concept forms the crucial framework for a more detailed study focusing on the partitioning behavior of elements between residual water-saturated melt and aqueous fluid at the magmatic-hydrothermal transition in the shallow magmatic system at Torres del Paine.

1 Introduction

Fluid inclusions have been established as valuable samples to study for example fluid evolution in pressure-temperature-time space and ore deposit formation (e.g. Sorby 1858; Roedder 1990; Audétat et al. 2008, and further references therein). Because they are trapped during the protracted growth of igneous host crystals that first precipitate from an ascending, cooling magma and later from a hydrothermal fluid, these small increments of fluid or solid phases represent ideal samples to study fluid related processes at the magmatic-hydrothermal transition. Regarding this stage, we are interested in studying the selective mobilization of elements that is associated with the exsolution of an aqueous fluid phase from the residual silicate melt, as this process is decisive for the mass transfer of elements between geological reservoirs and relevant to ore deposit forming processes.

Samples were taken from the shallow intrusive body of the Miocene Torres del Paine igneous complex, Chile, which is characterized by numerous fluid-features and a lack of significant post-emplacement deformation, justifying the assumption that fluid inclusions are present and well preserved.

Here, we present a first overview of this fluid and melt inclusion study, focusing on thick section petrography and preliminary microthermometry measurements that establish the framework for detailed geochemical analysis including LA-ICP-MS.

2 Geology

The Torres del Paine bimodal igneous complex in Patagonia, Chile intruded as a series of laccoliths at a depth of 2-3 km (~0.75 kbar) between 12.43 and 12.59 Ma into a series of early to mid-Cretaceous sediment formations (Leuthold et al. 2012, 2013). The numerous fluid exsolution features exposed in the field area range from miarolitic cavities (see Fig. 1) to pegmatoid and frothy zones, and document fluid processes during the complete magmatic-hydrothermal history of the igneous complex from 750 °C down to <300 °C as revealed by the local occurrence of zeolite minerals. The complex is thus a well-suited natural laboratory to investigate processes in shallow subvolcanic magma reservoirs that may ultimately trigger porphyry-type ore (Cu, Mo) deposit formation (Audétat et al. 2008).

Figure 1. Miarolitic cavities at Torres del Paine. a and b Cavities of variable size in granitic host rocks. c Thick section scan of cavity and surrounding graphic texture zone. d Schematic drawing of a miarolitic cavity with a transition zone marked by graphic texture in granitic host rock.
During field work, numerous miarolitic cavities were found and sampled in the exposed parts of magma-mingled mafic-felsic units, as well as in the lowest granite unit and in fallen blocks of all three granite units. These cavities range in size from mm up to about 1 m, and free-grown minerals are typically in the mm to cm range. The mineral assemblages of the cavities are mainly dominated by free-grown quartz and feldspar, in many cases also featuring a narrow eutectic graphic texture in the transition zone from the cavity into the surrounding rock (see Fig. 1). In the more mafic host rocks, the cavities show a more diverse mineralogy exhibiting also titanite, biotite, needle-shaped amphibole or allanite-epidote, and locally various zeolites.

3 Methods

Samples were selected from different textural regimes to cover host rock without fluid features, a transition zone marked by graphic intergrowth of quartz and feldspar, miarolitic cavity fillings and free-grown (hydrothermal) quartz crystals. They were prepared as doubly-polished 200 - 400 μm thick sections for inclusion petrography and microthermometry.

A transmitted light optical microscope was used to identify mineral assemblages, textural changes as well as inclusion types and the sequence of entrapment.

A Zeiss EVO-50 scanning electron microscope (SEM) was used to obtain variable pressure, secondary electron (VPSE) images that visualize internal structures such as growth zones, twinning and fluid alteration features in the host quartz crystals. We used imaging settings of 14 kV accelerating voltage, a spot size of 570 - 600 – which corresponds to a sample current of 1.5 - 2.4 nA – and a chamber gas pressure of 10 - 14 Pa for the quartz samples from Torres del Paine to achieve highest possible contrast in the VPSE images.

Preliminary microthermometry was performed on a Linkham THMS 600 heating freezing stage connected to a Linkham LNP controlling unit. This setup allows heating and cooling in a temperature range from -180 to +600 °C. The temperature control was calibrated using the melting points of CO$_2$ (-56.6 °C) and ice (0.0 °C) as well as the critical point of pure H$_2$O (374.1 °C). The observed temperatures of significant phase transitions in fluid inclusions are used to calculate bulk salinity data expressed as wt% NaCl equivalent (NaCl$_{eq}$), as well as to obtain first estimations of entrapment conditions. Last solid melting temperatures were converted into salinities according to Driesner and Heinrich (2007) for salty aqueous inclusions, while the formulation of Diamond (1992) was used for the system H$_2$O-CO$_2$-NaCl.

4 Results

4.1 Petrography

The studied samples cover several generations of quartz. The first one can be found in zones of unaltered igneous rock, while a second generation is present in the graphic texture surrounding most of the miarolitic cavities in a fine-grained, narrow zone, and an even later generation consists of the free-grown crystals inside cavities. We assume that the transition from crystal growth in a magmatic to a more hydrothermally dominated regime is documented in the latter two generations of quartz.

Figure 2. Types of inclusions preserved in the studied samples. a) Vapor-rich inclusions (Type I), b) Two-phase vapor-liquid (Type II), c) Three-phase-fluid inclusions (Type III), d) Simple brine (Type IV), e) Multiple crystal brine (Type V), f) Silicate melt (Type VI), g) Hydrous salt inclusions (Type VII).

During inclusion petrography, we were able to distinguish seven inclusion types in the samples from Torres del Paine by the presence and relations of characteristic phases at room temperature (Table 1, Fig. 2).

Vapor-rich inclusions (Type I) are found throughout all examined samples, while 2-phase vapor-liquid (Type II) and silicate melt now present as crystallized polyphase inclusions (Type VI) are less common. The latter mostly occur in quartz of generation 2 associated with graphic texture zones. Additionally, a large number of inclusions are comprised of several types of brines, all of which are characterized at room temperature by the presence of a vapor bubble and a halite crystal in aqueous liquid (Type IV), and many feature several additional crystal phases (Type V). In a few samples, 3-phase-fluid inclusions (Type III) containing liquid H$_2$O, liquid CO$_2$ and a gas bubble at
room temperature are also observed. Inclusions of a hydrous salt phase (Type VII) are very rarely observed. Type IV inclusions often contain tiny black and opaque crystals that are sometimes hidden by the inclusion walls or the vapor bubble. They are still counted as simple brines, as they share more characteristics with other Type IV than with the hypersaline Type V inclusions.

Additionally, several coexisting brine + vapor-rich fluid inclusions (“boiling assemblages”), as well as coexisting silicate melt + aqueous vapor-rich inclusions, have been observed in both quartz generations (1 and 2) in the samples from Torres del Paine.

**Table 1.** List of identified inclusion types and their respective characteristics.

<table>
<thead>
<tr>
<th>Type</th>
<th>Phase characteristics</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>&gt; 90% vapor</td>
<td>***</td>
</tr>
<tr>
<td>II</td>
<td>aqueous liquid + vapor bubble</td>
<td>*</td>
</tr>
<tr>
<td>III</td>
<td>aqueous liquid + liquid CO₂ + CO₂ gas</td>
<td>*</td>
</tr>
<tr>
<td>IV</td>
<td>aqueous liquid + vapor bubble + halite crystal</td>
<td>***</td>
</tr>
<tr>
<td>V</td>
<td>aqueous liquid + vapor bubble + multiple crystals</td>
<td>*</td>
</tr>
<tr>
<td>VI</td>
<td>multiple solid phases + deformed vapour bubble</td>
<td>**</td>
</tr>
<tr>
<td>VII</td>
<td>colorless mass + multiple small vapor bubbles</td>
<td>*</td>
</tr>
</tbody>
</table>

We were also able to observe general trends regarding overall inclusion distribution in the studied quartz crystals. For example, single crystals often have a core zone exhibiting a much higher inclusion density than the rim overgrowth, and inclusion assemblages are much harder to identify. This pattern is mostly found in samples that cover the transition from eutectic graphic texture to free-grown hydrothermal cavity quartz as can be seen in the example of TdP16a (Fig. 3). Another group of sample crystals is characterized by numerous secondary fluid inclusion trails that obscure most other inclusion features in the complete base of the crystals, and has therefore been mostly excluded from subsequent studies.

### 4.2 SEM-VPSE Imaging

VPSE imaging of the samples was implemented to visualize growth zones and inclusion related features in the quartz crystals. So far, all samples show at least two distinct hydrothermal growth phases identified by VPSE imaging of quartz crystals; an inner zone of higher intensity (light grey) overgrown by a narrow rim of low intensity (dark grey - black). The dark rim is supposedly related to late stage quartz precipitation from a hydrothermal fluid at lower temperatures, while the lighter inner part precipitated at more elevated temperatures as described by Rottier et al. (2016). VPSE images of a few crystals exhibit rhythmic growth zoning identifiable by alternating lighter and darker zones delineating former crystal faces. Additionally, in several samples, an internal zone of the crystal shows more complicated patterns in the VPSE images in darker shades of grey, that may be caused by fracturing and healing of the crystal associated with later fluid entrainment events (see Fig. 3).

Combining these observations with the identified inclusion types and distribution trends described in section 4.1, we derive a first hypothesis regarding the entrapment sequence of inclusions and the corresponding fluid evolution. We propose an early stage at magmatic conditions, during which silicate melt and vapor-rich inclusions are trapped, followed by a more complex transition phase which is documented by chaotic zones containing highly saline brines (Type V) likely associated with a second generation of vapor-rich inclusions. The rare Type II inclusions and some simple brine inclusions correspond to the late stage overgrowth phase at low temperature marked by lower VPSE intensities. Due to their rarity, type III (CO₂-bearing) and VII (hydrous salt) inclusions have not yet been definitely associated with a given growth stage.

**Figure 3.** Comparison of an optical microscope scan (left) and the corresponding VPSE image (right) of sample TdP16a. The marked zones are: i: graphic intergrowth, ii: inclusion-rich, hydrothermal core zone exhibiting an irregular VPSE pattern that we attribute to fluid induced recrystallization, iii: inclusion-poor, hydrothermal overgrowth with rhythmic zoning; iv: late stage hydrothermal overgrowth.

### 4.3 Microthermometry

To provide a first insight into the range of fluid salinities and entrainment conditions documented in our samples, a preliminary study was performed on a first set of inclusions in samples TdP01, TdP04, TdP17b. The preliminary results are presented as salinities versus homogenization temperatures in figure 4.

In the case of Type IV inclusions of TdP04, a second solid phase consisting of a cluster of small black needle-shaped crystals was present. This phase dissolved into the liquid around 355 °C, so we conclude that these additional solids are true daughter crystals that precipitated from
homogeneously entrapped fluid during cooling of the inclusion.

Calculated salinities and observed homogenization temperatures confirm the previously stated hypothesis of medium to highly saline fluids trapped at intermediate to high temperatures, followed by later entrapment of inclusions with low to medium salinities at lower temperatures.

A number of brine inclusions did not homogenize in the temperature range (<600 °C) as accessible by our microthermometry stage, but show only a small decrease in bubble size. Even though true homogenization temperatures could not be obtained on the current analytical setup, these inclusions already confirm fluid entrapment at high temperatures close to or even at the magmatic-hydrothermal transition.

**Figure 4.** NaCleq fluid salinities calculated from last solid melting temperatures are plotted against homogenization temperatures observed for a first sample set during preliminary microthermometry measurements. The inclusions which did not completely homogenize during heating up to >580 °C are included in the plot at 600 °C for completeness.

**5 Conclusions**

Combining inclusion petrography, VPSE imaging and preliminary microthermometry we conclude that the identified inclusion types document several generations of fluids present during the magmatic-hydrothermal evolution of the igneous system at Torres del Paine. These fluids cover a wide range of salinities, densities and entrapment conditions. The variety in fluids preserved in the sample crystals is promising for our on-going project as it will enable the study of element partitioning behavior during a long cooling history of the igneous system, as well as the effect of various fluid compositions and characteristics.

Discovering co-existing inclusions of brine and vapor, as well as melt and vapor-rich inclusion assemblages, is crucial for the subsequent analytical work because these inclusion assemblages make it possible to directly determine element partition coefficients, as has been shown before by e.g. Audéat et al. (2008) and Zajacz et al. (2008).

Future work will include measurements of the chemical composition of inclusions by LA-ICP-MS following procedures documented in Pettke et al. (2012). In combination with the previously determined succession of inclusion entrapment we will then be able to reconstruct the temporal evolution of melt-fluid chemistry upon cooling in the shallow intrusion of Torres del Paine.

**Acknowledgements**

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The Late Miocene Middle Cauca Au-Cu porphyry belt, Colombia: time-space distribution of magmatism and controls on Au mineralization

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Abstract. The Middle Cauca Belt in west-central Colombia contains a number of porphyry (e.g. Titribí, Nuevo Chaquiro) and low to intermediate-sulfidation epithermal deposits (e.g. Marmato, Zancudo), ranging in age from ~9 to 5.6 Ma. The deposits are hosted in the Romeral melange, a tectonized basement complex containing Mesozoic oceanic and older metamorphic rocks, overlain by Oligocene siliciclastic and middle to upper Miocene arc-volcanic rocks. The porphyry deposits are generally gold-rich although Nuevo Chaquiro is copper-rich. The igneous rocks related to porphyries are largely calc-alkalic and oxidized but at Titribí they are distinctly more alkalic. The current topography together with the volcanic stratigraphy and igneous geochemistry suggest that the gold-rich nature of the porphyries can largely be attributed to shallow emplacement and, in the case of Titribí to the alkalic character of the intrusions rather than a reduced oxidation state of the intrusions. The latter is likely the case at the 28.5 Moz La Colosa gold porphyry deposit, emplaced in early Paleozoic carbonaceous schists of the Cajamarca-Valdivia terrane to the S and E of the MCB.

1 Introduction
High gold content and Au/Cu ratios in porphyry deposits may be due to shallow-crustal emplacement (e.g. Murakami et al. 2010), alkalic nature of parental intrusions (e.g. Lang et al. 1995, Bissig and Cooke 2014) or the reduced character of basement and intrusive suites (e.g. Hart 2007). The Middle Cauca belt (MCB) in Colombia (Fig. 1) contains several gold-rich porphyry systems with associated low-sulfidation epithermal deposits. In this paper we summarize the geologic and petrochemical characteristics of key districts located in the MCB and adjacent areas and discuss these deposits in the context of the models outlined above.

2 The Middle Cauca belt

2.1 Geology
The Middle Cauca Belt is defined as a belt of late Miocene porphyry and related deposits hosted in the Romeral melange (Cediel et al. 2003; Shaw et al. 2011) of west-Central Colombia (Fig. 1). It is separated from the early Paleozoic Cajamarca-Valdivia terrane to the E by the NE to N-striking Romeral strike-slip fault system, and from the Pacific terranes and the Chocó Arc to the W by the Garrapatas-Dabeiba fault system (Cediel et al. 2003). The
basement of the Romeral melange comprises low-grade metamorphosed basaltic-gabbroic ocean floor assemblages interpreted as accreted remnants of a peri-cratonic continental margin basin (e.g., Quebradagrande complex; Nivia et al. 1996) containing local slivers and fragments of early Paleozoic and Permo-Triassic schists, gneisses and amphibolites (e.g., Arquía complex). Within the MCB, basement is overlain by upper Oligocene to lower Miocene siliciclastic rocks of the Amagá Formation and the mafic to felsic volcanic rocks of the middle to upper Miocene Combia formation.

2.2. Ore deposits

Key porphyry districts are briefly summarized from N to S below (Fig. 1).

The Titiribí Au-Cu porphyry cluster (4.6 Moz Au, ~0.3 Mt Cu), and overprinting low-sulfidation epithermal mineralization at Zancudo and Chisperos (Kantor and Cameron 2016), are located near the northern limit of the Romeral melange. Porphyry mineralization accompanies diorite stocks intruding the Amagá and Combia formations between 7.8 and 7.1 Ma. Sericite adjacent to epithermal mineralization at Chisperos is slightly younger (6.7 ± 0.1 Ma). Epithermal mineralization at Zancudo is hosted in Arquía Complex metamorphic rocks.

The Queradona district contains five porphyry centers emplaced in the Combia Formation between 8.0 and 7.4 Ma. The 566 Mt @ 0.64% Cu, 0.31 g/t Au Nuevo Chaquiro Cu-Au-(Mo) porphyry, located at the center of the district, was discovered at a depth of 250 m below surface (Bartos et al. 2017). Minor intermediate-sulfidation epithermal Au mineralization crops out above the porphyry Cu mineralization.

Caramanta includes a cluster of porphyry Au-Cu prospects also intruding the Combia Formation, some 30 km SE of Nuevo Chaquiro. Mineralization is centered on granodiorite porphyries dated at 7.2 - 7.1 Ma, spatially and temporally related to the eastern margin of the Tamesis Stock (Fig. 1; 7.8 - 7.2 Ma). Intermediate-sulfidation epithermal mineralization associated with E-trending structures cutting the Tamesis Stock 500 m to the west, yielded an age of ~8.2 Ma.

About 2.3 Moz Au have been produced at Marmato making it the most important gold producer in the MCB. Published reserves of 14.4 Moz Au and 90 Moz Ag are the largest within the MCB. The mineralization style is low- to intermediate-sulfidation epithermal, but Au-rich porphyry has also been identified at depth. 6.9 to 6.0 Ma diorite-granodiorite porphyries intruding the Arquía complex, host mineralization. Sericite related to epithermal mineralization yielded a K-Ar age of 5.6 Ma (Tassinari et al. 2008).

The Quinchía District includes several porphyry Au prospects including La Cumbre (2.5 Moz Au, 145 t Cu), Tesorito and Dosquebradas, as well as the Miraflores low-sulfidation epithermal breccia deposit (1.82 Moz Au). Age constraints range from 8.9 to 8.0 for granodiorite porphyries and 7.7 Ma for molybdenite at Dosquebradas.

At Tesorito, a ~9.1 Ma early phenocrystic garnet-bearing granodiorite porphyry hosts mineralization (Bissig et al. 2017).

El Poma, a porphyry Au (-Cu) prospect, recently discovered 40 km to the south of the Quinchía district, extends the southern end of the historically known Middle Cauca belt. Granodiorite porphyries at El Poma range in age from ~11.75 to 8.8 Ma, the latter likely representing the mineralization age. A post-mineral plagioclase porphyry dyke was dated at 4.65 ± 0.2 Ma. Extensive volcanic deposits associated with the presently active arc partially cover prospective rock units to the south of El Poma, indicating under cover exploration potential in the southern MCB.

Additional ore deposits of similar age to those of the MCB, but located outside the geological limits of the Romeral melange, include La Colosa and Buriticá (Fig. 1).

The 28.5 Moz La Colosa porphyry Au deposit, located some 50 km SE of El Poma, contains the largest gold resource in Colombia. Mineralization was dated at 8.43 Ma (Re/Os, molybdenite; Leal-Mejía 2011). It is hosted by early Paleozoic carbonaceous schists of the Cajamarca-Valdivia terrane and is not considered part of the MCB.

Buriticá (3.7 Moz Au, 10.7 Moz Ag) is a high-grade intermediate-sulfidation epithermal Au deposit located some 75 km N of Titiribí. It is hosted by 7.41 ± 0.4 Ma granodiorite porphyry which intrudes early-mid Cretaceous Cañas Gordas terrane oceanic sedimentary and volcanic rocks. The age of hydrothermal sericite associated with mineralization is within error of the host-rock age (Lesage et al. 2013).

3 Temporal and spatial trends

The oldest igneous rocks of the MCB (~12 - 11 Ma), are represented by felsic crystal tuffs of the Combia Formation and garnet-bearing granodiorite porphyries, both located in the south, at El Poma. Sericite, albeit of uncertain relationship to gold mineralization, was also dated at that age. Coeval 12 to 10 Ma plutons were documented in the Cauca belt. After 10 Ma, magmatism and porphyry mineralization migrated northward along the MCB to reach the Titiribí district by 7.5 Ma. After 7.3 Ma, magmatic activity and mineralization returned to the central part of the belt (e.g. Caramanta, Nuevo Chaquiro), and locally, an eastward-younging trend is recognized. The easterly-most deposit, Marmato, was emplaced after 6.8 Ma. Epithermal Au mineralization was formed shortly after porphyry mineralization in the Titiribí and Quinchía districts, but may be as old as, or older than, porphyry mineralization in the El Poma and Caramanta districts.

4 Igneous geochemistry

There is a general trend towards increasing SiO₂ content of porphyries and volcaniclastic rocks of the Combia Formation from N to S within the MCB (Fig. 2). Igneous
Figure 2. Lithogeochemistry of magmatic rocks of the Middle Cauca Belt. Abbreviations: wk weakly, med medium, sho shoshonite, Kspar K-feldspar.
rocks of most porphyry districts and age-equivalent porphyries unrelated to known mineralization exhibit “adakite-like” geochemical signatures and fall into the “porphyry fertile” compositions using Sr/Y and V/Sc diagrams (Loucks 2014). However, igneous rocks from Titiribí have a subtle but distinctly more alkaline character when compared to other districts to the South (Fig. 2). Igneous rocks from the Buriticá epithermal deposit, some 75 km N of Titiribí but located in the Cañas Gordas Terrane of the Chocó arc, have a similarly alkali affinity. Unlike the other porphyry districts in the MCB, but similar to other alkaline porphyry deposits elsewhere (Bissig et al. 2014), many igneous rocks from Titiribí and Buriticá do not fall in the porphyry fertile fields.

5 Discussion

The MCB and nearby Miocene porphyry-related ore deposits are generally gold-rich. The high Au/Cu ratios are herein largely attributed to shallow emplacement of porphyry systems (cf. Murakami et al. 2010). This can be inferred from the temporal relationship of porphyry stocks with only slightly older host-volcanic rocks, as well as from the proximity and similar age of epithermal and porphyry mineralization. Comparatively high Cu content is only reported from the Nuevo Chaqueiro deposit where 810m @ 1.65% Cu and 0.78g/t Au was intersected starting at 400 m depth (CHA-50 drillhole, AngloGold Ashanti 2014). Based on whole-rock geochemical and mineralogical characteristics (Bissig et al. 2017), mineralizing porphyries are water-rich and oxidized, and thus similar to other porphyry provinces around the world (Loucks 2014). A notable exception is the Titiribí district where the Au-rich nature of mineralization can potentially be attributed to the mildly alkalic nature of magmatism, as widely documented for other alkalic porphyry deposits (Lang et al. 1995; Bissig and Cooke 2014).

In contrast to the MCB porphyries, the Cu-poor but Au-rich nature of the giant La Colosa porphyry deposit is best explained by the relatively reduced nature of the causative intrusive rocks. The latter are hosted in strongly reducing Paleozoic carbonaceous schists of the Cajamarca-Valdivia terrane. La Colosa can best be classified as a reduced, gold-rich porphyry system within the clan of reduced terrane. La Colosa can best be classified as a reduced, Paleozoic carbonaceous schists of the Cajamarca – Valdivia rich nature of the giant La Colosa porphyry deposit is best compared to other districts to the South (Fig. 2).

Acknowledgements

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References


Abstract. At the Cantung mine; a mineralized zone which contains high concentrations of both gold and tungsten was identified from a drill hole underground at the contact between the Swiss Cheese (S.C.L.) and the Ore Limestones (O.L). The first part of this mineralized zone (beginning in the S.C.L.) consists of a massive sulfide (mainly pyrrhotite) rich lens with pyroxene-pyrrhotite and amphibole-pyrrhotite assemblages that transitions into a hydrous skarn (amphibole-biotite-muscovite) with very little to no sulfides. The gold and tungsten grades are highest within the hydrous skarn without the massive pyrrhotite. Gold is present as electrum (~30 wt% Ag) together with an assemblage with mainly native bismuth as well as bismuth tellurides and selenides. The textures exhibited by the gold and bismuth bearing phases are indicative of having been formed as low-temperature melts which were formed in equilibrium with the minerals containing Fe$^{2+}$ (biotite, allanite, pyrrhotite). Several studies have shown the ability for local reducing conditions to induce further precipitation of these low temperature melts directly from hydrothermal fluids. These melts can sequester a variety of metals from a fluid which is undersaturated with respect to those metals.

1 Introduction

The Cantung W-Cu mine is located within the Canadian Cordilleran in the Northwest Territories approximately 400 km to the northeast of Yellowknife, Yukon Territory. It is part of a suite of deposits known as the Tombstone-Tungsten Belt; a group of Mid-Cretaceous felsic intrusions which intruded into the ancient North American continental margin, resulting in the formation of a variety of different magmatic-hydrothermal systems (Hart et al. 2004; Lang 2000). The deposits in this belt all lie to the east of and form a trend subparallel to the major transverse terrane-bounding faults in the area known as the Tintina Fault (Mortensen and Jilson 1985).

A similar group of intrusion-related deposits known as the Tintina Gold Belt was also defined based on their spatial and temporal relations to these Middle Cretaceous granitoids (Hart et al. 2000). It is important to note that the Tintina Gold Belt has a similar trend to that of the Tombstone-Tungsten Belt. Most of the deposits of the Tintina Gold Belt are to the west of the Tintina Fault; however, some of the deposits (e.g. Dublin Gulch) do occur to the east of the Tintina Fault (Maloof et al. 2001).

The deposit is genetically associated with a peraluminous biotite monzogranite which intruded into Lower Cambrian limestones from the Selwyn Basin. This sequence of limestones and argillites form an overturned recumbent anticline at the location of the mine. Initial hydrothermal activity occurred at 450 to 500 °C and resulted in the virtually simultaneous development of the reduced anhydrous and hydrous skarns facies (garnet-pyroxene, pyroxene-pyrrhotite, amphibole-pyrrhotite, and biotite-pyrrhotite) (Mathieson and Clark, 1984). This zoning of the various skarn facies was believed to represent steep gradients in $\frac{dC_{Fe^{2+}}}{dA_{introduced~components}}$ in the fluid. Fluid inclusion data also suggested that the formation of the strongly mineralized hydrous skarn persisted down to temperatures of 270 °C, locally overprinting some earlier formed skarns.

2 Gold at Cantung

2.1 Previous research

Gold mineralization at Cantung was not identified until much later in the history of the mine development. Part of the reason the gold mineralization was not identified earlier is due to the “invisible” nature of the gold mineralization. Previous studies aimed at better understanding the gold mineralization at Cantung were conducted, but were unable to identify the phase or phases that host the gold mineralization. Elevated gold concentrations were identified using whole-rock geochemical analyses and their correlation with
other elements were defined. A strong positive correlation between gold and bismuth concentrations was observed \( (r^* = 0.76) \) (Fig. 1) (Palmer 2013). These whole-rock correlations were helpful in identifying the minerals which might be associated with gold mineralization. SEM-BSE imaging and EDS analyses were used to characterize the Bi-Te-Se-S-Ag bearing assemblages. Using in situ LA ICP-MS analyses; raster profiles across these assemblages of interest was conducted in attempt to locate any of the “invisible” gold which was potentially associated with these assemblages. One of these raster profiles contained highly elevated gold concentration (800-1000 ppm) which somewhat correlated with silver peaks and was near minerals which contained Bi and Te (Palmer 2013). Despite the fact that gold was detected using LA ICP-MS analyses; no positive confirmation was made as to the phases which host these elevated concentrations of gold. The author suggested that a possible reason for this was due to the fact that the gold was present as nano-inclusions along the grain boundaries between the bismuth tellurides and the silicates which surround them.

Figures 1. Log-log graphs of the concentration of elements with the highest positive Spearman Rank correlation coefficient value with Au. a Bi versus Au, with \( r^* = 0.76 \); b Ag versus Au, with \( r^* = 0.70 \); c Cu versus Au, with \( r^* = 0.64 \); and d Fe versus Au, with \( r^* = 0.64 \) (Taken from Palmer, 2013).

3 Current research

Drill hole U2083 began at the center of the anticline in the Older Argillite and was drilled sub horizontally towards the outside of the anticline. At approximately 316 feet a massive sulfide lens (pyroxene-pyrrhotite and amphibole-pyrrhotite) was intersected with ore grade scheelite mineralization as well as high copper and gold concentrations. The massive sulfide-rich skarn eventually transitioned into hydrous skarn (amphibole-biotite-muscovite) with locally minor pyrrhotite; this hydrous skarn contained very high Au and WO\(_3\) % concentrations. The orebody eventually ends in unaltered Ore Limestone. Due to the elevates gold and tungsten concentrations present in this drill hole it presents a good opportunity to study the distribution of gold throughout the various skarn facies in one of the main mineralized zones.

Polished thin sections were prepared from the samples throughout the ore body (also known as the “hanging wall” ore body) in hole U2083. The samples which contained the highest gold grades were characterized using reflected and transmitted light microscopy. Gold was identified in textural equilibrium with the native bismuth (Fig. 2). The native bismuth was present along with an assemblage containing bismuth tellurides and selenides. Scanning electron microscopy was used to quantify the major and minor element chemistry of the gold, bismuth, and bismuth tellurides (Fig. 3.). The gold contains an average of approximately 30% silver.

Figure 2. Reflected light photomicrograph of sample U2083-#205362-B2 showing gold in contact with native bismuth.
The textures exhibited by the gold and native bismuth are similar to those described by other authors, suggesting they formed as low-temperature polymetallic melts (Cepedal et al. 2006; Cook and Ciobanu 2004). The ability of bismuth melts to precipitate directly from hydrothermal fluids and their capacity to sequester gold from fluids which are undersaturated with respect to gold is now known (Tooth et al. 2011). Under reducing conditions bismuth melt can precipitate from a hydrothermal fluid more easily. The equilibrium concentration of gold in a bismuth melt is also greater under reduced conditions and increases with an increase in pH (Tooth et al. 2008).

Based upon the conditions inferred from the previous fluid inclusion work; chloride complexes were likely the main gold transporting species in the hydrothermal fluids (Mathieson and Clark, 1984; Williams-Jones et al. 2009). The abundance of Fe-bearing phases as well as the coexistence of native bismuth in textural equilibrium with both chalcopyrite and sphalerite suggest that metal transport through chloride complexes was active. The mineral assemblage present within the gold-rich zone suggests that it formed under relatively reduced conditions (pyrrhotite and allanite are both present). These reduced conditions are conducive to the precipitation of low-temperature bismuth melts and the scavenging of any gold from that fluid by those melts. The neutralization of generally acidic orthomagmatic fluids through reaction with limestone would also increase the solubility of gold within the bismuth melts. The textures present within scheelite are indicative of dissolution-reprecipitation reactions active within this mineralized skarn facies and the precipitation of bismuth and gold is directly associated with these reactions.

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I would like to acknowledge my mentor; without him, none of which would be possible. I would like to acknowledge Mr. A. Gebre for his knowledge and insight into the processes active within these systems. I would also like to acknowledge my family for supporting me through the toughest parts of my life.

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New insights into the formation of multiples mineralization events in the San Dimas District, Mexico

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Abstract. The San Dimas district is a reference world-class silver-gold epithermal low sulfidation deposit. We present a re-evaluation of this district based on new U/Pb ages and field observation of mineralization styles. We identify a Late Cretaceous volcanic succession of the Lower Volcanic Complex correlative with the Tarahumara formation of southern Sonora, which hosts subvolcanic Au-rich felsic mineralized bodies comparable to the Cu-Au porphyries of Sonora and Sinaloa. This succession is covered by intermediate lavas with hypabyssal intrusions (productive andesite) and is intruded by a Eocene batholith and several dike swarms. The final magmatic activity consists of silicic ignimbrites and less basaltic lava flows of Oligocene and early Miocene age.

The main epithermal mineralization consists of two kind of veins, silver-gold and gold types, possibly related to different magmatic sources. Our study shows that there is a genetic link between low sulfidation silver-gold veins and felsic intrusion with porphyry mineralization, which were recycled by the Eocene batholithic intrusion.

1 Introduction

Epithermal ore deposits are formed in the shallow portions of hydrothermal systems, at less than 2 km depth. The hydrothermal activity is related to contemporaneous igneous activity and the ore is typically hosted by volcanic rocks (Hedenquist & Arribas, 1999).

The San Dimas district is a world class silver-gold epithermal deposit located in the Sierra Madre Occidental (SMO) of western Mexico Fig. 1, which has been mined since 1700 (Clarke, 1986). The mining district contains more than 200 known Au-Ag veins, located in five blocks, which are separated by major NNW-striking normal faults (West Block, Sinaloa Graben, Central Block, Tayoltita Block and Arana Block). Au-Ag veins are found from the relative basement (Piaxtla batholith) to the erosional unconformity at the base of the Oligocene volcanic groups (Henshaw, 1953).

Despite San Dimas district being a world class deposit and a world reference for low sulfidation Au-Ag epithermal veins, a modern metallogenic model is lacking. The current model is based on the study of a limited portion of the district and on K-Ar ages that are not always reliable given the widespread alteration of the region (Enriquez y Rivera, 2001).

In this study, we present a revision of the local geology, supported by new U-Pb geochronology. We also describe the different mineralization styles, alteration assemblages, and mineralization textures observed in the mines. This allows to obtain a better understanding of mineralization episodes and characterization of ore-forming fluids from the deep magmatic sources, passing through hypabissal to shallow epithermal environment.

2 Regional tectonic and magmatic setting

The SMO includes Late Cretaceous to early Miocene rocks formed during two main periods of magmatic activity (Ferrari et al., 2017). The first period, concurrent with the Laramide orogeny, is made of dominantly intermediate batholiths and their volcanic counterpart, associated with a normal supra-subduction magmatic arc, active between ~100 and 45 Ma (Gastil, 1975; McDowell et al., 2001; Henry et al., 2003).

These rocks were traditionally named Lover Volcanic Complex (LVC; McDowell and Keitzer, 1977). After a transition period that lasted until the late Eocene, volcanism became dominated by silicic ignimbrites with less basaltic lavas, building one of the largest silicic volcanic provinces on Earth (Ferrari et al., 2007; Bryan y Ferrari, 2013). This second episode is concurrent with lithospheric extension of the Mexican Basin and Range that represents the initiation of the Gulf of California rift (Ferrari et al., 2017).

Two episodes of ignimbrite flare up are recognized in the SMO: at ~35-29 Ma along the entire province and at 24-20 Ma in its southern half. These rocks were traditionally called Upper Volcanic Supergroup (UVS; McDowell and Keitzer, 1977). The main SMO magmatic episodes are separated by erosional or angular
unconformities and continental deposits (Ferrari et al., 2002, 2007).

3 New geochronology and revision of the local stratigraphy

We have re-dated the whole local stratigraphic column using the LA-ICP-MS U-Pb method on zircon to avoid any uncertainty related to rock alteration. In our geological re-evaluation the stratigraphic column is divided in four groups: 1) the ignimbritic to porphyritic lavas of the LVC, 2) the intermediate lavas and hypabyssal intrusions locally named “productive andesite” and the coeval Las Palmas continental sedimentary deposit, 3) the Piaxtla batholithic intrusion, and 4) the Oligocene and early Miocene silicic ignimbrites and basaltic lavas, locally named “capping”, which belong to the UVC.

The LVC is sub-divided in three units composed of volcanic and subvolcanic rocks of rhyolitic to intermediate composition. We obtained U-Pb age of 76.6±0.9 Ma for the Socavón lower unit, 67.9±0.72 Ma for the Buelna intermediate unit, and 68.8±2.7 Ma for the Portal upper unit.

The productive andesite is dominated by andesitic lava flows intruded by porphyritic hypabyssal bodies of similar composition. Due to the low zirconium concentration in these kind of rocks no zircon crystal were found. However, the emplacement of these rocks was roughly concurrent with the Las Palmas continental conglomerate and sandstone, for which we obtained a maximum age of deposition of 43.1±1.2 Ma) with detrital zircon peaks of ~64 Ma and ~55 Ma.

The LVC and the productive andesite group are intruded by numerous rhyolitic or basaltic dyke swarms (Santa Rita and Bolaños dykes), subvolcanic felsic to intermediate bodies (Araña diorite) and several granitic to granodioritic bodies, collectively forming the Piaxtla batholith. The Santa Rita and Bolaños dikes both yielded U-Pb age of ca. 44 Ma. The Piaxtla batholith yielded similar ages of 49.0±0.22 Ma and 45.3±0.49 Ma.

An erosional unconformity separates the above rocks from the UVS, for which we obtained ages of 31.5±0.36 Ma for the lowermost ignimbrite and basaltic lavas.

4 New insights into alterations and mineralization style

The San Dimas mineralized district has been described as a long lived Au-Ag epithermal veins system (from ~38 to ~32 Ma; K-Ar on adularia and sercite; Enriquez y Rivera, 2001) with local petrographic and metals grade variations (Henshaw, 1953; Randall, 1971; Smith & Hall 1974; Henry, 1975; Nemeth, 1976; Clarke, 1986; Henry y Fredrikson, 1987; Clarke & Tittley, 1988). The vein thickness varies from less than 1 cm up to about 8 m, being ca. 1.5-2.0 m on average. The mineralization and alteration is pervasive in the LVC, the productive andesite group and its intrusive subvolcanic bodies (Araña), and the continental sedimentary sequence (Las Palmas).

Base on our details observations, the Au-Ag epithermal veins could be divided in two main groups according to their alteration type and structural control. (1) The main group is represented by veins with high Ag/Au ratio (2:1) that occupy east-west trending sigmoid fractures. These kind of veins are associated with quartz + rodenosite + adularia ± chlorite ± epidote ± calcite ± illite and traces of sercite. Pyrite + chalcopyrite + silver sulfosalts + galena ± sphalerite, are the main metallic minerals. (2) The second group is characterized by high Au/Ag (1:2), with chlorite + sercite + quartz + albite ± illite as a typical alteration assemblage. The sulphur mineralization is represented by pyrite + chalcopyrite ± sulfosalts in pots or weakly bands associated with gold mineralization. Its preferred orientation is north-northwest-south-southeast and they pinch and swell and commonly exhibit bifurcation, horse-tailing and sigmoidal structures.

Within the LVC, pervasively potassic alteration (secondary biotite) with intermediate to weakly intensity overprinted by sodic-calcic alteration (albite + actinolite ±epidote) is present in pots and halos around pyrite and chalcopyrite veinlets. This alteration is spatially associated with felsic subvolcanic intrusion that we dated at 73.9±1.6 Ma, characterized by fine disseminated pyrite, fine pyrite and chalcopyrite, and the iron sulfo-salts in pots. They are exposed in the Sinaloa Graben and the West Block.

5 Geologic and metallogenic evolution of San Dimas

Our new geochronologic data allow to identify for the first time the Late Cretaceous LVC at San Dimas, which correlate with the Tarahumara formation described in southern Sonora (Wilson y Rocha, 1949). In addition, at San Dimas the LVC is characterized by subvolcanic, Au-rich mineralized bodies dated at 73.9±1.6 Ma, which are comparable with the Cu-Au porphries described along the Sonora and Sinaloa coast (Barton et al., 1995) emplaced during the final stage of the Laramide Orogeny.

The productive andesite was likely emplaced in a transitional period (from ~60 to 48 Ma) partly concurrent with the intrusion of granitoids and subvolcanic bodies forming the Piaxtla batholith (from ~49 to 44 Ma). The top of these granitoids intrusions reach the productive andesite and locally assimilated the LVC subvolcanic Au-rich mineralized bodies.

A major extensional phase began in Early Oligocene, reactivating north-northwest structures and producing large scale normal faults that expose part of the veins. Large volume of rhyolitic ignimbrites and lavas, and less mafic lavas were emplaced at 32-29 and 24-20 Ma sealing the mineralized stratigraphic column.
Base on the new U-Pb ages of the stratigraphic column and our detail vein characterization, we propose to reinterpret the wide distribution of the K-Ar mineralization ages from ~38 to 32 Ma (Enriquez y Rivera, 2001) in two telescoped epithermal mineralization events. The older K-Ar ages (~38-34 Ma) correspond to the high Ag/Au ratio vein group. It is chronologically related to the end of intrusive cycle responsible for assembly of the Piaxtla batholith. The continuous intrusion of hydrated magma rich in tourmaline, hornblende, and muscovite for at least 5 Ma may have been able inducing and sustaining a Ag-rich hydrothermal cell. The duration of epithermal event apparently indicated by the K-Ar datings is probably overestimated because of adularia resetting by younger epithermal event. The younger K-Ar ages (~32 Ma) correspond to the high Au/Ag ratio vein group. These Au veins are found in proximity to Early Oligocene rhyolitic domes (~31-29 Ma) emplaced on north-northwest striking normal faults. This last episode of mineralization seems to have a regional extent that need to be assessed in more detail.

6 Conclusions

Based on our new geochronological, geological and mineralization studies at San Dimas district, we can conclude that:
- The style and nature of the different kind of mineralization are primarily controlled by the composition of the magma source.
- Low sulfidation epithermal Ag-Au veins may be critically linked to the input of Eocene magmatic fluids of the final intrusive stages of the Piaxtla batholith, accompanying the onset of the Basin and Range extension.
- The high Ag grades may be associated to hydrothermal fluids generated by continental magmatism with adakitic signature, represented by intrusives bodies with phyllic alteration styles. The low Au grades could be the result of the recycling produced by the Piaxtla intrusion into the Late Cretaceous porphyry Au mineralization. This is supported by the presence of porphyry clasts with potassic alteration and vitreous quartz veins into the epithermal breccias.
- Low sulfidation epithermal Au veins formed during silicic and bimodal magmatism of the Oligocene, associated with the initial opening of Gulf of California.

The San Dimas Ag-Au world class district is the result of overlapping of a porphyry and two low sulfidation epithermal events.

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References


First evidence of phreatomagmatic breccia at the Late Cretaceous Madneuli polymetallic deposit, Bolnisi district, Lesser Caucasus, Georgia

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Abstract. The producing Late Cretaceous Madneuli polymetallic deposit is a major deposit in the Bolnisi district, Lesser Caucasus, Georgia. It is interpreted as a felsic maar – diatreme system with rhyodacite dome, located out of the crater rim. The lower part of the tuff ring consist of a non-bedded pyroclastic sequence, where ore bodies are located. Several volcanic events were followed by the phreatomagmatic eruption, formation of volcanic domes, rhyodacitic extrusion and ignimbrites cropping out in the open pit, accompanied by hydrothermal fluid circulation and different types of mineralization. Detailed facies-oriented analyses allow us to suggest a shallow marine depositional environment for the host rocks of the Madneuli deposit. Matrix- to clast-supported phreatomagmatic breccia is described for the first time in the Madneuli open pit. According to SEM mineralogical studies of the breccia, mineralization is distributed differently in the matrix than in rock clasts, which enabled us to provide different possible models of formation of phretomagmatic breccias in the open pit and different stage of mineralization.

1 Introduction

The Madneuli deposit in the Bolnisi district belongs to the Somkheto-Karabakh island arc of the Lesser Caucasus (Kekelia et al. 1993; Moritz et al. 2016), which extends toward the west in the Eastern Pontides in Turkey (Fig. 1a). Both metallogenic provinces host various prospects and different type of ore deposits (Eguboglu et al. 2014). Therefore, it is extremely important to understand the distribution and genetic models of ore deposits in the Bolnisi district to improve regional mineral exploration in the future.

Numerous ore deposits are known in the Bolnisi district, which is associated with Late Cretaceous explosive volcanism at different stratigraphic levels. Due to an intensive exploration program in Georgia, new ore occurrences have been investigated, including Bnelikhevi and Kvemo Bolnisi. According to recent published data for Kvemo Bolnisi, the resources are 947,000 tonnes at an average grade of 0.93 copper (Cu) and 0.15 g/t gold (Au) (https://www.caesarsreport.com/category/reports/). It is believed that there is a laterally larger mineralized system at depth similar to the Madneuli Cu-Au deposit, located only 7 km away from the Kvemo Bolnisi system. The origin of the Madneuli deposit is still controversial and several models were proposed by previous studies: volcanicogenic massive sulphide (Little et al. 2007), porphyry-epithermal (Gugushvili et al. 2001), transitional volcanicogenic massive sulfide-epithermal (Migineishvili 2002) and transitional hydrothermal system with a magmatic input formed in a submarine environment (Gialli 2013).

Our facies-oriented investigation in the Madneuli open pit was based on physical volcanology and sedimentary basin analyses, and was applied for the first time in this region, allowing us to interpret several facies types (Popkhadze 2012, 2014; Popkhadze et al. 2014). As the Madneuli deposit is still operating, it is possible to study it at different operating levels of the open pit. Our investigations have revealed a phreatomagmatic breccia in the open pit allowing us to speculate about its formation and timing relationships with the mineralization at Madneuli. Preliminary observations of the phreatomagmatic breccia are reported in this paper.

2 Regional geology and stratigraphy

The Bolnisi ore district is part of the Artvin-Bolnisi belt, in southern Georgia and has a border zone with Armenia (Fig. 1a). It is the north-eastern extremity of the Somkheto-Karabakh arc system, which is known as the Artvin-Bolnisi zone in Georgia (Yilmaz et al. 2000) (Fig. 1b). The Artvin-Bolnisi zone is bordered to the north along the South-eastern Black Sea by the Adjara-Trialeti zone and the Imbricated Baiburt-Karabakh unit to the South (interpreted as an Upper Cretaceous fore-arc), part of the North Anatolian-Lesser Caucasus Suture (Fig. 1a). The Artvin-Bolnisi zone comprises a Hercynian basement, which consists of Precambrian and Paleozoic granite, gneiss and plagiogranite, cropping out in the Khrami and Loki massifs, overlain by Carboniferous volcano-
sedimentary rocks. This is followed by shallow marine sedimentary rocks, alternating with Middle Jurassic to Early Cretaceous volcaniclastic rocks (Yilmaz et al. 2000). Within the Artvin-Bolnisi zone, the 3000-4000 m thick Late Cretaceous section is dominated by calc-alkaline basalt, andesite, dacite and rhyolite (lava, and pyroclastic rocks). Volcanic rocks were belonging shallow marine to subaerial settings.

The ore deposits in the Bolnisi district are hosted by Late Cretaceous volcanic and volcano-sedimentary rocks, which are subdivided into six volcanogenic suites; they are Cenomanian to Campanian and Maastrichtian in age (Apkhazava 1988). Based on lithological correlations, the age of the host rocks of the Madneuli deposit, named the Mashavera suite, have been assigned to late Turonian-early Santonian formations. According to nannoplankton fossil determinations, the age is Campanian (Migineishvili et al. 2010). Recent TIMS U-Pb dating of zircons from mafic dikes located in the southeastern part of the Madneuli open pit and crosscutting the rhyodacitic extrusion yielded ages of 87-86 Ma (Moritz et al. 2016). In conclusion, according to the TIMS U-Pb dating of zircons the age therefore supports a Coniacian-Santonian age and is consistent with radiolaria ages obtained for the host rocks of the Madneuli deposit (Dumitrica 2014; Popkhadze 2014; Popkhadze et al. 2014).

3 Phreatomagmatic breccia host rocks within the Madneuli open pit

3.1 Host rock architecture of the Madneuli deposit

The host rocks of the Madneuli deposit are composed of stratigraphically lower volcano-sedimentary (VS) and upper volcanic sequences, which consist of different facies types (Popkhadze 2014; Popkhadze et al. 2014). The VS bedded sequence is predominant in the open pit and represented by tuff ring and post eruptive crater infill facies in the maar - diatreme system of the Madneuli deposit. Volcanic facies mostly is connecting with formation of out of crater lobe hyaloclastites (two type) creating a dome structure with peperites in the contact with tuff ring VS sequence. Rhyodacite extrusion and ignimbrites are cropping out in the uppermost part in the open pit. The relatively complete section of tuff ring is best exposed in the eastern flank of the Madneuli deposit, thickness is about 80-100m. It consists of two stratigraphic units: lower non-bedded and upper bedded separated by an undulating contact. Lower unit (which begins from the bottom of the mined open pit nowadays) represented my massive, non-bedded pyroclastic rocks – ash rich, reversely graded pumice-fiamme breccias. This unit is strongly silicified and mineralized. The upper part is an indurate bedded unit, where the vesiculated tuff is exposed within a sequence of base surge and ash-fall deposits. This bedded VS sequence in the open pit hosts different styles of mineralization, including a deep, vertical stockwork and breccia composed of veins and matrix with a quartz - pyrite - chalcopyrite assemblage with enargite, covellite and sphalerite, passing upward into quartz – barite – sphalerite – galena – pyrite subvertical veins, and into stratiform massive sulfide ore bodies with sphalerite, galena, chalcopyrite, pyrite and tennantite - tetrahedrite, and sandstone lenses cemented by barite in the uppermost levels (Gugushvili et al., 2001; Migineishvili, 2002, Gialli, 2013). In addition to these two facies sequences, a granodioritic- to quartz dioritic porphyry intrusion was intersected by drilling at a depth of 800 to 900 m beneath Madneuli.

3.2 Phreatomagmatic breccia

A phreatomagmatic breccia was recognized for the first time in the Madneuli open pit and coincides with a SE-
oriented major fold (dip azimuth 140°) in the eastern flank of the Madneuli open pit. The breccia is mostly matrix-supported and consists of juvenile clasts and a mixture of comminuted clasts of fine-grained tuff from the host rocks (Fig. 2a).

The breccia contains a chaotic mixture of clast types. The clast shapes range from angular to well rounded, but those with a more rounded shape predominate. Open spaces is also characteristic in the matrix. In the eastern flank, it is possible to observe subhorizontal layers of a breccia, representing the stratigraphic sequence of the host rocks, which was affected by the breccia (Fig. 2b). In the open pit, the contact of phreatomagmatic breccia with the host rocks is sharp, locally underlined by ring faults (Sillitoe 1985; Sillitoe et al. 1985; Baker et al. 1986). Fragments of wood or lacustrine sedimentary were not identified in the breccia.

The breccia is an endogenous (non-eruptive) phreatomagmatic breccia (Lawless et al. 1990), as it does not extend to the uppermost horizons of the host stratigraphic sequence. This may be evidenced also by the fact, that bedded texture was recognized within the breccia in the eastern part of the open pit (Fig. 2c). Such bedded texture may caused by the gravity of the above located VS sequence and possible water column. Well preserved radiolarias were described in petrographic observations from the matrix of the breccia.

Mineralization is hosted by the breccia units. Mineralization has several models at occurrence the open pit. It occurs locally as veins, in the breccia matrix and also localized the open spaces and also licalized in some clasts. This is confirmed by SEM observations of the different clasts and matrix of the phreatomagmatic breccia from the eastern part of the Madneuli deposit. The irregularity and discontinuity of some sulfide-bearing post brecciation mineralized veinlets in the eastern flank of the Madneuli deposit that crosscut the breccia (including clasts and matrix) (Fig. 2d) indicates that they were emplaced while the breccia was still poorly lithified and incompetent (Sillitoe et al. 1985).

![Figure 2. Phreatomagmatic breccia from the eastern part of the Madneuli open pit. a juvenile magma clast in the phreatomagmatic breccia. b lateral extension of the phreatomagmatic breccia within bedded host rocks. c bedded texture in the breccia. d postbrecciation mineralized veins in the eastern flank of the Madneuli deposit crosscut the entire breccias (including clasts and matrix). e block of previously formed breccia in the rebrecciated part of breccia. f the scanned thin section of phreatomagmatic breccia with minor milling to sub-angular fragments, evidence of rebrecciation.](image)

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![Figure 3. Simplified scheme for the formation of phreatomagmatic breccia in the Madneuli deposit a) first stage of formation: during the first stage formation of the non-eruptive, matrix-supported phreatomagmatic breccia, when intruding rhyodacitic magma interacts with water from the surface; b) Second stage of brecciation: breccias from the first stage can be rebrecciated and it can be incorporated in the form of clasts in the second stage of breccias.](image)
Several phreatomagmatic breccia generations can be recognized in the open pit. We have identified two types of breccias, because there are clasts with dimensions of 10s of decimetres from the first stage of breccia that have been incorporated into the second stage breccia Polyphase brecciation (Fig. 2e). Phreatomagmatic breccia facies has undergone minor milling sub-angular fragments with evidence of rebrecciation (Fig. 2f). There is selective and different style of mineralization in clasts. Several possible explanations for the observed relationship of brecciation and mineralization should be discussed (Fig. 3): during the first stage, there were two zones (mineralized and non-mineralized) in the Madneuli deposit. Below the mineralized zone, the hydrothermal fluid penetrated, which was associated with a porphyry intrusion recognized beneath the Madneuli deposit (Fig. 3a). During the second stage of brecciation (Fig. 3b), breccia was rebrecciated and incorporated in the form of clasts in the second stage polyphase breccia. Both breccia facies were affected by later stage fluids, which were accompanied by the formation of a volcanic dome.

3.3 Conclusions and recommendations

In conclusion, we can recognize at least two types of brecciation and connected mineralizing events at the felsic maar – diatreme system of the Madneuli. There is evidence of a shallow marine environment, and no evidence for a lacustrine sedimentary environment. So, it still remains open to question in what setting the maar was formed (subaerial or shallow marine setting). Juvenile fragments in the breccia provide evidence for a phreatomagmatic origin (Sillitoe 1985). Although brecciations are not directly related to mineralization (Lawless et al. 1990), phreatomagmatic breccia in the Madneuli deposit might be a prime candidate for selective mineralization. In terms of exploration, the extend of breccia can only be used empirically as a guide to location of ore.

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References

Late Cretaceous to Cenozoic subduction-, post-
subduction- and post-collision-related porphyry and
epithermal Au-Cu systems of the Anatolide-Tauride
metallogenic belt, Turkey

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Abstract. The Anatolide-Tauride block (ATB) of southern central Turkey has experienced two successive orogenic cycles since the Mesozoic caused by the closure of Neotethys oceanic basins between the Laurasia and Gondwana continents. The complex tectonic evolution of the ATB has been accompanied by fertile magmatism and associated porphyry and epithermal mineralization in various tectonic settings that include arc, back-arc, post-
subduction slab tear and break-off, and post-collisional extension. Magmatism peaks in the Late Cretaceous (87 - 65 Ma), early Eocene (53 - 41 Ma), Oligocene (26 - 25 Ma), Miocene (22 - 9 Ma) and Pliocene-Quaternary (< 6 Ma). Porphyry and epithermal gold mineralization forms in 16 mineral districts, dominantly generated in response to early Eocene (52 - 42 Ma) and Oligo-Pliocene (26 - 3 Ma) magmatism. Magma fertility is primarily controlled by the degree of alkalinity that increases due to the upwelling of hot asthenosphere into the subduction-modified mantle wedge after subduction and collision. The fertility window in ATB was brief (< 10 m.y.) and occurred at the early stage of each magmatic episode. This contrasts with conventional models for global arc-related porphyry and epithermal provinces that traditionally emphasize long-lived subduction zone, crustal thickening and magmatic maturation as optimal first-order factors for the formation of porphyry copper systems.

1 Introduction

Tectono-magmatic processes controlling post-subduction and post-collisional magmas as causative hosts for Au-Cu porphyry and epithermal mineralization in space and time are less constrained than those controlling petrogenesis in classical subduction-related arc setting (Richards 2009, 2015). The closure of Neotethyan oceanic basins along the Anatolide-Tauride orogenic belt of southern central Turkey produced widespread subduction-, post-subduction- and post-collision-related magmatism since the Late Cretaceous. These magmas resulted in the formation of numerous significant porphyry- and epithermal-style deposits. The temporal, spatial and metal distribution of these deposits and similar prospects is controlled by geological and tectonic factors that remains poorly understood despite recent efforts (e.g. İmer et al. 2013; Kuşcu et al. 2013; İmer et al. 2014; Baker et al. 2016). In this study, we provide new geochronological and lithogeochemical data from Anatolian magmatic units and associated Au-Cu mineralization produced in various tectonic settings including arc, slab tear and break-off, and post-orogenic extension, and evaluate magma fertility.

2 Tectono-magmatic setting

The Anatolian-Tauride block (ATB) of southern central Turkey is a Gondwana-derived micro-continent that collided into the southern Laurasia, now Eurasia, closing the northern Neotethys Ocean along the present Izmir-Ankara-Erzincan suture zone in the Late Cretaceous (Şengör and Yılmaz 1981; Fig. 1). This tectonic event produced Jurassic to Cretaceous arc-type magmatism in the Sakarya block followed by Eocene post-collisional magmatism emplacement in both the ATB and Sakarya blocks (Şengör et al. 1991; Yılmaz and Boztuğ 1996; Keskin et al. 2008). The northward convergence of the African and Arabian plates, south of the ATB, has been responsible for the second orogenic event since the Late Cretaceous that produced Late Cretaceous arc and Late Cretaceous to Eocene back-arc magmatism in the eastern ATB (e.g. Kuşcu et al. 2013; Fig. 1). The indentation of the Arabian promontory into the ATB has contributed to the break-off of the Arabian segment of the southern Neotethyan slab and its westward propagation to the Cyprus domain of the central ATB since the late Oligocene. Subsequently, a north-south slab tear developed between the Aegean and Cyprus ATB domains since the middle Miocene to accommodate the differential roll-back rates between the Aegean (fast) and Cyprus (slow) slabs (Jolivet et al. 2015). These successive orogenic episodes, caused by the closure of the northern and southern Neotethys Oceans since Jurassic, has produced widespread arc-, back-arc-, slab tear-, slab-break-off- and post-collision-related magmatism, spatially and temporally associated with porphyry and epithermal-style mineralization.
**Figure 1.** Tectonic-magmatic map of Turkey showing the location of the tectonic terranes (grey background), magmatic units (MTA, 2002), and mineral districts and provinces. Late Cenozoic ATB tectonic history is divided into three tectonic domains: Aegean, Cyprus and Arabian. Scale: 1:6,000,000; Projection: Lambert Conformal Conic; Datum: ED50.
3 Anatolian porphyry and epithermal Au-Cu systems

Anatolian mineral deposits occur in clusters. These can be grouped into districts that share similar geological, structural, metallogenic, tectonic, geochemical and geochronological features centered on key deposits. A total of 16 porphyry and epithermal districts occur within four newly defined mineral provinces (Fig. 1). The Late Cretaceous Baskil and Göksun districts consist of arc-related porphyry Cu-Au-Mo prospects that were emplaced along the Bitlis suture zone (Kuşcu et al. 2013). The Late Cretaceous Keban porphyry Cu-Mo prospect formed in the back-arc domain behind the arc-hosted Baskil district (Kuşcu et al. 2013). The Eocene porphyry Cu-Au and intermediate-sulfidation epithermal Au deposits, including Çöpler and Karakartal in the Erzincan and Malatya districts, formed during the regional extensional phase that followed the Late Cretaceous magmatic arc in eastern ATB (Imer et al., 2013). In contrast, the Eocene porphyry Cu-Mo prospects (e.g. Karapınar and Gelemiç) of the Bursa districts were emplaced in a post-orogenic extensional setting following the closure of the northern Neotethys Ocean in northwest ATB.

The roll-back of the southern Neotethyan slab in the Aegean domain has been responsible for the southwestward migration of the magmatic front (e.g. Dilek and Altunkaynak 2009) and associated Au mineralization. Aegean metallogeny in western ATB is characterized by early Miocene, low-sulfidation epithermal Au veins in the northerly Simav district (e.g. Red Rabbit deposit), porphyry (e.g. Pınarbaşı, Kışladağ and Afyon-Sandıklı) and low- to intermediate-sulfidation epithermal Au mineralization in the middle Miocene (e.g. Efemçukuru), east and west of the Menderes Massif, respectively, and late Miocene high-sulfidation epithermal systems in the southerly Bodrum district (Fig. 1).

Slab break-off-related magmatism that initiated after the indentation of the Arabian platform into ATB in the Oligocene produced late Oligocene to early Miocene porphyry and epithermal Au-Cu systems such as the Hasançelebi high-sulfidation epithermal Au-Ag prospects, and the Tunceli (e.g. Cevizlidere deposit) and Ağrı porphyry Cu-Au districts (e.g. Taşkapı and Taşçıay prospects). The westward migration of fertile, slab break-off-related magmatism produced mineralized high-sulfidation Au-Ag-Cu systems in the Central Tauride Province such as Doğanbey, İnlice (Konya district), Altunhisar (Niğde district) and Öksüt (Kayseri district; Fig. 1).

4 Timing of magmatism and associated Au-Cu mineralization

New U-Pb and compiled geochronological data integrated with geological information from along the Anatolide-Tauride metallogenic belt reveal that widespread subduction to post-collisional ATB magmatism occurred in five episodes since the Late Cretaceous during: 1) Late Cretaceous (87 - 65 Ma), 2) early Eocene (53 - 41 Ma), 3) Oligocene (26 - 25 Ma), 4) Miocene (22 - 9 Ma) and 5) Pliocene-Quaternary (< 6 Ma).

The Eocene and Miocene magmatic units are responsible for the formation of most of the economic porphyry and epithermal systems (53 Moz Au and 2 Mt Cu in total) and link the westerly Aegean and easterly Arabian domains of the Neotethyan accretionary margin. Mineralization timing peaks during early Eocene (52 - 42 Ma) and late Oligocene-Pliocene (26 - 3 Ma) such as at Karapınar (51.7 ± 0.2 Ma by Re-Os), Çöpler (ca. 44 Ma by Re-Os; İmer et al. 2013), Cevizlidere (ca. 25 Ma by Re-Os; İmer et al. 2014), Hasançelebi (20.44 ± 0.86 Ma by 40Ar/39Ar), Kışladağ (14.49 ± 0.06 Ma by Re-Os; Baker et al. 2016), Afyon-Sandıklı (11.63 ± 0.05 Ma by Re-Os) and İnlice (8.16 ± 0.25 Ma by 40Ar/39Ar). Nevertheless, the presence of small porphyry systems in the Late Cretaceous belts suggests that the porphyry fertility is not necessarily restricted to the two major early Eocene and late Oligocene-Pliocene metallogenic periods.

5 Magma fertility

Documented post-subduction to post-collisional porphyry Cu-Au deposits are characterized by high-K calc-alkaline to alkaline magmatism (Wang et al. 2006; Richards 2009). New litho-geochemical results from ATB mineralized magmatic rocks and data compiled from the literature indicate medium-K calc-alkaline to shoshonitic character with an alkalinity content (K2O + Na2O) between 5 and 9.5 wt % K2O + Na2O)

![Figure 2. K2O + Na2O (wt %) vs. age (Ma) diagram illustrating the alkalinity evolution through time (arrows). New litho-geochemical data are coloured and their shape represents the degree of fertility. The two horizontal dashed lines indicate the fertility interval (5 to 9.5 wt % K2O + Na2O).](image-url)
wt %, regardless of the rock age (Fig. 2). The successive alkalinity increases through time during each tectonic episode appear to reduce magma fertility for porphyry and epithermal mineralization. This geochemical evolution implies an increase of heat caused by asthenosphere upwelling in the hydrous mantle wedge controlled by the complex slab geometry (i.e. subvertical or subhorizontal tearing) and post-orogenic extension during the ATB tectonic evolution. In addition, the rapid tectonic changes through time and space in ATB hinder the development of a long-lived subduction zone, with stabilizing crustal thickening, and magmatic maturation that are identified as optimal first-order factors for the formation of porphyry Cu deposits (e.g. Kay and Mpodozis 2001; Chiaradia 2014). However, Anatolian Miocene porphyry systems are richer in gold (e.g. Baker et al. 2016) while Cretaceous and Eocene Cu-Au porphyry systems are relatively small in tonnage and metal content compared to their arc-hosted Andean and Iranian counterparts, apparently independent of exploration and mineral preservation factors.

6 Conclusion

The successive episodes of magmatism during the complex Late Cretaceous to Cenozoic tectono-magmatic evolution of the Anatolide-Tauride metallogenic belt show spatial, temporal and geochemical variations reflecting various tectonic settings and complex slab geometries during the closure of Neotethyan oceanic basins. While the Late Cretaceous porphyry systems formed during arc formation, the better-endowed Eocene to Pliocene hydrothermal gold-rich systems formed in response to post-subduction tectonism including slab tear and break-off, and back-arc and post-collisional extension. Magma fertility was primarily controlled by the degree of alkalinity that increased due to the upwelling of hot asthenosphere in the hydrous mantle wedge during post-subduction to post-collision tectonism. The fertility window in ATB was brief (< 10 m.y.) and preferentially occurred at the early stage of each magmatic episode, which contrasts with well-established models in the worldwide arc-related porphyry and epithermal provinces.

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Epithermal gold in felsic maar-diatremes

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Abstract. Felsic maar-diatreme volcanoes are excellent hosts for epithermal gold-silver ore deposits, for both high- and low-sulfidation types. Felsic maar-diatremes can be thought of as formed by dome-like eruptions strongly modified by explosive underground magma-water interaction (phreatomagmatism). A maar crater sits on top of a diatreme; the crater is surrounded by a relatively thin ejecta ring; both the diatreme and ejecta ring consist mostly of pyroclastic deposits; the crater can be filled by remobilized pyroclastic debris as well as lacustrine and other sediments after the eruption. Epithermal mineralization forms veins, stockworks, hydrothermal breccias and disseminations which are most often found within the diatreme (e.g., Cripple Creek, Montana Tunnels, Mt. Rawdon), but sometimes just outside as well (e.g., Acupan, Kelian, Martabe), depending on the permeability of the diatreme infill and the style of mineralization. Ore can also sit in the ejecta ring (e.g., Wau). Felsic maar-diatremes are prospective because they have a direct connection with the magma feeding system and the source of magmatic-hydrothermal fluids.

1 Introduction

Felsic maar-diatreme volcanoes can host metallic ores, such as epithermal gold-silver deposits (e.g., Sillitoe and Bonham 1984) and Cordilleran base metal deposits (e.g., Baumgartner et al. 2009). Other felsic diatremes cross-cut porphyry-type ore deposits (e.g., Howell and Molloy 1960). This extended abstract focusses on epithermal gold-silver deposits in felsic diatremes, based on a review of the literature and the authors’ preliminary work at Mt. Rawdon in Australia. We first summarize the volcanology of felsic maar-diatremes, then describe their mineralization.

2 Volcanology of felsic maar-diatremes

Felsic maar-diatreme volcanoes have not been well described in the volcanology literature, even though economic geologists have known about them for decades. In contrast, mafic and kimberlitic maar-diatremes have been intensely scrutinized by volcanologists due to natural hazard implications (several maars and other phreatomagmatic volcanoes have erupted in the last few centuries) and the presence of primary diamond deposits in some kimberlites (e.g., White and Ross 2011; Brown and Valentine 2013; and references therein).

Ross et al. (2017) summarized the volcanology of felsic maar diatremes and showed that they have much in common with their ultramafic to mafic counterparts (Fig. 1):
- They can occur in groups, which has implications for the exploration of epithermal deposits.
- The overall structure of the volcano (maar crater with ejecta ring around it and a diatreme underneath) is largely the same.
- The dimensions are comparable.
- Phreatomagmatism is the dominant eruptive style but magmatic explosive activity and effusive activity can also occur.
- Features such as low-angle cross-bedding, dune bedforms, undulating beds, and channels, are typical of deposition from pyroclastic surges and commonly occur in ejecta rings.
- Bomb sags, soft-sediment deformation and accretionary lapilli indicate water in the eruption column and in the deposits of ejecta rings; pyroclastic fall deposits also occur there.
- Pyroclastic deposits in ejecta rings and diatremes contain mixtures of juvenile and lithic clasts in variable proportions. The abundance of lithic fragments is an indication that the diatreme is being excavated in the country rocks and that the source of external water is typically groundwater.
- Diatreme deposits are mostly poorly sorted, relatively coarse (lapilli tuff to tuff breccia), heterolithic deposits.
- In the deeper portions diatremes, the pyroclastic deposits tend to be non-bedded (Fig. 2a), whereas bedding can occur in the upper portions (Fig. 2b).
- The margins of diatremes are sometimes occupied by country rock breccias, and megablocks of country rocks or bedded pyroclastic rocks can occur.
- Juvenile fragments may have a range of vesicularities, since external water can meet the rising magma at any stage in its vesiculation and degassing history, but the clasts are often dense to poorly vesicular.
- Crater lakes can form in maars, and become filled with remobilized pyroclastic deposits from the ejecta ring, plus a range of sediments, including lacustrine sediments.
- Both the upper diatreme beds and the post-eruptive
crater infill can display centroclinal dips, which indicates subsidence, occurring during and/or after the eruption.

There are some differences too, given the variations in magma composition and the impact on magma viscosity:

- The dikes and plugs feeding and invading felsic diatremes seem larger (Fig. 1b) than most of the dikes related to mafic to ultramafic ones (Fig. 1a).

Wider conduits appear to be needed for the more viscous felsic magmas to ascend to surface (Carrasco-Núñez and Ort 2012). Some of the plugs are extruded as domes.

- The composition and some textures of the juvenile pyroclasts are different (e.g., mineralogy, flow banding, Fig. 2a).

- The processes of phreatomagmatic explosions involving felsic magmas may be different too (see Austin-Erickson et al. 2008).

- The eruption of the largest felsic maar-diatreme volcanoes, by analogy with felsic domes, may have lasted years to decades, compared to the days to months typically envisaged for mafic to ultramafic maar-diitremes.

3 Gold mineralization in felsic maar-diatremes

3.1 Description

Epithermal gold deposits occur in or near maar-diitremes at Acupan, Philippines (Cooke et al. 1996); Cripple Creek, USA (Thompson et al. 1985; Jensen 2003); Kelian, Indonesia (Davies 2002; Davies et al. 2008a,b); Lagunas Norte, Peru (Cerpa et al. 2013); Martabe, Indonesia (Sutopo 2013); Montana Tunnels, USA (Sillitoe et al. 1985); Mt. Rawdon, Australia (Brooker and Jaireth 1995); Pascua, Chile and Argentina (Chouinard et al. 2005); Roşia

Figure 1. Schematic cross-sections through a ultramafic to mafic, and b felsic maar-diitreme volcanoes, modified from Ross et al. (2017).

Figure 2. Photos from the Mt. Rawdon diatreme, SE Queensland. a Coarse, poorly sorted, non-bedded pyroclastic rocks showing a rare flow-banded dacitic clast (J) in MRDD204240-1. M/S means mafic or sedimentary. b Bedded tuff and lapilli tuffs in DDH12.
Montana, Romania (Wallier et al. 2006); and Wau, Philippines (Sillitoe et al. 1984), among other examples.

Epithermal mineralization can sit within the diatreme (Acupan, Cripple Creek, Martabe, Kelian, Montana Tunnels, Mt. Rawdon, Roșia Montana; Fig. 3), next to it in the country rocks or in hydrothermal breccias (Acupan, Kelian, Martabe; Fig. 4), and within the ejecta ring (Wau). Tonnages tend to be high and grades relatively low, so open pit mining is the preferred method of production.

Mineralization occurs in hydrothermal breccias, veins, stockworks and disseminations (Sillitoe 1997). Precious metals are commonly associated with pyrite (Kelian, Mt Rawdon, Montana Tunnels), but base metals associations are also known. Types of alteration present include sericitic (Acupan, Mt Rawdon, Montana Tunnels), advanced argillic (Martabe), adularia (Acupan, Roșia Montana), propylitic (Acupan, Martabe). Siliceous and argillic alterations have also been reported.

3.2 Discussion

Among the 14 largest circum-Pacific epithermal gold deposits reviewed by Sillitoe (1997), three or four occur in or near felsic diatremes, making this the most common volcanic setting for that deposit type, along with flow-dome complexes. Ross et al. (2017) propose that the type of magma degassing and eruptive rates typical of domes also apply to felsic maar-diatremes. In other words, dome-like eruptions strongly modified by phreatomagmatism create felsic maar-diatreme volcanoes.

In both cases (flow-dome complexes versus maar-diatremes), the setting is highly favourable for epithermal mineralization because there is a direct permeable connection between the magma chamber at depth and the newly emplaced volcanic features in the subsurface or surface (Sillitoe 1997). This allows magmatic-hydrothermal fluids to rise quickly to sites favourable for precious metal deposition. In the case of maar-diatremes, the permeability is represented by regional faults, diatreme margin faults, and the diatreme infill (Sillitoe 1997). Also, in these settings (domes and maar-diatremes), the magma and its contained volatiles (and presumably, precious metals) are not, for the most part, catastrophically evacuated from the magma chamber directly into the atmosphere, as opposed to what occurs during large caldera-forming eruptions.

The pyroclastic rocks in felsic maar-diatremes can still be permeable when hydrothermal fluids arrive, and therefore form good hosts for epithermal mineralization. However, the muddy matrix of the diatreme infills at Kelian means that some higher grade zones are outside the diatremes (Davies et al. 2008b; Fig. 4) and at Lagunas Norte mineralization is mostly around the margins of diatremes because of differences in the matrix in the margins versus centre (Cerpa et al. 2013). Because felsic diatremes contain a variety of clast types (felsic juvenile fragments, but also country rock clasts that can include mafic or sedimentary lithologies), they may be good sites for hydrothermal deposition because they react with fluids and cause the dumping of ore elements. At Mt. Rawdon for example, pyrite precipitated preferentially in dark (mafic) country rock clasts.

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Figure 3. Cross-section through the Montana Tunnels diatreme, USA, simplified from Sillitoe et al. (1985). The gold mineralization (>0.6 g/t Au, green dashed lines) is restricted to the middle portion of the diatreme.
Figure 4. Cross-section through two diatremes (Burung Breccia, Tepu Breccia) and multiple ore zones at the former Kelian mine, Indonesia, modified from Davies (2002) and Davies et al. (2008b). The gold mineralization (>0.5 g/t Au, green dashed lines; higher grade zones, red dashed lines) lies both in the diatremes and outside, including in hydrothermal breccias.

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Sodic-calcic skarn hosted by ultramafic rock in the Ulsan skarn deposit, Gyeongsang Basin, South Korea

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Abstract. The Ulsan Fe-W skarn deposit is located within the Cretaceous Gyeongsang basin in the southeastern part of the Korean Peninsula. The skarn and mineralization formed along the contact of the Tertiary Gadaeri granite and the limestone (age unknown) with partially serpentinized ultramafic rocks (dunite and harzburgite) and volcanic/sedimentary rocks (hornfels). Calcic skarn developed within limestone progressively as clinopyroxene-magnetite skarn, clinopyroxene-garnet skarn and garnet skarn. Sodic-calcic skarn formed by chemical interactions between albitized granites and adjacent ultramafic rocks. The sodic-calcic skarn contains unusual Na-rich clinopyroxene, Na-rich amphiboles, Cr-rich clinopyroxene, Cr-rich amphiboles, and Sr-bearing plagioclase, Ba-bearing K-feldspar as accessory phases. The clinopyroxene and amphibole have Na\textsubscript{2}O concentrations up to 6.5 wt.%, and these minerals have up to 12.1 wt.% and 2.5 wt.% Cr\textsubscript{2}O\textsubscript{3}, respectively. The Na was derived from albitite and the formation of Cr-bearing acmite (kosmochlor) and Na-amphibole (richterite) appears to be related to the release of Cr into the fluid phase by the breakdown of chromite in the ultramafic rocks during prograde skarn.

1 Introduction & geology

The Ulsan Fe-W skarn deposit is located within the Cretaceous Gyeongsang volcano-sedimentary basin at the southeastern edge of the Korean Peninsula (Fig. 1A). The Cretaceous sedimentary and volcanic rocks within the Gyeongsang basin unconformably overlie highly deformed Precambrian basement of the Yeongnam Massif. In this area, partially serpentinized ultramafic rocks (dunite and harzburgite) and carbonate rocks (mainly calcite) are exposed as a small roof pendant within the Upper Cretaceous sequence. All of these rocks have been intruded by the Gadaeri granite. Although the ages of both the ultramafic rock and carbonate rocks are unknown, they are considered to represent the basement to the Cretaceous volcano-sedimentary rocks. The Ulsan ultramafic rocks and carbonate rocks undergo the serpentinization and hydrothermal alteration with associated iron mineralization. The Gadaeri granite mainly consists of hornblende-biotite granite, K-Ar biotite age of 58 Ma (Lee and Ueda 1977), which is related to the Ulsan Fe-W skarn deposit (50.3±1.7 Ma by K-Ar K-feldspar; unpublished data) in the northeastern part of Gadaeri granite.

Figure 1. a Simplified regional geological map of South Korea. b Study area in Ulsan, Gyeongsang Basin in A.

There has been some controversy about the origins of host rocks (carbonates and ultramafic rocks) in previous studies (Kim et al., 1990; Choi et al. 2003; Yang et al. 2003). Based upon the carbon and oxygen isotope compositions of fresh unaltered host limestones (δ\textsuperscript{13}C\textsubscript{V-PDB} = 1.2 – 4.6‰, and δ\textsuperscript{18}O\textsubscript{V-SMOW} = 13.5 – 22.1‰), the Ulsan carbonate rocks are interpreted to be of marine origin. The Ulsan ultramafic rocks have a mantle restite origin, based on their whole rock geochemistry (Choi et al. 2003).

Various skarn types formed in the different protoliths. Calcic skarn typically developed in limestone, progressively forming clinopyroxene - magnetite skarn, clinopyroxene - garnet skarn and garnet skarn, ultramafic rock + albitite sodic-calcic skarns. The calcic skarn occurs as a nearly vertical ore pipe within recrystallized limestone at the contact with the Upper Cretaceous volcanic rocks that carbonates thin layers of pelitic sedimentary rocks. The Na-Ca skarn formed by chemical interactions between albitized granites and adjacent ultramafic rocks (Fig. 2). The Na-Ca skarn formed at the contact zone between ultramafic rock and albitite.
2 Petrography and geochemistry

2.1 Ultramafic rock

The Ulsan ultramafic rocks are dunite and harzburgite. They are coarse-grained, equigranular to porphyroblastic texture. They consist of olivine, orthopyroxene, amphibole, clinopyroxene, chromite, magnetite, serpentine, and talc. Olivine is abundant as subhedral grains with spinel inclusions. Orthopyroxenes occur as porphyroblasts. Spinel occurs as inclusions in olivine and amphibole. These dunite and harzburgite have undergone serpentinization. Anthophyllite the contact zone between ultramafic rock and, granite-albitite intrusion.

The ultramafic rocks have SiO$_2$ in the range of 40.1–44.0 wt.%, 37.1–45.0 wt.% MgO, 5.7–9.4 wt.% Fe$_2$O$_3$, 0.9–2.4 wt.% Al$_2$O$_3$, 0.9–2.7 wt.% CaO, <0.1 wt.% Na$_2$O. They have high Mg# (88.9–93.6), Ni (1520–2581 ppm), Cr (2000–3033 ppm). Ultramafic rocks have almost REE pattern (La$_N$/Yb$_N$ ratios of 2.0–10.7) using the Chondrite-normalized (Sun and McDonough, 1989). The REE patterns are similar to the average REE pattern of harzburgite (Fig. 3A; Lesnov, 2010). The bulk compositions of the Ulsan ultramafics and these REE patterns suggest that the formed by 10–20% partial melting of residual mantle restite.

2.2 Granite and albitite

The Gadaeri granite mainly consists of fine to medium grained porphyritic hornblende-biotite granite. The granite is composed of K-feldspar (36.7–52.6 vol.%), quartz (26–32.9 vol.%), plagioclase (14.9–29.2 vol.%), minor biotite (<3 vol.%), hornblende (<2 vol.%), and accessory magnetite, hematite, sphene, and apatite. It has porphyritic, micrographic, perthitic and/or granophyric textures strongly evolved magma. Intergrowths of quartz and alkali feldspar are arranged along euhedral plagioclase phenocrysts. It most of the plagioclase is altered to sericite, and partly replaced by chlorite. The albitite consists mainly of fine to medium grained plagioclase (mostly albite) and variable contents of the K-feldspar.

The Gadaeri granite has 69.3 – 73.0 wt.% SiO$_2$, 13.4 – 14.7 wt. % Al$_2$O$_3$, 1.9 – 3.5 wt.% FeO$^m$, 0.7 – 1.7 wt.% CaO, 4.5 – 5.1 wt.% Na$_2$O, 3.4 – 4.1 wt.% K$_2$O. The albitite has lower contents of SiO$_2$ (between 61.4 and 66.8 wt.%), FeO$^m$ (10.01 – 1.2 wt.%), K$_2$O (0.4 – 0.7 wt.%), and CaO (0.3 – 2.6 wt.%), and higher Al$_2$O$_3$ (9.6 – 21.7 wt.%) and Na$_2$O (9.3 – 11.2 wt.%). On the total alkali (Na$_2$O+K$_2$O) vs. silica diagram (Cox et al. 1979), the granite plots in the subalkaline field. On the SiO$_2$ vs. K$_2$O binary diagram (Peccerillo and Taylor 1976), the granites have a high-K calc-alkaline signature, with Na$_2$O+K$_2$O of 8.5 – 8.8 wt.%, and Ba concentrations of 677 – 856 ppm. The granites are I-typewith weakly metaluminous to peraluminous geochemical affinities on the A/NK vs. A/CNK diagram (after Maniar and Piccoli 1989). On tectonic discrimination diagrams (after Pearce 1996), the granites plotted of the volcanic arc granite (VAG). A correlation between SiO$_2$ and K/Rb ratios is a characteristic factor for the degree of evolution of igneous intrusions (Meinert et al., 2005). The K/Rb ratios of the Gadaeri granites are about 200–500, which is highly evolved magma in a continental margin setting. The granites and albitite have total REE concentrations of 236 – 441 and 307 – 409 ppm, respectively. The granites and albitite display different LREE-enriched chondrite-normalized REE patterns. The granites have relatively more enriched patterns, with La$_N$/Yb$_N$ ratios of 6.7–10 compared with 49 – 109 for the albitite. The granites show distinctive negative Eu anomalies (Eu/Eu$^*$=Eu$^*/\sqrt{[\text{Sm}_{N}\times\text{Gd}_N]}$) of the (0.5–0.7), while the albitite does not have Eu anomalies (Fig. 3B; Eu/Eu$^*$ = ~1.0; except for sample US89110-3 = 0.7).
granites have distinctive negative high-field strength element (HFSE) anomalies (Nb, Ta, P, Ti) on primitive mantle-normalized multi-element plots, indicating a subduction-related contribution to the magma (Fig. 3C).

2.3 Albitite endoskarn & ultramafic skarn

Albitite is located at several localities in contact between ultramafic rock and granite. These contact zones contain both exoskarn formed within the ultramafic rocks and endoskarn formed within the granite and albitite (Fig. 2). Textural evidence indicates that the first stage of skarn formed as a result of chemical interactions between albitized granites and adjacent ultramafic rocks. Sodium-enrichment in the serpentinized ultramafic rocks near the contact with the albitized intrusive is characterized by distinctive metasomatic textures (Fig. 4).

![Figure 4. Cr-bearing acmite of the Na-Ca exoskarn within the ultramafic rock (a to e) and Na-cpx (acmite) within the albitite endoskarn (d to f), respectively. Abbreviations: chm–chromite, cpx–clinopyroxene, pl–plagioclase, src–sericite.](image)

The albitite Na-Ca endoskarn have SiO$_2$ in the range of 52.0 – 65.5 wt.%, 0.9 – 2.5 wt.% MgO, 0.5 – 1.0 wt.% Fe$_2$O$_3$, 19.0 – 22.5 wt.% Al$_2$O$_3$, 0.3 – 15.8 wt.% CaO, 4.3 – 6.3 wt.% Na$_2$O. The Na-Ca skarn have SiO$_2$ in the range of 55.9 – 58.1 wt.%, relatively higher 17.5 – 17.8 wt.% MgO, 3.1 – 4.8 wt.% Fe$_2$O$_3$, 6.7 – 7.6 wt.% Na$_2$O, and lower 5.6 – 6.9 wt.% Al$_2$O$_3$, 1.8 – 5.7 wt.% CaO. Both endoskarn (L$_{Na}$/Y$_{Na}$ = 48.3 – 100.4) and ultramafic Na-Ca exoskarn (L$_{Na}$/Y$_{Na}$ = 62.7 – 73.8) display similar REE patterns, which are also similar to the fresh albitite (L$_{Na}$/Y$_{Na}$ = 49.4 – 108.7; Fig. 3E).

3 Na-Ca skarn and mineral chemistry

The sodium contents hydrothermal fluid derived from locally presented albitite have created unique skarn assemblages at Uljan. The albitite skarn (Na-Ca endoskarn) mainly consists of garnet, clinopyroxene, Sr-bearing plagioclase, Ba-bearing K-feldspar, minor prehnite, and wollastonite. The ultramafic skarn (Na-Ca exoskarn) contains unusual Na-rich clinopyroxene (acmite), Cr-bearing acmite (kosmochlor), Na-rich amphiboles (winchite, richterite), Cr-bearing richterite, and albite, Sr-bearing plagioclase and Ba-bearing K-feldspar as accessory phases.

![Figure 5. Compositional variation of the prograde skarn minerals. a. Garnet and b. clinopyroxene. Abbreviations: Ad–andradite, Di–diopside, Gr–grossular, Hd–hedenburgite, Jo–johannesenite, Pyr–pyralspite.](image)

Garnets in the endoskarn are part of the grossular–andradite solid solution from early (Gr$_{58-100}$, Pyr$_{0-4}$) to late (Ad$_{39-100}$, Pyr$_{0.4}$), whereas garnet in the Na-Ca skarn are mostly Al-rich (Gr$_{1.0}$, Pyr$_{0.5}$; Fig. 5A).

Clinopyroxenes in the endoskarn are part of the diopside–hedenbergite solid solution early (Di$_{73}$-100, Jo$_{0.5}$) to late (Hd$_{3}$-83, Jo$_{7}$-16) stage containing less than 15 mol.% johannesenite (Fig. 5B). Some clinopyroxenes from the Na-Ca skark display an increase in Na-Cr contents. The Na increase reflects coupled replacement between Na$^+$, Cr$^{3+}$, Fe$^{3+}$ and (Ca$^{2+}$, Mg$^{2+}$) (Fig. 6). This substitution has been inferred from the (Na$_{0.4}$Ca$_{25.6}$)Mg$_2$Cr$^{3+}$$_{0.2}$Fe$^{3+}$_{0.2}Si$_2$O$_6$ formula mineral chemical data. Maximum Na$_2$O concentrations of 6.44 wt.% are observed in clinopyroxene. Pyroxenes in the Na-Ca skark show a wide range of compositions (diopside–hedenbergite and/or kosmochlor–acmite solid solution). Clinopyroxenes in ultramafic rocks are mainly kosmochlor, whereas clinopyroxenes in the albitite mainly have acmite compositions. Amphiboles have a high contents of Na$_2$O (max. 6.5 wt.% and Cr$_2$O$_3$ (max. 2.5 wt.%), respectively.
4 Discussion and conclusions

The formation of the Ulsan skarn deposit related to the Gadaeri granite, iron mineralization began above 464ºC from a fluid containing greater than 45 equiv. wt.% NaCl, formed at about 350–450ºC and shallow depths (about 0.5 kbar, Choi and Youm 2000). The Gadaeri granite is characterized by strongly evolved porphyritic texture. It has high-K calc-alkaline signature and I-type, weakly metaluminous to peraluminous geochemical affinities. Based on field relations and geochemical characteristics, the albrite appears to be derived from the Tertiary Gadaeri granite. Meinert et al. (2005) suggests that a correlation between skarn assemblages and geochemistry of the related igneous rock. The Gadaeri granites have the characteristics of igneous rocks that form Fe and W skarn deposits (Choi and Wee, 1994).

Typically, Ca skarn developed within limestone, while Na-Ca skarn formed of the ultramafic + albrite contact zone. Textural evidence indicates that the first skarn stage garnet + diopside + Na-Sr-Ba silicates formed as the result of interaction between highly evolved albitized granites and adjacent ultramafic rocks. Hydrothermal fluid was derived from albrite, skarn assemblage. The formation of Cr-bearing acmite (kosmochlor) and amphibole appears to be related to the release of Cr breakdown of chromite within the ultramafic rocks during prograde skarn alteration.

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References

Mineralogy of low temperature argillic alteration in the porphyry-epithermal Çöpler gold deposit, Erzincan, East Central Turkey

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Abstract. The Çöpler porphyry-epithermal gold deposit, is associated with middle Eocene dioritic and granodioritic intrusive rocks. It is a porphyry Cu-Au system characterized by a potassically altered (biotite-K-feldspar-magnetite) core overprinted by extensive phyllic (quartz-sericite) and argillic (quartz – montmorillonite – kaolinite - cristobalite) alteration zones. The low temperature (argillic) alteration zone was investigated by optical microscopy and X-ray diffraction (XRD) methods. Bulk mineralogical compositions of the altered samples are quartz + feldspar + clay. Hydrothermal alteration-related clay mineral compositions of the argillic zone samples are quartz + smectite (montmorillonite) + kaolinite in the outer parts, and quartz + mixed-layer illite-smectite (I-S) and pure cristobalite in the inner parts (toward phyllic zone). Dioctahedral smectites are mainly Ca-montmorillonite, while samples close to inner parts include minor amounts of Na-smectite. Clays were neoformed within the pores of groundmass, and as replacements of plagioclase crystals. I-S has an R3 ordering type (85% illite, 15% smectite). Mineralogical associations indicate lowest grade of alteration (argillic zone), at low temperatures (< 200°C). In general pure smectite and I-S minerals represent potential minerals to aid in elucidating the origin of late stage hydrothermal fluids and the duration of hydrothermal activity which can be obtained from their stable and radiogenic isotope data.

1 Introduction

The Çöpler porphyry-epithermal gold deposit is associated with middle Eocene (⁴⁰Ar/³⁹Ar plateau ages of igneous biotite and hornblende are 43.75±0.26 to 44.19±0.23 Ma) intrusive rocks related to an extensional tectonic phase in the Tethyan Alpine-Himalayan orogenic belt (Kuşçu et al., 2013; Imer et al., 2013; 2016). The intrusive system is contained within a 1×2 km wide, ENE-trending structural window (the Çöpler window), along which block-faulted rocks have been exposed underneath the regional thrust sheet of the Munzur carbonate allochthon (Figure 1 and 2, Imer et al., 2013; 2016).
The intrusive rocks were emplaced into Late Paleozoic–Mesozoic metamorphosed sedimentary basement and overlying carbonate rocks, and created the porphyry epithermal Cu-Au deposit and an area of extensive hydrothermal alteration zones. The main alteration zones at the deposit are defined by the potassic, phyllic, propylitic alterations, with local carbonate, skarn and supergene alterations (Imer et al. 2016). The above authors have stated that the apparent absence of argillic or advanced argillic assemblages above the phyllic-altered zone can be explained either as a consequence of lithologic controls during the evolution of the hydrothermal system or by deep erosion within the Çöpler window. They assumed that the estimated depth (~1.5 km) of the veinlets suggested that erosion within the Çöpler window was mostly restricted to the carbonate rocks and, therefore, that low-temperature argillic alteration assemblages were never formed. According to this scenario, weakly acidic magmatic-hydrothermal fluids were neutralized upon contact with the limestone/marble, precluding evolution to more acidic compositions during cooling.

Epithermal environments are typified by extreme acid leaching, and therefore argillic alteration provides a very useful guide to mineralization. The leaching of aluminosilicates may result in silica enrichment, so that argillic alteration may in fact grade into zones of silica-rich material. Clay minerals primarily replace the plagioclases and the mafic silicates (hornblende, biotite). Argillic alteration is characterized by the formation of clay minerals due to intense H⁺ metasomatism and acid leaching, at temperatures of between 100 and 300 °C. This alteration inwardly grades into phyllic zones, whereas outwardly it merges into propylitic zone. This type of alteration is common in porphyry systems, but erosion may eliminate evidence of this type of alteration (Pirajno 2010).

In this study, we have investigated low-temperature related clay alterations (argillic alteration) from the late stage of hydrothermal system, in terms of the mineralogical and textural properties. Thus, it may be possible that these minerals are suitable to investigate the origin of fluids and the duration of hydrothermal activity.

2 Geological setting and lithology

The basement in the Çöpler area consists of regionally metamorphosed Permo–Triassic siliciclastic sedimentary rocks of the Kebar metamorphic massif (Figs. 1, 2). The metasedimentary succession consists of low-grade metamorphic (subgreenschist facies) clastic rocks (Figure 3) in conjunction with Late Cretaceous obduction of ophiolites onto the northern Tauride margin. These rocks are characterized by a mineral assemblage of chlorite + quartz ± sericite ± epidote. The metamorphic basement was structurally overlain by the Late Triassic to Cretaceous allochthonous Munzur carbonate platform (Figs. 2, 3).

The Middle Eocene igneous rocks (granodiorite porphyry and hornblende diorite porphyry) intrudes the meta-sedimentary basement and overlying limestones (Figure 2, 3) as several stocks that range in width from a few hundred meters to several kilometers (Imer et al., 2013, 2016). Brown-colored biotite-rich and pale green-colored diopside-rich hornfels are locally developed at contacts with the Eocene intrusions. These calc-alkaline intrusives were emplaced into a narrow structural corridor along the northern flank of the eastern Taurus mountain range within a region of structural complexity where the modern Eurasia–Arabia collision zone is juxtaposed against at least two different suture zones marking the closure of former Neo-tethyan ocean basins (Kuşçu et al., 2013; Imer et al., 2013). Early-stage porphyry mineralization is developed within the granodiorite porphyry intrusion, which is exposed primarily in the Main zone, and is confined to a 300 × 500 m area (Figure 2). Biotite-rich and pale green-colored diopside-rich hornfels are locally developed at contacts with intrusions (Imer et al., 2013, 2016). This zone also contains minor epithermal-style mineralization as a shallow overprint on the porphyry system (Imer et al., 2016).

3 Results

3.1 Optical microscopy

The samples from the alteration zone which is hosted by metasediments and granodiorite porphyry, show intense argillization. In the granodiorite porphyry samples different clay minerals were developed as different micro layers (Fig. 4 a-b). The more intense argillized samples exhibit homogenously distributed clay and quartz occurrences. Illite-smectite minerals are present as very fine-grained crystals (Figure 4 c-d). Smectite-rich altered granodiorites show an original igneous porphyritic texture formed by plagioclase phenocrysts which is replaced mainly by smectites and partly by kaolinites (Figure 4 c-f).

3.2 X-ray diffraction (XRD)

Whole rock and clay fraction mineralogical compositions of the argillized samples, obtained from GNS APD 2000 X-ray diffractometer, are given in Table 1, figures 5 and 6.
Quartz and feldspar (plagioclase) are the main minerals in almost all samples, except for two samples that contain appreciable cristobalite and have nearly pure clay fractions (smectite and I-S). Clay minerals, obtained from oriented smear slides, are determined as smectite, kaolinite and mixed-layer illite-smectite (Fig. 6). Clay mineral assemblages are quartz + smectite + kaolinite at outer parts, and quartz + I-S at inner parts (toward phyllic zone).

Two samples have nearly pure clay fraction (smectite and I-S). Smectites have dioctahedral composition (d006 < 1.500 Å). According to first peak locations (2θ = 6°) of smectites they are mainly a Ca-montmorillonite type. But the samples from the inner parts, where the first peaks show broadening toward higher 2θ values, represent the presence of Na-montmorillonite (Fig. 6).

### Table 1. Bulk and clay fraction composition of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Qz</th>
<th>Fsp</th>
<th>Crs</th>
<th>Clay</th>
<th>Sme</th>
<th>Kln</th>
<th>I-S</th>
<th>Ilt</th>
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<tr>
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<tr>
<td>M2-33</td>
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<tr>
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<td>M2-81</td>
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</table>

Qz= Quartz, Fsp= Feldspar, Crs= Cristobalite, Sme= Smectite, Kln= Kaolinite, I-S= Mixed-layered illite-smectite, Ilt= Illite.

### 4 Discussion and conclusion

Argillic alteration is characterized by the formation of clay minerals due to intense H⁺ metasomatism and acid leaching, at temperatures of between 100 and 300 °C. This alteration inwardly grades into phyllic zones, whereas outwardly it merges into propylitic zones. In the porphyry epithermal Çöpler Au deposit, clay samples, collected from outer and inner parts of the phyllic zone, contain argillic
alteration related minerals (smectite, kaolinite and cristobalite), and indicate low temperature (< 200 °C) conditions. Clays are mainly observed replacing plagioclases and have a neoformed origin within the groundmass of the porphyry intrusive rocks.

Imer et al. (2016) stated there was an absence of argillic assemblages above the phyllic-altered zone in the Çöpler deposit, and explained either as a consequence of lithologic controls during the evolution of the hydrothermal system or by deep erosion within the Çöpler window. They mentioned supergene kaolinite replacement of sericite and possibly feldspars was possibly due to reaction with sulfuric acid generated by pyrite oxidation. The authors seem to omit the presence of argillic alteration zones, and suggested a short-lived (<1 my) magmatic (43.7-44.2 Ma) and hydrothermal (43.8-44.2 Ma) history. They concluded that no suitable minerals were found that could be used to date the epithermal system, but it was inferred to be close to the age of the precursor porphyry system. However, Akçay et al. (2016) obtained U/Th-He dating on zircons, which indicates closing temperatures of around 200°C, suggested that cooling intrusion of Çöpler to below this temperature took place at 36.6±0.7 Ma.

The argillic alteration related mineral composition of the Çöpler deposit is very similar to the argillic zone of theBizmîşen skarn-type iron deposit (Bozkaya et al. 2016). Both are associated with intrusive rocks of similar age (43.75±0.26 to 44.19±0.23 Ma for Çöpler, 44.16±0.23 and 43.51±0.51 Ma for Çaltı and Bizmîşen plutons) and developed in the same extensional tectonic phase. Therefore, the mineral assemblages in Çöpler deposit may well be associated with the argillic alteration processes around these other plutons. We conclude that smectite and I-S minerals can play an important role in understanding the origin of late stage hydrothermal fluids and here suggest a longer period of hydrothermal activity from their stable and radiogenic isotope data.

References


Abstract. The Pirquitas epithermal Sn-Ag deposit is located near the Bolivian border in the Argentinian Puna Plateau and used to be historically a great source of Sn and Ag in the country. The Pirquitas deposit is considered to be an analogue to the Bolivian Sn-Ag epithermal deposits but the origin of the ore-bearing fluids is still controversial. Fluid inclusions studies in quartz, Sn-Ag minerals and sphalerite from e.g., the Oploca vein system in transmitted and near infrared light show variable salinity from 10.6 to 0.8 wt.% NaCl equiv. and homogenization temperature from 274° to 190° interpreted as a mixture of saline metal-rich [magmatic] fluids and meteoric water. Fluid inclusion evidence for flashing and boiling, as suggested in previous studies from the Cortaderas breccia body, was not observed in samples from the Oploca vein system. All results obtained are in agreement with data from Bolivian epithermal Ag deposits (e.g. Potosi, San Antonio de Lipez).

1 Introduction

Pirquitas is a Bolivian-type epithermal Sn-Ag deposit located in Jujuy Province of NW Argentina (Rosas et al. 2013). The Pirquitas mine is one of the most important economic Sn-Ag mines in Argentina, with both primary Sn-Ag sulfide mineralization as well as alluvial tin and gold accumulations (Paar et al. 2000). Between 1933 and 1989 Pirquitas was the largest producer of tin and silver in Argentina (Board 2011). Production in 2015 was 309 t of silver and 2,134 t of zinc (www.silverstandard.com).

The source of ore fluids in the Pirquitas deposit is still controversial. In this contribution, we report results of fluid inclusion studies in quartz, sphalerite and silver ore minerals from the Oploca vein which is the most southern vein-type mineralization in the Pirquitas deposit (Fig. 1). The results are compared with fluid inclusion data from breccia-hosted ores from the Cortaderas breccia, 500 m north of the open pit (Soler et al. 2008).

2 Regional setting

Pirquitas mine is located on the Altiplano-Puna Plateau, near the Bolivian border, at an elevation of about 4200 m. Vein type mineralization at Pirquitas is hosted in metamorphosed Ordovician marine sedimentary rocks covered by Tertiary continental sedimentary units and salars (Gorustovich et al. 2011). The main tectonic structures are NNE striking faults, and faults sub-parallel to the Neogene N-S to NNE-SSW fold axes with compressive or transpressional nature (Slater 2016).

Although the mineralization at Pirquitas is considered as an analogue to the Bolivian Sn-Ag epithermal deposits, there is no direct association with magmatism. The closest intrusion is the granodioritic Cerro Galán some 12 km to the east of the Pirquitas mine (Soler et al. 2008). The Bolivian epithermal deposit model and geophysical results suggest a subvolcanic body or breccia pipe between 400 and 600 m beneath the Pirquitas open pit whereas a 800 m deep borehole did not confirm its existence so far (Soler et al. 2008).

2.1 Local geology

![Figure 1. Location map of the Pirquitas mine also showing major structures and ore bodies. Modified after Rosas et al. (2013) and Slater (2016).](image-url)
veins are deep-dipping (N to S) polymetallic veins striking close to 105°. Disseminated mineralization occurs north of Potosí, San Miguel area, and comprises the Veta Blanca and Colquechaca veins with a NW-SE trend near 305°. (Rosas et al. 2013; Salter 2016). Veins and breccia-hosted mineralization consists of iron and zinc sulfides with accessory cassiterite and a large variety of Ag-Sn-Zn (-Pb-Sb-As-Cu-Bi) sulfides and sulfosalts. All mineralized veins are subvertical with an average thickness of 30 to 50 cm (Malvicini 1978; Paar et al. 1996). Disseminated ores occur with small veins and stockworks as disseminate minerals in the host rock, especially common in the San Miguel area. Hydrothermal breccia bodies, characterised by sulphide and quartz mineralization occur in the Oploca and Potosí vein systems. A subject of recent exploration (Slater 2016) is the Ag-Zn-rich breccia system in the Cortaderas zone, north of the current open pit (Fig. 1).

2.2 Paragenesis and mineralogy
In the southern veins system, Oploca, San Miguel and Chacoya, four ore assemblages were distinguished by Paar et al. (1996): (1) sphalerite (ZnS), pyrrargyrite-miargyrite (Ag₃SbS₃ to AgSbS₂), freibergite ((Ag,Cu,Fe)₄(As,Sn)₄S₁₃), wolframite ((Fe,Mn)WO₄) and cassiterite (SnO); (2) stannite (Cu₂FeSnS₄) and other tin sulphides; (3) Pb-Ag sulfoantimony minerals; and (4) bismuth minerals including frankelite ((Pb,Sb)₃Fe²⁺Sn_Sb₂S₁₄) and andorite (AgPbSb₂S₆).
Malvicini (1978) described two stage of ore deposition. The first stage is dominated by early pyrrhotite (Fe₇S₈) partly replaced by pyrite with accessory cassiterite and arsenopyrite (FeAsS); the second stage comprises colloform bands of sphalerite (“schalenblende”) with stannite and other Sn-sulfides, minor galena and various Sn-Ag sulfosalts replacing pyrrhotite, cassiterite, stannite and galena (PbS). Most of the Pb-Sb-Ag minerals were deposited during this second stage of ore formation. (Fig. 2)

3 Results
3.1 Fluid inclusion petrography
The samples studied here mostly come from the veins of the Oploca and San Miguel systems. Fluid inclusions occur in quartz as well as in ore minerals hocartite-pirquitasite (Ag₅(Fe²⁺,Zn)S₄ to Ag₅ZnS₄), pyrrargyrite, sphalerite and cassiterite. Fluid inclusions in quartz, pyrrargyrite and bright sphalerite were studied in transmitted light whereas fluid inclusions hosted in dark sphalerite, miargyrite and hocartite-pirquitasite were studied using an infrared light microscope.

![Figure 2](image-url)
Fluid inclusions hosted in different ore minerals are always aqueous two-phase but show variable L-V ratios (Figs. 3 and 4). Quartz samples from various occurrences within the Pirquitas mine are mostly recrystallized and a clear classification of primary vs. secondary inclusions is difficult or even impossible due to the high frequency of fluid inclusions in most samples. Furthermore, the Ordovician host rocks contain older metamorphic quartz segregations and veins that are not always easy to distinguish from the Pirquitas veins. To avoid potential ambiguity, our emphasis here is on fluid inclusions hosted in the ore minerals.

Primary and/or pseudosecondary inclusions in sphalerite show variable shapes and mostly occur along growth zones. Secondary inclusions are oriented along healed microfractures. Primary inclusions in hocartite-pirquitasite are clearly defined by regular prismatic or near spherical shapes. They occur isolated or are arranged in fluid inclusion assemblages (FIAs) within individual crystal grains. Pyrargyrite contains primary and secondary inclusions that are clearly distinguishable. The shape of primary inclusions is rectangular prismatic and spherical and they occur as isolated inclusions or in small FIAs. Secondary inclusions have more irregular or spherical shapes and are arranged along healed microfractures. Cassiterite only rarely hosts fluid inclusions and, when present all inclusions are very small and show rectangular prismatic shape. The L-V ratios of cassiterite-hosted fluid inclusions are considerably lower compared to those hosted in quartz, sphalerite and Ag-sulfosalts (Figure 3 and 4).

Figure 3. IR photomicrographs of fluid inclusions hosted a, b and c hocartite-pirquitasite, d in Pyrargyrite.

### 3.2 Microthermometry

Fluid inclusions hosted in quartz from the ore stages yield salinity between 0 to 9.2 wt. % NaCl equiv. and a broad range of homogenization temperatures in the range between 175° and 300° C.

Fluid inclusions in colloform sphalerite (dark and light), in banded wurzite, hocartite-pirquitasite, and pyrargyrite show variations in salinity and homogenization temperatures from 10.6 to 0.8 wt. % NaCl and 274° to 190° C, respectively. (Fig. 5). In general, fluid inclusions hosted in hocartite and pyrargyrite yield higher salinity and homogenization temperatures than those in sphalerite.

![Figure 4. Photomicrographs of fluid inclusions in a sphalerite, b and c cassiterite.](image)

### 4 Discussion

The observed general trend of decreasing salinity and homogenization-temperatures in fluid inclusions hosted in early and late ore minerals from the Oploca vein system (Fig. 5) suggests fluid mixing between a higher temperature and higher salinity fluid with a cooler, low salinity fluid. The origin of the two fluids is still unknown but mixing of a metal-rich (magmatic?) fluid and meteoric water appears likely. The rare and small cassiterite-hosted fluid inclusions showing low L-V ratios can be due to a higher trapping temperature. However, vapor-rich inclusions may also be indicative for boiling of the ore-forming fluid (Bodnar et al. 1985).

Slater (2016) interpreted fluid inclusion data from the Cortaderas breccia to indicate flashing, where liquid is instantaneously converted to steam, and simple boiling due to rock dilation and depressurization (Brown 1986). The colloform structure of sphalerite was also attributed to such processes. According Slater (2016), the Ag-Sn sulfosalts formed in the last stage of mineralization when the system was sealed and temperature gradients were higher.
However, no clear evidence for boiling was observed in the Oploca samples.

Figure 5. Results of fluid inclusion microthermometry in ore minerals from Oploca and San Miguel vein compared with Slater (2016) data from sphalerite in the Cortaderas breccia zone.

The fluid inclusions results are in agreement with studies of fluids from typical Sn-Ag epithermal deposits in Bolivia. Fluid inclusions in sphalerite from the Potosí district in Bolivia show a range of homogenization temperature and salinity of 174° - 311° C and 6.6 - 9.5 wt.
% NaCl equiv., respectively. Similarly, the San Antonio de Lipez deposit near the Argentine border yielded Th between 157° and 317° C and 1.2 - 16 wt% NaCl equiv. (Sugaki and Kitakaze 1988).

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Mineralogical characterization of a gold-rich porphyry in Tolima, Colombia

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Abstract. The California prospect is located 200 km west from Bogotá, Colombia and only 8 km SE from the La Colosa gold-rich porphyry. The mineralization is associated with two porphyritic dacites which intruded muscovite-quartz-graphite schist of Palaeozoic age. Gold occurs with disseminated pyrite and minor chalcopyrite, pyrrhotite, sphalerite, galena and marcasite. The ore minerals are accompanied by a strong phyllic alteration which affects both the host rock and the dacites. All these features may indicate the presence of an unroofed gold-rich porphyry system; however, further investigation is needed.

1 Introduction

A gold-rich porphyry deposit was defined like a porphyry copper deposit that contains more than 0.4 g/t Au (Sillitoe 1979). Few gold-rich porphyry deposits have been found worldwide; there are some examples in the Maricunga Belt in Chile (Vila and Sillitoe 1991), Cajamarca in Peru (Teal and Benavides 2010) and Luzon in Philippines (Cooke et al. 2011). Sillitoe (2008) defined the Middle Cauca Belt according to the occurrence of Miocene gold rich deposits (porphyry and epithermal); Leal (2011) defined the Cajamarca-Salento district where a series of gold deposits occur associated with hypabyssal intrusives. In 2006 the AngloGold Ashanti greenfields exploration team discovered the world’s largest gold-rich porphyry deposit, La Colosa. It is located within the Cajamarca-Salento district and they inferred a mineral resource of 470Mtonnes with a gold content of 0.9g/t (Gil-Rodriguez 2010).

The California prospect is located about 8 km southeast from La Colosa. In 1960’s there was a gold mine operated by an English geologist. A couple of years later, the mine closed due to Colombian armed conflict. But no geological study has been developed in this area. So, this will be the first work in which some data is reported there (Fig. 1).

2 Geological framework

The Central Cordillera of Colombia is limited at east from Romeral Fault System and west from the Otú-Pericos fault. It is divided in four lithodemic megaunits (Maya and Gonzalez 1995): Cajamarca Complex, Quebradagrande Complex, Arquía Complex and Mesozoic oceanic vulcanites (Amaime Formation). There are some reported ages, using 40Ar/39Ar and 238U/206Pb, for the Cajamarca Complex revealing an average age of 236.2±6.3 Ma (Villagomez et al. 2011). Villagomez et al. (2010) proposed a synchronous exhumation process occur during 117-107 Ma for Arquía complex Villagomez et al. (2011) reported an U/Pb dating on zircons from a metatuff in Quebradagrande Complex, yielding an age of 114.3±3.8 Ma; in (Sinton et al. 1998) and average age of 77 Ma was given for Amaime Formation.
A seven-stage genetic model for the Central Cordillera was proposed by Villagomez and Spikings (2013), explaining the subduction model and the accretion of terrains over the Paleozoic and Triassic basement, following the chronological order exposed before.

In the Central Cordillera, an important gold belt had been reported: The Middle Cauca Belt is a structure that starts at north in the Antioquia Batholith with deposits like Titiribí ending at south in El Poma (Bissig et al. 2017). It was formed in a transtensional tectonic setting and the gold mineralization is associated with Miocene magmatism (Sillitoe 2008). Another important gold region is the Cajamarca-Salento district, which is located at the southeast of the Middle Cauca Belt. The most important deposit in this district is La Colosa, a gold-rich porphyry deposit associated to the intrusion of andesitic to dacitic porphyries, hosted by black schists and quartzites from the Cajamarca Complex (Gil-Rodriguez 2010).

2 Methodology

Twenty rock samples were collected during a field trip through series of outcrops on a creek, (Fig. 5). Respective macroscopic descriptions were done, characterizing the hydrothermal alteration and the types of veinlets. Six significant samples were selected for petrographic and metallographic studies using polished thin sections. Furthermore, some points were analyzed using TerraSpec with the aim to identify alteration minerals. Data was taken with an equipment model 350-2500 ASD inc® and it was analyzed with the software SpecMin-Pro-3.1. Version.

3 Results

In the creek three different rocks were identified. The hypabyssal bodies were classified using the QAPF triangle for volcanic rocks of Streckeisen (1980) like:

-Dacite 1: Dacite with a green matrix product of chloritization and tourmaline product of hydrothermal alteration (Fig. 2).

-Dacite 2: Dacite with a whitish colour, with quartz, sericite and disseminate pyrite, hints for a phyllic alteration (Lowell 1970).

Field observations show that Dacite 1 cuts Dacite 2. In muscovite-quartz schists with graphite, a phyllic alteration was recognized by the presence of quartz and sericite. Additionally, some veinlets of pyrite clearly cuts the foliation planes of the rock, this means hydrothermal influence which brought sulphides to the system.

In field, a tectonic breccia was found and petrographically contains three different types of clasts, graphite quartz-muscovite schists, dacites and chlorite-schists (Figs. 3 and 4).

Figure 2. Photomicrograph of a Dacite with quartz (Qtz), plagioclase (Pl) and tourmaline (Tur) as alteration mineral.

Figure 3. Photomicrograph of tectonic breccia with clasts of: Muscovite-quartz schists with graphite (Qz-Musc-Gph Sch.) and chlorite schists (Chl Sch.).
3.1 Structural control

In La Colosa, the deposit is affected by Palestina fault, which allows the ascent and the emplacement of the porphyries that initiated the mineralization. A similar geological control exists in California by Ibague and Palestina faults, considering that: Cauca-Romeral faults system, Ibague fault and Palestina fault is a conjugate dextral-fault set.

3.2 Mineralization

The mineralization is dominated by the presence of disseminated pyrite. In Dacite 2 (Figs. 6 and 8), pyrite is accompanied by a strong phyllic (illite-bearing) alteration with the following mineral assemblage: Marcasite, pyrrhotite, sphalerite and chalcopyrite. In Dacite 1 (Fig. 7), the mineralization is associated with a Chloritic-carbonatic alteration with: pyrite, sphalerite, chalcopyrite and galena. In the host rock some gold-bearing veinlets of massive pyrite, quartz and minor tourmaline were observed, associated with a strong phyllic alteration. The presence of tourmaline in the system indicates an important volatile phase in the mineralizing fluids. A schematic paragenetic sequence is represent in Table 1.

Table 1. Paragenetic sequence of the mineralization. Pyrrhotite (Pn), pyrite (Py), marcasite (Mrc), chalcopyrite (Cpy), sphalerite (Sp) and galena (Ga).

<table>
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(Fig. 6). Reflected light photomicrograph with crossed nicols of Dacite 2. Illustrating the relation between pyrrhotite and chalcopyrite. Pyrite (Py), chalcopyrite (Ccp) and pyrrhotite (Pn).

(Fig. 7). Reflected light photomicrograph with crossed nicols of Dacite 1. Note chalcopyrite disease in sphalerite. Pyrite (Py), chalcopyrite (Ccp), sphalerite (Sp) and galena (Gn).
4 Conclusions

The presence of chalcopyrite disease in sphalerite indicates a range of temperature for the mineralization of 200°-400°C. This temperature is in agreement with the presence of illite (White and Hedenquist 1995) which occurs both in the dacites and in the host rock.

The occurrence of gold is associated with a disseminated mineralization accompanied by phyllic alteration; these features may suggest the existence of an unroofed porphyry system; however, more field, geochemical and isotopic evidence is needed to confirm this supposition.

The presence of pyrrhotite could be an indicator of the interaction between the mineralizing fluids and the host rock. This feature is observed in other deposits in Colombia, like Marmato (Santacruz 2011) where pyrrhotite indicates a redox change in the fluid due to the reaction with carbonaceous-rich rocks.

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Figure 8. Reflected light photomicrograph with crossed nicols of Dacite 2. It shows euhedral crystals of marcasite (Mrc).
Hypogene copper isotope trends in the Pebble porphyry Cu-Au-Mo deposit, Alaska

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Abstract. This study presents Cu isotope ratios for copper sulfides from 12 samples from the Pebble porphyry Cu-Au-Mo deposit in Alaska. The $\delta^{65}$Cu isotope ratios show linear correlations with the $\delta^{18}$O isotope ratios calculated for the fluid in equilibrium with the hydrothermal alteration in each sample. Samples with sodic-potassic, potassic and illite alteration display a negative linear correlation between the Cu and O isotope results. This suggests that the fractionation of Cu isotopes between the fluid and precipitating chalcopyrite is positive as the hydrothermal fluid is evolving from magmatic to mixed magmatic-meteoric compositions. Samples with sericite- and pyrophyllite-rich advanced argillic alteration display a weak positive linear correlation between Cu and O isotope results consistent with small negative fluid-chalcopyrite Cu isotope fractionation during fluid evolution. The hydrothermal fluids that formed sodic-potassic, potassic and illite alteration transported Cu as CuHSO. Hydrothermal fluids that resulted in acidic advanced argillic alteration likely transport Cu as CuCl$_2$. The difference in transporting species may explain the differing fractionation behavior of the Cu isotopes.

1 Introduction

The Pebble porphyry Cu-Au-Mo deposit in Alaska provides a case study for increasing our understanding of the geological processes responsible for Cu isotope fractionation in the magmatic-hydrothermal environment. At Pebble the hydrothermal fluid compositions, sources and temperatures are defined and their role in forming hydrothermal alteration and mineralization are understood based on a dataset that includes stable isotopes of O and H, and fluid inclusion analysis (Gregory 2017). This study uses Cu isotope data for hypogene chalcopyrite mineralization together with O isotope data (Gregory 2017) for hydrothermal alteration minerals coexisting with chalcopyrite to attempt to understand the behavior of Cu isotopes during high temperature hydrothermal processes.

2 Mineralization and alteration

The Pebble porphyry Cu-Au-Mo deposit is one of the world's largest porphyry deposits. The deposit is related to 90 Ma granodiorite porphyry intrusions and is dominated by chalcopyrite-pyrite-rich mineralization. A succession of hydrothermal alteration assemblages accompanied and overprinted sulfide deposition (Gregory et al. 2013; Lang et al. 2013). These alteration assemblages have been attributed to two major mineralizing magmatic-hydrothermal events; the earlier generated large zones of sodic-potassic and potassic alteration, and the later generated a relatively restricted advanced argillic overprint (sericite-rich and pyrophyllite-rich alteration assemblages). Illite-kaolinite alteration formed in the interval between the two mineralization events, overprinting sodic-potassic and potassic alteration assemblages. Quartz-sericite-pyrite alteration forms a halo around the deposit.

3 Samples

Copper isotope analyses were undertaken on 12 Cu sulfide separates. Three samples from sodic-potassic and potassic alteration mineral assemblages are characterized by K-feldspar-quartz-biotite-chalcopyrite-pyrite±albite. Fluid inclusion data from quartz veins associated with these assemblages suggest alteration was occurring as hydrothermal fluids cooled from ~600°C to ~330°C with average temperatures of ~400°C for sodic-potassic alteration and ~375°C for potassic alteration (Gregory 2017). Sulfide minerals precipitated late in the alteration event between ~375 and ~330°C. Interpreted $\delta^{18}$O and $\delta^D$ data for biotite in both assemblages suggest a magmatic fluid source that has evolved via wallrock interaction and quartz precipitation (Gregory 2017).

Five samples are characterized by illite-kaolinite alteration that overprints earlier alteration assemblages. Three samples from the deposit core, where illite overprints potassic and quartz-sericite-pyrite alteration assemblages, are associated with ~280°C fluids that are dominantly meteoric in origin (Gregory 2017). These samples have a silicate assemblage of K-feldspar-quartz-illite. Previously formed chalcopyrite was dissolved and reprecipitated during this illite alteration (Gregory 2017). Two samples are from the deposit margins where illite overprints sodic-potassic alteration and forms quartz-illite-pyrite alteration. Fluid temperatures during this alteration are ~280°C and fluids are dominantly magmatic in origin (Gregory 2017). These samples have a silicate assemblage of quartz-illite-minor K-feldspar-albite.

Four samples are from the advanced argillic alteration zone. Two samples are sericite-rich, are associated with fluid temperatures of ~340°C and have magmatic $\delta^{18}$O and $\delta^D$ values. Two samples are pyrophyllite-rich, are associated with fluid temperatures of ~300°C and have $\delta^{18}$O and $\delta^D$ values that indicate the alteration was formed...
by mixed magmatic and meteoric fluids (Gregory 2017).

4 Copper isotope results

This study uses the data for six of the samples from Mathur et al. (2013) together with six new analyses. The Cu isotope values for Cu sulfide minerals in the 12 samples range from -2.09 to 1.11 ‰ δ65Cu. All but one sample are chalcopyrite dominant, one sample is a mixture of digenite and bornite. There are distinct populations in the data set when subdivided by hydrothermal alteration type. Samples with high temperature sodic-potassic or potassic alteration have Cu isotope values between -2.09 and -0.65 ‰ δ65Cu. Samples with sulfide minerals that were dissolved and reprecipitated during illite alteration have heavier Cu isotope values between -0.33 and 0.82 ‰ δ65Cu.

Samples with advanced argillic mineral assemblages have the heaviest Cu isotope values that range from 0.28 to 1.11 ‰ δ65Cu. The digenite-bornite sample is included in this advanced argillic sample group and has a value of 0.28 ‰ δ65Cu, the lowest in the group. This lower value reflects the different fluid-mineral Cu isotope fractionation systematics for chalcopyrite compared with digenite-bornite. As the digenite-bornite in this sample has replaced chalcopyrite it is likely the isotopic signature has shifted to lower values by approximately 0.4 ‰ (Larson et al. 2003). Adding 0.4 ‰ to the digenite-bornite value results in a signature of 0.68 ‰ which is very similar to the corresponding sericite-rich sample that has a chalcopyrite-rich sulfide assemblage.

5 Discussion

5.1 Relationship between hydrothermal fluid type and variations in copper isotope signature

Oxygen and H isotope data together with temperatures estimated from fluid inclusion data have been interpreted to characterize the fluids that formed each of the hydrothermal alteration assemblages at Pebble (Gregory 2017). The calculated δ18O values for fluids related to alteration minerals in each sample are plotted against the measured δ65Cu values for the Cu sulfide mineral in each sample in order to understand how changing fluid compositions relate to Cu isotope fractionation (Fig. 1).

Samples from the sodic-potassic, potassic and some illite alteration assemblages plot to form a linear array in δ18O-δ65Cu space (trend 1 on Fig. 1). The negative correlation shows that lighter δ65Cu values are related to heavier δ18O values typical of magmatic fluids and heavier δ65Cu values are related to lighter δ18O values associated with meteoric fluid. The array represents a mixing line between the two fluid sources in terms of δ18O values. The same interpretation cannot be used for the δ65Cu values because all the chalcopyrite originally precipitated from the magmatic fluids and has been dissolved and reprecipitated in samples where the host rock underwent significant illite alteration.

The change in the Cu isotope signature between the sodic-potassic and potassic samples can be interpreted to represent the fractionation of Cu isotopes between the magmatic fluid and precipitating chalcopyrite during cooling. The first chalcopyrite that precipitated at ~400°C from this fluid occurs in the sodic-potassic sample which has the heaviest δ18O value, and therefore the most magmatic signature, and the chalcopyrite has a δ65Cu value of -2.09 ‰. The two potassic samples represent the cooling of magmatic fluid through ~375°C where the δ65Cu signature of the fluid evolves to heavier values due to Rayleigh fractionation between the fluid and precipitated chalcopyrite (δ65Cuchalcopyrite values of -1.01 and -0.65 ‰). Based on this data, the lighter δ65Cu isotope is preferentially incorporated into the chalcopyrite. The fluid-chalcopyrite isotopic fractionation factor (Δ65Cufluid-chalcopyrite) is approximately 0.4 ‰, based on a Rayleigh fractionation model for the sodic-potassic and potassic sample data.

Theoretically, all the samples on the linear trend 1 (Fig. 1) contain chalcopyrite that was originally precipitated from magmatic fluids, and therefore it is assumed to have had original δ65Cu values of less than approximately -0.5 ‰. The illite overprint on some of these samples has resulted in isotopic re-equilibration of this δ65Cu signature, suggested by δ65Cuchalcopyrite values between 0.14 and 0.82 ‰. It is unlikely that these Cu isotopic values are a function of the same Rayleigh fractionation processes discussed above because signatures greater than 0.14 ‰ occur when there is less than 2% of the total Cu left in the fluid and therefore should be very low grade. However, these illite-altered samples are from the core of the mineralized zone where the majority of Cu was deposited.

Figure 1. Plot of δ65Cu data for copper sulfide minerals and δ18O data for hydrothermal fluids in equilibrium with silicate minerals. Open triangle represents measured δ65Cu value for bornite-rich sample; 0.4 ‰ has been added and point plotted as a filled triangle so it can be compared with other data.
Illite alteration at Pebble results from a fluid formed by the mixing of a magmatic vapor phase and meteoric fluid (Gregory 2017). Different stages of illite alteration can be distinguished based on the relative amount of magmatic vapor present in this mixture. Based on the O and D data presented in Gregory (2017), the three illite alteration samples that lie on the same trend as the magmatic samples (trend 1 in Fig. 1) all interacted with a fluid that had a significant proportion of magmatic fluid and represent alteration that has overprinted potassic alteration resulting in a stable mineral assemblage of quartz-K-feldspar-illite. This fluid is interpreted to have evolved to heavier $^{65}$Cu isotope based on the Rayleigh fractionation trend observed in the sodic-potassic and potassic altered samples. In theory the vapor fraction that is mixing with the meteoric water is the same fluid that originally precipitated chalcopyrite during the earlier magmatic alteration. This mixed fluid is assumed to have a low Cu content at this point in the evolution as it has already deposited most of its original Cu. As this fluid flowed back into the core of the deposit it dissolved and locally remobilized the pre-existing chalcopyrite (Gregory 2017).

The data suggest that isotopic exchange has occurred between the magmatic chalcopyrite and the illite alteration fluid resulting in heavier $^{65}$Cu isotope signatures in the newly formed chalcopyrite. There is no evidence that the Cu grade of illite altered mineralization has increased, rather it is found to slightly decrease (Lang et al. 2013). Therefore, during the dissolution and reprecipitation of the chalcopyrite the hydrothermal fluids have removed some Cu and the isotopic data presented here suggests that it is the lighter $^{63}$Cu isotope that is being removed generating heavier $^{65}$Cu chalcopyrite values. This is consistent with the findings of Maher et al. (2011) who reported that hydrothermal fluids at temperatures between 250 and 300°C and pH of 4-7, very similar to the hydrothermal fluids responsible for illite alteration at Pebble, preferentially leached the light Cu isotope from chalcopyrite resulting in up to -1 % fractionation.

Overall, the linear trend is reflecting the coupled process of Rayleigh fractionation between chalcopyrite and a magmatic fluid and Cu leaching by meteoric-rich fluids. The lower the $\delta^{18}$O value, the larger the proportion of magmatic water in the hydrothermal fluids, the greater the degree of dissolution and Cu leaching resulting in progressively increasing $^{65}$Cu values of the chalcopyrite.

Two samples of illite-rich alteration plot above trend 1 at higher $^{64}$O values consistent with a fluid dominated by magmatic vapor with no meteoric input (Fig. 1). Based on the above discussion, the absence of meteoric fluid input suggests there was no leaching of $^{63}$Cu and these samples plot at slightly higher $^{65}$Cu values of -0.33 and -0.11 % which is only just above the values for potassic altered samples. These samples are characterized by low Cu grades on the periphery of the deposit with sulfide textures dominated by the replacement of chalcopyrite by illite-sericite. Based on the Rayleigh fractionation model the Cu isotope signatures for these samples are consistent with a fluid that has deposited 95% of its Cu in agreement with the location on the deposit margin. Compared with the three illite-altered samples related to meteoric-rich fluids, the silicate assemblage in these two samples is dominated by quartz and illite-sericite and an absence of K-feldspar suggesting the alteration took place at lower, more acid, pH conditions. The experiments of Maher et al. (2011) showed that there was limited to no measureable fractionation of Cu isotopes during leaching of chalcopyrite by fluids at pH conditions lower than 4, and this could explain the limited shift in isotopic signature.

### 5.2 Reversal in copper isotope correlations

Results from the advanced argillic alteration zone samples do not plot on the negative linear array discussed above, but instead plot above the main array, and have heavier Cu isotopic values (Fig. 1). As one sample is dominated by bornite-digenite (0.28 %; open triangle on Fig. 1), in order to compare it directly with the other samples that are all chalcopyrite dominant, the fractionation factor between chalcopyrite and bornite of 0.4 % has been added to the measured value (0.68 %; filled triangle on Fig. 1) (Larson et al. 2003). Three of the four samples from the advanced argillic alteration plot on a horizontal to weakly positive array (trend 2 on Fig. 1). The fourth sample plots above this array at higher $^{65}$Cu. The samples plot across a range in $\delta^{15}$O values with sericite-rich samples at high $\delta^{15}$O signatures consistent with a magmatic fluid and pyrophyllite-rich samples at lower $\delta^{15}$O values consistent with meteoric fluid mixing with magmatic fluids. The absence of a significant change in $\delta^{65}$Cu values (excluding the high $\delta^{65}$Cu sample) across a large range in $\delta^{15}$O values is very different to trend 1, and although there are too few samples to draw strong conclusions, the data suggest a significant change in Cu isotope fractionation behavior during sodic-potassic, potassic and illite alteration compared with advanced argillic alteration.

Advanced argillic alteration resulted from a second pulse of magmatic fluid (Gregory 2017). Graham et al. (2004) showed that the Cu isotope signature became heavier with each successive intrusion in the Grasberg porphyry Cu-Au deposit, suggesting that the Cu isotope signature of the fluid source fractionates as the magmatic system evolves. At Pebble, the advanced argillic-related mineralization has a heavier Cu isotope signature than the initial mineralization related to sodic-potassic and potassic-alteration, at the same $\delta^{15}$O values. This suggests the offset in Cu isotope values from the main linear trend 1 may be the result of a change in the source Cu isotope signature.

The O and D data suggest that magmatic fluids generated sericite-rich alteration, and mixed magmatic-meteoric fluids formed pyrophyllite alteration. As the fluids responsible for the alteration and mineralization evolve from magmatic to meteoric, recorded by decreasing $\delta^{15}$O values, the corresponding Cu isotope signatures evolve to slightly lower $\delta^{65}$Cu values. The three points on trend 2 can be modeled assuming Rayleigh fractionation with a fluid-chalcopyrite isotopic fractionation factor ($\Delta^{65}$Cu fluid-chalcopyrite) of -0.05 %.
The sample of pyrophyllite-rich alteration that sits off the trend at higher $\delta^{65}$Cu values has a sulfide texture characterized by replacement of chalcopyrite by pyrophyllite. This texture together with the heavy $\delta^{65}$Cu signature is consistent with leaching of $^{65}$Cu by the mixed magmatic-meteoric fluid similar to the interpretation for the illite-rich samples on trend 1, however unlike trend 1 this assemblage formed under highly acidic conditions. These are the conditions that Maher et al. (2011) found were not favorable for significant isotope fractionation.

5.3 Controls on copper isotope fractionation

The results of this study could support the idea that different complexes transporting Cu result in different degrees of Cu isotope fractionation. Fluid inclusion data from Pebble suggests that the magmatic fluids responsible for sodic-potassic and potassic alteration exsolved from a magma as a single phase that underwent separation to form a high salinity brine and low density vapor prior to the formation of the hydrothermal alteration and mineralization (Gregory 2017). Copper was likely transported by and precipitated from both the brine and the vapor (Lerchbaumer and Audetat 2012; Seo and Heinrich 2013). The fluids responsible for illite alteration are interpreted to be dominated by the vapor that has mixed with meteoric water and interacted with the sodic-potassic and potassic-altered wallrock (Gregory 2017).

Pokrovski et al. (2008) found that the complex transporting Cu in a given fluid phase varies due to liquid-vapor partitioning and pH conditions. Copper in a liquid phase is transported as CuCl$_2^-$ under acidic conditions and as Cu(HS)$_3^-$ under alkaline conditions. In the vapor phase Cu is transported as CuHS$^0$ (Pokrovski et al. 2008). Therefore, at Pebble during sodic-potassic, potassic and illite alteration it is likely that Cu was transported as CuHS$^0$ in the vapor phase and, where present, as CuCl$_2^-$ and/or Cu(HS)$_3^-$ in the brine depending on pH.

The hydrothermal fluid responsible for the advanced argillic overprint at Pebble was a low salinity, single phase magmatic-meteoric fluid similar to the interpretation for the advanced argillic alteration fluids. Therefore, it is postulated that sulfur complexes are most important in transporting Cu in sodic-potassic, potassic and illite alteration fluids, especially the CuHS$^0$ species, and chloride complexes (CuCl$_2^-$) dominate Cu transport in advanced argillic alteration fluids.

Overall, the data suggest there is significant Cu isotope fractionation between the sulfide species and precipitating chalcopyrite under neutral pH conditions compared with the chloride species and precipitating chalcopyrite under acidic conditions where there is limited fractionation.

6 Conclusions

Variations in Cu isotope data in the Pebble porphyry deposit can be linked to changes in pH conditions and Cu speciation during hydrothermal alteration. Initial hydrothermal fluids at Pebble dominantly transported Cu as CuHS$^0$ and resulted in near neutral hydrothermal alteration assemblages. Chalcopyrite in these assemblages has Cu isotope signatures that evolve towards heavier $\delta^{65}$Cu values consistent with positive fluid-chalcopyrite fractionation factors. Subsequent hydrothermal fluids that resulted in acidic advanced argillic alteration at Pebble likely transport Cu as CuCl$_2^-$. Chalcopyrite that precipitated from this fluid has Cu isotope signatures that evolve towards slightly lighter $\delta^{65}$Cu values consistent with small negative fluid-chalcopyrite fractionation factors. The pH conditions control the magnitude of the Cu isotope fractionation with large fractionation factors occurring under neutral conditions compared with only limited fractionation occurring under acidic conditions. Therefore, understanding the hydrothermal fluid evolution, likely Cu speciation and the pH conditions during hydrothermal alteration in a deposit is the key to being able to interpret Cu isotope variations in the hypogene mineralization environment.

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References


The origin and evolution of fluids associated with gold deposits in the basement of Sulawesi, Indonesia

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Abstract. The gold deposits in the Latimojong Metamorphic complex are mainly hosted by metasedimentary rocks. The conditions of ore formation are estimated from fluid inclusion microthermometry, crush-leach analyses on bulk samples and Raman spectroscopy on carbonaceous materials. The fluid inclusion assemblages are dominated by moderately saline H2O-rich fluids with minor aqueous-carbonic (CO2) inclusions. Fluid inclusions in quartz veins indicate that the temperature of hematite-quartz and sulfide-sulfosalt quartz veins does not exceed 250°C at 1 kbar pressure. Fluid inclusion assemblages in hematite-quartz veins and sulfide-sulfosalt quartz veins are characterized by a moderate salinity, in average 5.1 and 4.5 eq. mass% NaCl, respectively. Microthermometry from dolomite and barren veins indicates highly variable homogenization temperatures ranging from 165 to 387°C. Crush leach analyses on bulk samples reveal fluid compositions that are probably derived from mixing of different fluid sources. These results are comparable to orogenic gold deposits and give evidence for the influx of meteoric water during late-stage metal precipitation. Raman spectra of organic material in graphitic schist confirm that the region underwent blueschist- to greenschist facies metamorphism, followed by hydrothermal gold precipitation during decompressional uplift. We conclude that gold is retrograde and post-dates regional metamorphism.

Keywords. Latimojong, gold in Indonesia, fluid inclusion, Awak Mas, Salu Bullo, Raman spectroscopy on carbonaceous material

1 Introduction

Gold deposits in metamorphic terrains such as the Awak Mas and the Salu Bullo gold fields are considered one of the main exploration targets in Indonesia. The Awak Mas and the Salu Bullo gold fields are situated in the Latimojong metamorphic complex, part of a Late Cretaceous accretionary complex, situated in South Sulawesi, Indonesia (Wakita 2000). This complex forms the basement of Sulawesi, consisting of thick successions of turbidites, weakly metamorphosed pelitic and psammitic rocks with intercalations of volcanic rocks metamorphosed within the pumpellyite- to greenschist-facies.

Gold in the Awak Mas and Salu Bullo deposits precipitated in oblique normal faults, extensional shears and fractures as well as in the host sediments. Early and late-mineral faulting dominates the structures observed in the deposits, with late-mineralization faults forming the main mineralized vein systems.

Querubin and Walters (2012) distinguished two main styles of mineralization, namely (i) steeply dipping quartz veins and stockwork along pre-mineralization faults and (ii) quartz veins parallel to foliation. Total resources in the Awak Mas and Salu Bullo deposits yield 60 Mt at 1.4 g/t Au, equal to 80 tonnes of gold (One Asia Resources Company report 2016). To date, the role of fluids during gold precipitation has not been studied.

In order to investigate the fluid evolution, eleven boreholes from the Salu Bullo and Awak Mas gold fields covering a sequence of mineralized and barren veins and host rock were studied by crush leach and microthermometric analysis. Furthermore, Raman spectroscopy was carried out to constrain the compositions of the gas phase in fluid inclusions and the crystallinity of carbonaceous materials.

2 Samples and analytical methods

The main rock types encountered in the area comprise phyllite, mica or graphitic schist, metabasite, metatuff and metavolcanic rock with disseminated sulfide mineralization. Samples from veins and host rock were collected from outcrops and eleven boreholes.

Microthermometric studies were carried out in quartz and dolomite because most inclusions in abundant hydrothermal albite occur as clouds of irregular and small inclusions (< 5µm). Selected quartz and carbonate samples were crushed and distilled for crush leach analysis, as described in Banks and Yardley (1992). Carbonaceous materials from graphitic schist were separated chemically from all other mineral phases (Rantitsch et al. 2004). We focus on Raman spectra in the 700-2000 cm\(^{-1}\) region. Numerical analysis of the Raman spectra was performed using the fitting procedure of (Lünsdorf et al. 2014). All analyses were performed at the Montanuniversität Leoben.

3 Results

3.1 Mineralogy

Based on the presence of sulfide-sulfosalts and oxide assemblages, three types of veins were distinguished: (i)
hematite-Au quartz vein, (ii) sulfide - sulfosalt-Au veins, and (iii) barren veins. The main mineral assemblages of hematite and sulfide - sulfosalt veins are hematite + pyrite ± gold and chalcopyrite - tetrahedrite - covellite - famatinite - luzonite ± gold (Fig. 1), respectively. The result of electron microprobe on gold analysis indicate that the Au:Ag ratio is 9:1.

Most of the alteration products are strongly influenced by the host rock composition. Silica, white mica, dolomite and albite alteration are distinguished. Silica alteration is characterized by the replacement of initial minerals by quartz. In metasedimentary host rocks, white mica is the most common alteration. Chlorite and dolomite-ankerite are found in mafic host rocks. Albite alteration is observed in host rocks of all compositions.

![Figure 1](image1.png) **Figure 1.** Replacement of pyrite by luzonite. Gold and galena are disseminated in the pyrite grain.

### 3.2 Microthermometry

Based on the composition of fluid inclusions, three different types are distinguished: low salinity aqueous inclusions with CO₂ (type I), H₂O-NaCl (type II) and H₂O-NaCl containing a solid phase (type-III). Quartz + hematite veins contain all types of fluid inclusions, whereas type-I inclusions are absent in sulfide-sulfosalt and barren veins.

The volume fraction of vapour in type-I inclusions is about 0.14-0.15. The final dissolution of ice (T_m) occurs in a narrow temperature range between -3.6 and -2.8°C, clathrate dissolves at 8.6 and 11.6°C, and liquid-vapour homogenization temperatures range from 146 to 178°C.

Fluid inclusion type II is most abundant. Mineralized veins contain relatively homogenous vapour volume fractions, between 0.10 and 0.20, whereas barren veins have highly variable volume fractions from 0.10 to 0.46. Quartz + hematite veins show a bimodal distribution of dissolution temperatures, ranging from -4.60 to -2.50°C and from -1.80 to -0.80°C, corresponding to a wide range of salinities between 1.4 and 7.3 eq. mass% NaCl. The salinities of sulfide-sulfosalt veins is between 2.1 and 5.9 eq. mass% NaCl. Both homogenize at a temperature <250°C. The dolomite contains exceptional fluid inclusion assemblages with a wide range of vapour volume fractions (0.10 to 0.46), and homogenization temperatures up to 387°C.

Inclusion type-III comprises one or two phase inclusions with a trapped solid phase, identified as quartz, calcite, tourmaline or anatase by Raman spectroscopy.

### 3.3 Crush leach

The ratios of (Na/Cl) versus (Br/Cl) of fluids leached from mineralized and barren veins fall into two groups: (i) Na/Cl molar ratio less than 1.80 with Cl/Br ratio ranging from 1068 to 5433, and (ii) Na/Cl molar ratio higher than 1.80 with Cl/Br ratios restricted between 734 and 2874. Furthermore, barren materials are characterized by Na/Cl and Cl/Br molar ratios higher than 0.68 and lower than 3065, respectively (Fig. 2).

![Figure 2](image2.png) **Figure 2.** Na-Cl-Br molar ratios from the quartz and carbonate veins in the Latimojong are plotted in a diagram proposed by Landis and Hofstra (2012).

### 3.4 Raman spectroscopy on carbonaceous materials

The D₁ band was measured between 1344 to 1354 cm⁻¹, whereas the G band between 1581 to 1600 cm⁻¹. Intensity of D₁ in all samples is higher than the intensity of the G peak. In some samples, peak fitting demonstrates the presence of the D₂ band at ca. 1610 cm⁻¹.

### 4 Discussion

#### 4.1 Fluid evolution

In order to illustrate the fluid evolution, a plot of total homogenization temperature versus salinity was constructed (Fig. 3). Type-I aqueous-carbonic inclusions represent the minimum homogenization temperature (146-177°C), whereas maximum temperatures up to 387°C are recorded in dolomite. Aqueous-carbonic inclusions of type I are rare and overprinted by a later generation of fluid inclusions type-II.

Dolomite contains fluid inclusions with highly variable homogenization temperatures and volume area fractions. Interestingly, microthermometric data of veins are clustered and yield homogenization temperatures lower than 250°C, whereas barren veins scatter considerably (Fig. 3).

In a system with a temperature lower than 350°C, gold
transport is mostly controlled by bisulfide (HS\(^{-}\)) with \(\text{AuHS}^{2-}\) predominating at lower pH and \(\text{Au( HS)}^{2+}\) at higher pH (Gammons and Williams-Jones 1997), whereas at temperatures higher than 350°C, gold mostly occurs as \(\text{AuCl}^{+}\). Considering the homogenization and salinity data, the bisulfide complex is considered as the main ligand for gold transport in the Latimojong Metamorphic Complex.

**Figure 3.** Scatter plot of homogenization temperature versus salinity of mineralized and barren veins.

During early stages of ore precipitation, a relatively small increase of \(f(O_2)\) is inferred to have led to a precipitous drop in HS\(^{-}\) concentration and gold solubility. As a result, deposition of gold was favoured by oxidation and occurs through interaction of the ore-bearing fluid with an iron-bearing host rock (Gammons and Williams-Jones 1997). The evidence of oxidation processes in Latimojong are the precipitation of gold in iron-bearing host rock within pyrite (hematite) - Au quartz veins.

The first ore stage is followed by the precipitation of sulfide-sulfosalt Au veins at moderate salinity, and moderate temperature. Sulfosalt-rich assemblages with minor oxide precipitated in an neutral pH under reducing sulphur conditions, with typical minerals such as tetrahedrite\(_{\text{as}}\), chalcopyrite, covellite and bornite. Barren veins precipitated during and/or after ore precipitation at all stages, suggested by the scattered data obtained from the microthermometric study (Fig. 3).

Isochores of the quartz + hematite, quartz + sulfide - sulfosalt and barren veins were constructed to illustrate \(P-T\) conditions. Trapping conditions of the veins are at 250°C at a maximum pressure of 1 kbar. The barren quartz and dolomite veins records a distinct trapping event at about 400°C at a maximum pressure of 1 kbar.

**4.2 Fluid sources**

\Na/\Cl/Br\ diagrams based on Landis and Hofstra (2012) (Fig. 2) show that the halogen data of Latimojong veins scatter and plot into several fields. This is similar to metamorphic fluids of Phanerozoic orogenic gold deposit, and magmatic fluids of porphyry Cu-Mo deposits with some data shifting into the albitization field. The introduction of sodium through albitization may be regarded as metasomatic alteration during the cooling process and metal deposition.

Using Na/Cl/Br diagrams, data points differ from residual evaporative brines of Mississippi Valley-type (MVT) Pb-Zn deposits; therefore, dissolution or precipitation of halite are considered to be less important factors (Landis and Hofstra 2012) and the fluids in the Latimojong complex are assumed to derive from different fluid sources.

Fluid mixing and interaction controlling gold precipitation were suggested by several workers (Mikucki 1998; Boiron et al. 2003). Mikucki (1998) suggested that ore depositional mechanisms in Archean lode-gold systems likely vary with crustal depth. With decreasing depth of formation, phase separation and fluid mixing appear as most important gold precipitation mechanisms, rather than fluid-rock interaction and wallrock sulfidation. Boiron et al. (2003) also discuss the role of fluid mixing in Hercynian gold systems in western Europe, which show the contribution of shallow and deep-seated fluids, similar to those in the Latimojong Complex.

**4.3 Formation temperature**

The transformation of carbonaceous material to graphite is illustrated by Raman spectra on carbonaceous materials (RSCM) in response to rising metamorphic conditions. With increasing structural order, the G and D2 peaks are clearly distinguishable. Our Raman data are comparable to lower greenschist-facies metamorphic samples (Rantitsch et al. 2016) and a blueschist facies metamorphic sample from Western Alps (Beyssac et al. 2002). Formation temperature calculations using equations from IFORS software suggest that the metamorphic conditions vary between 316 to 395 °C (+ 39°C) (Lünsdorf 2015).

Interestingly samples containing ore minerals yield higher temperatures than barren samples.

**5 Discussion**

It is important to note that gold veins in the Latimojong Complex are dominantly associated with metasedimentary rocks. Host rocks are metamorphosed within the pumpellyite to greenschist facies. High pressure and moderate temperature were reached during NW –directed subduction in the Late Cretaceous (van Leeuwen and Muhardjo 2005). These rocks were subsequently deformed and uplifted above sea level. This may have been associated with the obduction of Eocene-Oligocene back-arc rocks (Lamasi Complex) (White et al. 2017).

Pitcairn et al. (2015) studied the effects of increasing metamorphic grade on the concentration of Au and related elements (As, Sb, Se and Hg) in metabasaltic samples from the Otago and Alpine schist of New Zealand. The results show that metasedimentary rocks are much more
suitable source rocks for fluids and metals in orogenic gold deposits than metabasaltic rocks as they show mobility during metamorphism of all elements commonly enriched in this style of deposit. Large et al. (2011) consider that carbonaceous metasedimentary rocks are required to form large deposits in metasedimentary host rocks (Carlin-type and orogenic gold deposits). Gold and arsenic were introduced early into black shale and turbidites during sedimentation and diagenesis, later concentrated to ore grades by hydrothermal, structural or magmatic processes.

It is proposed that the greenschist metamorphism was responsible for the element mobility, which resulted in the enrichment of Au and related elements (As-Sb-Hg) in the veins within the Latimojong Metamorphic Complex. A thick carbonaceous metasedimentary rock in this region may be regarded as the source of metals. Although the sulfosalt mineralogy indicates a component of high sulfidation state mineralization, however, epithermal alteration mineral assemblages (e.g. alunite, barite, kaolinite, diaspore, pyrophyllite, etc) are absent. The deposit is characterized by low-silver content (Au:Ag ratio is 9:1), which does not support an epithermal model. Furthermore, veins are hosted in a thick package of metasedimentary rocks and minor volcanic rocks post-dating mineralisation. The fluid inclusion results from single inclusion and bulk samples record multiple pulses of H$_2$O-rich, moderately salinity, oxidized and reduced fluids.

6 Conclusion

Fluid inclusion data from the Latimojong Complex show that the fluids are composed of H$_2$O-NaCl-CO$_2$ (type-I), H$_2$O-NaCl (type-II) and aqueous inclusions with daughter minerals (type-III).

Crush-leach analyses on quartz and carbonate underline that the fluids were derived from various sources, including a deep-seated fluid with some addition of meteoric water. Fluid mixing appears to be the most important factor of gold precipitation.

Formation temperatures calculated from carbonaceous materials indicate that the region was metamorphosed to blueschist- to greenschist-facies. The deposit post-dates the regional metamorphism.

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Hiekkapohja ore showings in Paleoproterozoic Central Finland Granitoid Complex - a Hydrothermal System?

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Abstract. Porphyritic Cu-Mo mineralizations can be found in modern and old convergent plate-tectonic settings. They are more abundant in younger successions than in older, oldest know economical deposits of this type are Paleozoic. In the Fennoscandian shield, the largest deposits proposed to be porphyritic origin is Aitik in Northern Sweden located in volcanic succession and related to quartz monzonite intrusions. Paleoproterozoic Central Finland Granitoid complex (CFGC) can be considered as a potential host for porphyry type deposits, as it formed in convergent setting and is volumetrically dominated by granitoids. So far only the Kopsa deposit in western CGFC has been properly studied, although several indications and potential areas are known. One being the Hiekkapohja area, where small high grade mineralizations (Zn, Pb, Cu, Ag, Au) and mineralized boulders with unknown sources are known from a geographically constrained area.

1 Geological setting

Bedrock of Central Finland was formed during the Paleoproterozoic Svecofennian orogeny, during which volcanic arcs amalgamated with the Archean Karelia craton (eg. Nironen 1997; Lahtinen et al. 2005). Oldest Svecofennian rocks are found north of the CGFC and they are 1.93–1.91 Ga in age. The main phase of the orogeny occurred at 1.89–1.87 Ga, rocks of this age include arc volcanic rocks and granitoids, which of two most voluminous groups are synkinematic and younger postkinematic groups (Nironen 2005). The first has arc type geochemical signature and the latter displays A-type affinity. Although the age differences are clear in the field, based on the age determinations the two types overlap in age as available age determinations cluster at 1.88 Ga. Third, less voluminous granitoid group is formed by leucogranitoids interpreted as small degree partial melts of pre-existing crust. Rocks belonging to this group typically yield ages close to 1.875 Ga (Mikkola et al. 2016). The sedimentary-volcanic sequences in the area show geochemically arc type characteristics A significant feature of CFGC are crustal scale shear zones, which can be divided to three age groups, which are from oldest to youngest; 1) 20°-40° trending, 2) 120°-135° trending, and 3) 0° trending. Group 1 could be related to extensional or transtensional stage (Mikkola et al. 2016).

2 Results

2.1 Hiekkapohja area observations

In the Hiekkapohja area a ca 9 x 4.5 km local aeromagnetic low (Figure 1) is observable in an area dominated by typical variably deformed K-feldspar porphyritic granites of CFGC, age of which is 1882±4 Ma (Mikkola et al. 2016). On the west side of the aeromagnetic low is a porphyritic granite variant with two cross-cutting unfoliated granitic hypabyssal dykes (max. width 130 m). In the northern part of the aeromagnetic low two round intrusions, less than 1.3 km across are known. Age of these unfoliated, evengrained pale grey granite intrusions, referred to as Soimavuori type, is 1879 ± 4 Ma. Based on field observations Soimavuori type intrusions cross-cut the surrounding porphyritic granite could be the youngest intrusions in the area. It is readily observable on the geophysical map that the magnetic low is transected by a large scale dextral fault belonging to the 120°-135° trending group.

Both target scale ore prospecting and more general mineral potential mapping has been carried out in the Hiekkapohja area, the first in 1980s and latter in the recent years. Mineralizations and ore showings contain variable combinations of the following elements: Cu, Mo, Zn, W, Ag, As and Au. The highest concentrations reported for 1 meter drill core sample are: Cu 0.7 %, Zn 230 ppm and Ag 17 ppm (Ikävalko et al. 1986). This sample is from the Ruutamäki mineralization located in conjugant shears of the major 120°-135° trending shear system. Highest concentrations from boulder/outcrop samples are: Cu ≤7.7 %, Zn ≤ 6.7%, Pb ≤ 8%, Ag ≤500 ppm, Au ≤1 ppm (Figure 2).

Samples enriched in Au and As most often coincide with the outermost parts of the aeromagnetic low, forming a ring structure. Ag-Zn-Pb showing concentrate closer to the centre of the aeromagnetic low, whereas Cu and the few known Mo showings occur in the middle of the aeromagnetic low. The boulder samples support the observations made from outcrop showings, albeit it is based on average glacial transport in the area (Figure 1).
2.2 Geochemistry of granitoids

All of the granitoids are calc-alkalic to alkali-calcic and ferroan showing I-type composition. The dominant porphyritic granite in the area is compositionally similar to other parts of CFGC. The younger Soimavuori type is enriched in from K₂O (~5 wt. %) and SiO₂ (~75 wt. %). In respect to main elements the hypabyssal dykes do not differ significantly from the other granitoids, despite the fact that its REE pattern is almost flat [(La)ₙ =17.4 and (La/Lu)ₙ = 1.7]. At this stage it is unclear if this peculiarity is due to later alteration or if it represents original composition. Based on geochemistry as well as field observations we propose that Soimavuori belongs to the typical younger leucogranitoid group (Mikkola et al. 2016).

2.3 Ore mineralogy observations

The mineralized boulder samples include granitoids, volcanic rocks and altered samples whose protholith(s) cannot be recognised. The ore mineralogy doesn’t correlate with the host rock. Almost all outcrop and boulder samples contain arsenopyrite, sphalerite, chalcopyrite, and pyrrhotite as well as galena, magnetite and pyrite as minor amounts (Figure 2). In microscope studies ore minerals display evidence for multiple events that are not in line with textbook evolution of epithermal porphyritic deposits, but more likely represent several events of hydrothermal activity. Most typical is alternation of pyrrhotite and pyrite to marcasite during cooling (Figure 3; Halonen 2015).

3 Prospecting

Geochemical study of basal till was executed in central part of the aeromagnetic low. Based on this sampling significant mineralizations are unprobable in Hiekkapohja area (Heilimo and Niemi 2015).

4 Summary

As based on bedrock mapping the aeromagnetic low in the Hiekkapohja area does not correlate with lithological boundaries it must be a younger feature unrelated to the original rock forming events. We propose that fluids released from Soimavuori type intrusions during their crystallization could have hydrated the overlying granitoids, and altered the magnetite to hematite. The same fluids could have caused the small scattered mineralizations. The mineralization processes concentrated in existing fractures, possibly due to limited fluid flux. The observed ring structure of the mineralizations is typical for porphyrite systems. Alternatively the mineralizations could
be linked only to the fault system in the area, but as similar faulting and host rocks occur over the whole CFGC this does not explain the concentration of the mineralizations in Hiekkapohja area. Based on till geochemical studies it is relatively certain that Hiekkapohja area does not host significant porphyry type deposits, at least in current erosion level. However it demonstrates the potential for such deposits within the CFGC.

References


Gold-porphyry mineralization of the Toupugol-Khanmeyshorsky ore district (the Polar Urals, Russia): geochronology and geological controls on ore genesis

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Abstract. The paper presents the geological characteristics of the Toupugol-Khanmeyshorsky ore district, including results of satellite imagery analysis and precise U-Pb zircon geochronology on the host intrusive rocks. Geological, morphostructural, basin and facies analyses were used in reconstructing of the Novogodny volcanic dome structure. Regional-scale controls on gold mineralization include concentric and arcuate faults crosscut by NE- and NW-trending radial lineaments. Gold porphyry mineralization, including the Petropavlovskoe deposit, is associated with subvolcanic porphyry diorite bodies preferentially located at the intersection with the radial faults. The pre ore to ore-associated, diorite-dominated second phase of the Sobsky intrusive complex is precisely dated at 410 ± 2 Ma. Zircons from gabbro sill of the Novogodnee-Monto deposit and lamprophyre dikes of the Malohanmeysky complex are dated 256 ± 5 Ma and 248 ± 7 Ma respectively.

1 Introduction

The Toupugol-Khanmeyshorsky ore district is located in the Polar Uralian region, ~ 40 km to the north of the Salekhard city. The ore district includes two gold deposits and series of ore occurrences. The Novogodnee-Monto gold-magnetite-skarn deposit (Soloviev et al. 2013) with 7 t of Au was discovered in 1995. The Petropavlovsk gold-porphyry deposit was discovered in 2005 (26 t Au).

2 Geological setting

The Toupugol-Khanmeyshorsky ore district is a large volcano-tectonic structure. It is located in the northeast of the Malouralsky volcano-plutonic belt (Fig. 1).

The ore district comprises a variety of volcano-sedimentary rocks (the basalt-andesite-basalt series) (Fig. 2). The ore host rock complexes are characterized by interlayering of volcano-sedimentary rocks with basalt and andesite-basalt flows. These rocks are intruded by three plutonic complexes: the Sobsky (Early Devonian-Eifelian), the Kongorsky (Late Devonian – Early Carboniferous), and the Malohanmeysky (Triassic?) ones (Zyleva et al. 2014).

Hydrothermal and metasomatic alterations include skarnification, albitization, beresitization, silicification, and propylitization. Gold-rich mineralization (2–3 ppm of Au) is accompanied by the quartz-sericite beresite-like alteration zones. Skarn-magnetite bodies are characterized by low gold grade (~ 1 ppm of Au).

Skarn-magnetite (the Novogodnee-Monto deposit) and gold-porphyry (the Petropavlovskoe deposit) mineralization are dominant in the Toupugol-Khanmeyshorsky ore district with minor Cu, W, Mo mineralization.

Fe-Au mineralization is abundant because of mafic component predominance in the basement of the Malouralsky volcano-plutonic belt (Ozherel’eva et al. 2014).

3 Methods

Spectrozonal satellite imagery Landsat 8 (ground resolution 30 m, 35,000 m² area, and 3-channel RGB raster) was used in the process of decoding. The geological, morphostructural (satellite imagery and topographic base); basin and facial analyses were used in reconstructing of the Novogodny volcanic dome structure. We cannot use geological-structural field analyses because of bad outcropping.

Precise U-Pb (LA-ICP-MS) zircon geochronology on the host intrusive rocks in the Geological Institute of Siberian Branch of the Russian Academy of Sciences, Ulan-Ude city using magnetic-sector mass spectrometer Thermo Scientific Element XR and laser ablation system UP-213, New Wave Research (method see Khubanov et al. 2016). The criteria for selection of valid analysis were discordance range (D) from –10 to 10.

4 Decoding of satellite imagery and the predication of the gold mineralization

Major oval structure of the central type (6 x 10 km) and
small ring structures were decoded in ore district using satellite imagery analysis (Fig. 3). The major structure was reconstructed as paleovolcanic edifice (the Novogodny volcanic dome structure).

Figure 2. The schematic geological cross-section through the Toupugol-Khanmeyskoy ore district (modified from TsNIGRI and Yamalzoloto companies): 1 – volcano-sedimentary rocks (Late Silurian – Middle Devonian); 2 – marbled limestone; 3 – andesite-basalt porphyry; 4–5 – the Sobsky complex (Early – Late Devonian): 4 – second phase: micro gabbro, quartz diorite, tonalite, plagiogranite, 5 – third phase: quartz diorite porphyry, tonalite-porphry, plagiogranite-porphry; 6–8 – the Malohanmeysky complex (Triassic?): 6 – gabbro; 7 – lamprophyre dolerite, and basalt dike; 8 – montsodiorite porphyry dike; 9 – epidote-garnet-pyroxene skarn; 10 – magnetite ore body; 11 – zone of gold-quartz-sulphide mineralization (gold grade > 0.3-0.5 ppm); 12 – contour of the predicted gold-sulphide-quartz mineralization; 13 – drill holes.

Figure 3. a Interpreted satellite imagery for the eastern slope of the Polar Urals. b Interpreted satellite imagery for the Toupugol-Khanmeyskoy mineral district: 1–3 – lineaments: 1 – arc; 2 – concentric; 3 – radial; 4 – probable radial morphological structure under of thick cover of Cenozoic sediments of the West Siberian plate; 5 – the contour of the Toupugol-Khanmeyskoy ore district; 6–9 – gold occurrences: 6, 7 – deposits; 8, 9 – ore occurrences (6, 8 – gold-quartz/porphry type, 7, 9 – skarn-magnetite type with gold); 8 – subvolcanic bodies of diorite porphyry according Pryamonosov et al. (2001).

The Novogodny paleovolcanic structure (morphological structure of the central type) is consists of ring, arcuate, and radial elements. Ore deposits and occurrences are located in the central part of this structure.
Large ring and arcuate structures were formed in the relation with subcrustal activation of magmatism and represent burial volcanic structure. Structures less than 5 km in diameter are traced supraintrusive zones of subvolcanic bodies.

We used morphostructural analysis for the prediction of radial faults (visual inspect of the hydrographic network and relief by maps, distribution of water races and lineaments and satellite imagery, and the correlation with a geological maps). Decoded radial zones are a long length ~ 15 km (structures are the 1st orders). They correspond to the basement faults. Ore deposits and occurrences of ore district are associated with radial faults of NE and NW directions. They are structures of the 2nd order. These morphostructures are decompression zones.

The ore district mineralization is controlled by permeable zones of the Earth's crust. Therefore, ore-controlling role of these morphostructures is very important. Structural control of mineralization consists of two aspects: tectonic and volcanic. Tectonic control indicate that mineralization belongs to specific combinations of ring structures and lineaments. Volcanic control indicate that mineralization corresponds to paleovolcanic structures and subvolcanic bodies.

5 The results of U-Pb (LA-ICP-MS) dating of zircons of intrusive complexes

U-Pb dating of 40 individual zircon crystals (45 analyzes) from diorite of the second phase of the Sobsky plutonic complex revealed the ages from 2,860 Ga to 385 Ma. The results of 30 analyzes are clustered with concordant age 410 ± 2 Ma (2, MSWD = 3.4). These results are probably corresponded to the real time of diorite formation. Ages of single zircons are constituted 450 ± 6,494 and 2,860 ± 24 Ma.

Zircons (40 crystals, 45 analyzes) from microgabbro sill revealed a wide range of ages from 239 to 2,623 Ma. The concordant age of two grains was 256 ± 5 Ma (26, MSWD = 0.046). These results are probably corresponded to the time of microgabbro formation.

Zircons (37 crystals, 38 analyzes) from lamprophyre dikes revealed a wide range of ages from 245 to 2,643 Ma. The two youngest zircon grains calculated concordant age is 248 ± 7 Ma (26, MSWD = 0.046). This time corresponds to intrusion of lamprophyre dikes at the Novogodnee-Monto deposit.

6 Paleovolcanic reconstruction of the Novogodnny structure

Paleovolcanic reconstruction of the Novogodnny dome structure revealed three stages: Late Silurian, Early Devonian – Eifelian, and Givetian – Late Devonian.

Stage one (Late Silurian). The Novogodnny ore field territory was an active submarine volcanic zone with basalt-andesite-basalt series accumulation. The large complex diorite massif (first phase of the Sobsky complex) was formed. Sediments were accumulated on the flanks of the Novogodnny volcano synchronously with the volcanism.

Stage two (Early Devonian – Eifelian). Volcanic activity was reactivated after short interruption. The composition of lavas and tuffs was changed to andesite-basalt.

New portion of the diorite melt was intruded (second phase of the Sobsky complex) at this time. Skarn-magnetite mineralization was formed (the Novogodnee-Monto deposit) as the result of high-temperature post-magmatic fluids interaction with limestone and carbonate-bearing rocks. Processes of skarnification were manifested at the Petropavlovskoe deposit (southern part of deposit) locally (because of rarity of carbonate rocks) with skarn-magnetite formation associated with the 2nd phase the Sobsky intrusive complex.

Stage three (Givetian – Late Devonian). At this time volcanic activity is attenuated. The territory of the ore district is occupied by the shallow internal pool. Quartz diorite porphyry and zones of gold-sulphide-quartz mineralization (thin gold-sulphide-quartz veins and streaks) were formed in the Late Devonian because of intruding of the third phase of the Sobsky complex.

Disseminated gold mineralization was superimposed onto skarn-magnetite mineralization (the Novogodnee-Monto deposit). The radiometric age of micas from Au-bearing sericite–quartz–carbonate-pyrite veins crosscut the lamprophyre dikes at the Novogodnee-Monto deposit (Rb–Sr data is 360±1.3 Ma according to data of Volchkov et al. (Soloviev et al. 2013).

Gabbro sill and lamprophyre dikes of the Malohanmeysky complex (Triassic?) were the final manifestations of magmatism. Bodies of this intrusive complex intersect all magmatic, and hydrothermal-metasomatic complexes, as well as the gold ore bodies.

7 Significance of the Petropavlovskoe deposit

The Petropavlovskoe gold-porphyry deposit is a new type of gold deposits in the Northern-Polar Urals region. The Petropavlovskoe deposit is ascribed to gold-porphyry type on the basis of following features: the deposit pertains to polygenetic and polychronous isometric volcano-tectonic structure with porphyry bodies and mineralization confined to the centers of large concentric ring structures; the host rocks are subvolcanic porphyry diorite (including subalkaline ones) stocks; gold-skarn-porphyry and gold vein mineralization occur in close spatial association; both mineralization types are related to the Sobsky complex; the mineralization was found in zones of hydrothermal alteration (albititization, biotitization, epidotitization, silicification); the ore bodies have the complex stockwork-like morphology and low Au content (~ 1.4 ppm); mineralization occurs as rare scattered impregnations and thin veins of sulphide (mainly pyrite) or quartz-sulphide; stable complex of main opaque (predominant pyrite and minor magnetite and chalcopyrite) and non-metallic minerals (quartz, carbonate, sericite, chloride); Au is mainly observed as native gold, forming nanosized and finely-dispersed grains; according to LA-ICP-MS the Au contents in the pyrite ranges from 0.03 to 50 ppm (Vikenetiev et al.)
2016); diverse telluride mineralization (hessite, petzite, altaite).

The closest analogue of the Petropavlovskoe deposit among the other gold-porphyry deposits of the world is the Lobo deposit in the Maricunga belt of Chile (Muntean and Einaudi 2001; Conca et al. 2014).

8 Conclusions

The Toupugol-Khanmeyskory ore district is polygenetic and polychronous (Late Devonian-Early Carboniferous) volcano-plutonic structure of the central type. It belongs to the Malouralsk volcano-plutonic belt. Gold-porphyry mineralization in the ore district is confined to the intersection zones of concentric or arcuate faults crosscut by NE- and NW-trending radial lineaments of various ranks and to the clusters of small ring structures.

Gold porphyry mineralization is associated with subvolcanic porphyry diorite bodies preferentially located at the intersection with the radial faults.

We distinguished three stages of the Novogodnensk paleovolcano formation: Late Silurian, Early Devonian – Eifelian, and Givetian – Late Devonian. Gold-sulphide-quartz mineralization was related to the third phase of the Subsky complex (Early Devonian-Eifelian).

The pre-ore ore-associated, diorite-dominated second phase of the Subsky intrusive complex is precisely dated at 410 ± 2 Ma (the Petropavlovskoe deposit). Zircons from gabbro sill of the Novogodnee-Monto deposit and lamprophyre dikes of the Malohanmeysky complex are dated at 256 ± 5 Ma and 248 ± 7 Ma, respectively (the Novogodnee-Monto deposit).

Variations in zircon ages of plutonic rocks indicate that the basement of the Malouralsky island arc had a heterogeneous structure in the Early Devonian time and included Silurian, Cambrian, Neoproterozoic, and Mesoarchean complexes.

The Lobo deposit (Chile) is the closest analogue of the Petropavlovskoe deposit.

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Geology, fluid inclusion, and stable isotope constraints on the mineralization of the Nuocang skarn Pb-Zn polymetallic deposit, western Gangdese, Tibet

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Abstract. The Nuocang Pb-Zn polymetallic deposit is located in the Linzizong volcanic area of western Gangdese, Tibet, China. Three types of fluid inclusions including type L, type V, and type S have been discussed in the Nuocang deposit. The ore-forming fluids evolved from moderate to high temperature and moderate to high salinity in the pre-ore stage through low to moderate temperature and low salinity in the syn-ore stage, and to low temperature and low salinity in the post-ore stage. The δ34S CDT values of −0.6 to 2.7‰, and 206Pb/204Pb, 207Pb/204Pb, 208Pb/204Pb values of 18.629 to 18.738, 15.646 to 15.793, and 38.907 to 39.340, respectively, indicate the ore-forming materials are dominantly derived from an upper crustal source mixing with minor amounts of mantle–derived components from the subducted slab of Neo-Tethys. The calculated δD H2O and δ18O H2O values of the gangue minerals in different ore-stages range from −180 to −106‰ and from −8.6 to 3.0‰, respectively, suggesting the original fluids was magmatic hydrothermal. Significant addition of meteoric water to the magmatic-hydrothermal system considered to be responsible for metal deposition. Locally, boiling has also been considered as another mechanism for ore precipitation in the Nuocang hydrothermal system.

1 Introduction

Skarn deposits have long been studied by many researchers (e.g. Meinert et al., 2003; Meinert et al., 2005). However, controversies still exist, regarding whether ore-forming materials originate from magmas, a mixing of intrusive and sedimentary rocks, or from the local wall rocks. The related controversy of ore-forming fluids sourced from magmatic or meteoric sources is still debated, as a result of the mixing, or boiling. This paper discussed possible ore-forming processes and fluid sources for the Nuocang Pb-Zn deposit in western Gangdese, based on fluid inclusion and H-O–S-Pb isotopic data.

2 Geology

The recently discovered Nuocang Pb-Zn polymetallic deposit is located in the Linzizong volcanic region of the western Gangdese belt, Tibet (0.2 Mt at 5.36% Zn, 4.26% Pb, 0.26% Cu, and 70.8 g/t Ag). The outcropping strata consist of Lower Permian carbonates, sandstones and slates of the Angjie Formation and Linzizizong Group volcanic rocks of the Dianzhihong Formation, and a granite porphyry that intruded them. The main Pb-Zn orebodies occur at the contact of the Linzizong volcanic rocks and the Permian limestones. Subordinate Cu orebodies are hosted in interlaminar fractures in the sandstones and slates. Three ore-stages can be identified; these are composed of 1) the pre-ore stage, containing contact metamorphic quartz, feldspar, and cordierite, prograde metasomatic skarn minerals garnet, pyroxene, and wollastonite, and early retrograde metasomatic skarn minerals of epidote, tremolite, actinolite, quartz, ilvaite, magnetite, and hematite, 2) the syn-ore stage including the late retrograde metasomatic minerals of muscovite, chlorite, quartz, chalcopyrite, pyrite, sphalerite, and galena, 3) the post-ore stage of quartz, calcite, and chlorite, and the weathering minerals of azurite, malachite, and limonite (Fig. 1).

Figure 1. Geological map of the Nuocang skarn Pb-Zn polymetallic deposit, western Gangdese belt, Tibet.

3 Analytical methods

Microthermometric measurements of the fluid inclusions selected from the Nuocang deposit were conducted on a Linkam THMSG-600 heating-freezing stage with a temperature range from −190 to 600 °C attached to an Olympus BX-50 transmitted light microscope at the Fluid
Inclusion Laboratory, China University of Geosciences (Wuhan). Sulfur and lead isotopic compositions were analysed at the Analytical Laboratory of Beijing Research Institute of Uranium Geology. Sulfur isotopic compositions were measured on a Finnigan MAT-251 isotope mass spectrometer. The results are expressed relative to the international standard V-CDT with a precision better than ± 0.2‰. Lead isotope analyses were carried out by using the GV Isotope-T Thermal Ionization Mass Spectrometer. Analytical results for the standard NBS 981 are $^{208}\text{Pb}/^{204}\text{Pb} = 36.611 ± 0.004 (2\sigma)$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.457 ± 0.002 (2\sigma)$ and $^{206}\text{Pb}/^{204}\text{Pb} = 16.937 ± 0.002 (2\sigma)$, in agreement with the reference value. Both the hydrogen and oxygen isotope analyses were performed on a MAT-253 EM spectrometer at the Isotopic Laboratory of the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China. All the resulting values are reported relative to the V-SMOW standard, with an error of ± 0.2‰ for $\delta^{18}\text{O}$ and of ± 2‰ for $\delta^D$.

4 Analytical results

4.1 Fluid inclusions

Fluid inclusions hosted in garnet, pyroxene, and epidote from the pre-ore stage, quartz and sphalerite from the syn-ore stage, and quartz and calcite from the post-ore stage were investigated. Three types of fluid inclusions include Type V (pure vapor or vapor-rich, 5–10% content), Type L (pure liquid or liquid-rich, 85–90% content), and Type S (daughter mineral-bearing, S-L-V, 1–5% content). The homogenization temperatures for pre-ore stage inclusions range from 210 to 571°C. The ice melting temperatures vary from −16.2 to −2.1°C, and the halite dissolution temperatures are from 378.7 to 405.5°C, which correspond to salinities from 3.5 to 48 wt.% NaCl equiv.. The homogenization temperatures, ice-melting temperatures, and salinities in syn-ore stage are 135 to 381.6°C, −11.6 to −0.3°C, and 0.5 to 15.6 wt.% NaCl equiv., respectively. Fluid inclusions for post-ore stage have homogenization temperatures ranging from 103 to 330 °C, and ice melting ranging from -10.9 to -0.1 °C, which correspond to salinities from 0.2 to 14.8 wt.% NaCl equiv. (Fig. 2).

4.2 H-O-S-Pb isotopic compositions

The $\delta^D$ values for garnet, pyroxene, epidote, quartz, and calcite for the different stages from Nuocang range from −180 to −106‰. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values vary from -1.2 to 3.0‰ in the pre-ore stage, -4.7 to -2.3‰ in the syn-ore stage, -8.6 to -5.8‰ in the post-ore stage, respectively, decreasing from the pre-ore to post-ore stages (Fig. 5). Sulfur isotope compositions (Fig. 3) of chalcopyrite, sphalerite and galena from the Nuocang yield uniform $\delta^{34}\text{S}_{\text{CDT}}$ values (−0.6%o to 2.7%o, average 0.83‰). The temperatures calculated from S isotope geothermometry for co-existence galena-sphalerite range from 181 to 300°C, and are in good agreement with the fluid inclusion homogenization temperatures. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 23 sulfides from the Nuocang deposit vary from 18.629‰ to 18.738‰, 15.646‰ to 15.775‰ and 38.907‰ to 39.340‰, respectively.

5 Discussion

5.1 Fluid and metal sources

The $\delta^{34}\text{S}$ values of −0.6‰ to 2.7‰ for sulfides from Nuocang are similar to those from magmatic hydrothermal deposits (−3‰ to +1‰; Hoefs, 2009), which is indicative of a magmatic sulfur source. Most of the Pb isotope ratios for sulfides from Nuocang plotted in the field of upper crust and overlapped with those of Pb isotope compositions in the Nyainqentanglha basement, indicating a primary upper crust source for Pb. Some Pb isotope ratios plot between the orogenic and upper crustal curves, and have similar characteristics with those of sulfides from the Narusongduo Pb-Zn deposit (Ji et al., 2013). The Pb isotope ratios plot a steep linear array feature in the tectonic evolutionary diagram (Fig. 4). Pb isotope compositions of from Nuocang are therefore dominated by an upper crust source, mixing with minor amounts of mantle Pb compositions derived from the subducted slab of Neo-Tethys (Fig. 4).

The homogenization temperatures of primary fluid inclusions and the hydrogen and oxygen isotopic compositions at Nuocang are similar to those of the typical Pb-Zn skarn deposits elsewhere. The high homogenization temperatures (380 to 580 °C) and salinities (up to 48 wt.%
NaCl equiv.) of the primary fluid inclusions in the pre-ore stage garnet are consistent with magmatic-hydrothermal fluid. The $\delta^{18}$O$_{H2O}$ values of the pre-ore stage (2-3.9‰) are close to that of magmatic water (5.5-9.0‰; Taylor, 1974) suggest that the initial ore-forming fluid could be dominantly of magmatic origin. However, the $\delta^{18}$O$_{H2O}$ values show a decreasing trend, much closer to the meteoric values from the pre-ore to post-ore stage, indicative of a mixing with significant meteoric water. The $\delta D$ values from Nuocang (-180 to -106‰) are lower than those for magmatic fluids (–40 to 80‰), but overlap with those of Tibetan meteoric water (–66 to –160‰), which could be due to the continuous degassing from a crystallizing magmatic source in an open system during late crystallization (Hedenquist et al., 1998). Consequently, the initial ore-forming fluid was dominantly magmatic-hydrothermal in origin, but mixed with significant meteoric water during late stage hydrothermal activity.

**Figure 3.** Frequency histogram plot of $\delta^{34}$S$_{V-CDT}$ values.

**Figure 4.** Lead isotope plot showing $^{207}$Pb/$^{204}$Pb vs. $^{206}$Pb/$^{204}$Pb for sulfides from the Nuocang deposit (Zartman and Doe, 1981). Data sources: sulfides from the Narusongduo deposit (Ji et al., 2013); Yarlung Zangbo ophiolite (Liu et al., 2014); Nyqentanghla Basement (Gariépy et al., 1985).

5.2 Fluid evolution and depositional mechanisms

Relatively high homogenization temperatures (380 to 580 °C) and salinities (up to 48 wt.% NaCl equiv.) in the pre-ore stage, and $\delta^{18}$O$_{H2O}$ values (2-3.9 ‰) suggest a typical magmatic hydrothermal fluid sources in the pre-ore stage. The prograde system associated with supercritical fluid (6–8 wt.% NaCl equiv.) exsolved from the magma chamber at shallow levels (6–8 km) of the upper crust (Meinert et al., 2003) rose and separated into a hypersaline liquid (44-48 wt.% NaCl equiv.) and moderate salinity fluid (13.3 to 19.0 wt.% NaCl equiv.). During interaction with carbonate rocks, the hydrothermal fluid produced prograde skarn minerals, such as garnet and pyroxene through metasomatic reactions. Subsequently, a low temperature and low salinity meteoric water mixed with magmatic hydrothermal fluids, leading to abundant retrograde assemblages of epidote, actinolite, and tremolite. Gradually decreasing oxygen isotopic values of skarn minerals from the prograde to the retrograde stage and a significant linear array in the homogenization temperatures vs. salinities diagram (Fig. 6). The syn-ore stage is characterized by the occurrence of sulfides quartz and calcite, and have isotopic compositions consistent with a significant component of meteoric water. The continuous influx of meteoric water and greater water-rock reaction resulted in moderate-low temperatures (200-320 °C),
salinities (6-12 wt.% NaCl equiv.), a relatively high pH, and reducing fluids. In this case, the reduced sulphur ions increased and reacted with the metal ions of the ore-forming fluid, producing abundant of sulphides, such as pyrite, chalcopyrite, galena, and sphalerite. Prograde skarn minerals were partly altered to chlorite, sericite, and quartz. The co-existence of type L and type V inclusions with similar homogenization temperatures observed in quartz-hosted fluid inclusions implied that boiling possibly represent another mechanism for ore precipitation in the Nuocang hydrothermal system.

Figure 6. Homogenization temperatures vs. salinities diagram for the fluid inclusions from the Nuocang deposit.

6 Conclusions

Three types of fluid inclusions have been recognized in ore and gangue minerals from the Nuocang deposit, including types L, V, and S. The ore-forming fluids evolved from moderate to high temperatures and moderate to high salinities during the pre-ore stage through low to moderate temperatures and low salinities in the syn-ore stage, and to low temperature and low salinity in the post-ore stage. The metal and fluid sources were originated from the upper crustal magmas. Significant addition of meteoric water to the early magmatic-hydrothermal system is considered to be responsible for the metal deposition. Local fluid boiling is another mechanism for ore precipitation in the Nuocang deposit.

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References


Decompression of overpressured fluids and its role in the localization of intrusion-related orebodies: Evidence from field and computational modeling

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Abstract. Many intrusion-related ore deposits are closely associated with hydrothermal breccias that indicate sharp fluctuations of fluid pressure during mineralization. Using field investigations and computational modeling for two intrusion-related deposits in different tectonic regimes, we present evidence to demonstrate that decompression of over-pressured fluids is capable of playing an important role in localizing ore bodies.

1 Introduction

Ore deposits related to hydrous intrusions are both important and complicated (Meinert 1992; Candela et al. 2005). The intrusions related to hydrothermal mineralization are emplaced under lithostatic load (Fournier 1999). Many intrusion-related deposits show obvious evidence of pressure fluctuations during ore formation (Liu 2011). In this paper, through field and computational modeling on coupled MTH (mechanothermal-hydrological) dynamics in one porphyry Cu-Mo deposit in northern China and one skarn Cu deposit in southern China, we present evidence for decompression of over-pressured magmatic-hydrothermal fluids and discuss its role in localization of ore bodies.

2 Study sites

2.1 Chehugou porphyry Cu-Mo deposit

The Chehugou porphyry Cu-Mo deposit is located in the Chifeng district, Inner Mongolia, eastern north China. It is a major Cu-Mo deposit in the Xilamulun metallogenic belt on the northern margin of the North China Craton (Zeng et al. 2012). The host rocks are mainly breccias, Archean metamorphic rocks (including hornblende plagioclase gneiss, granitic gneiss and migmatitic granite) and granite porphyry (Fig.1). The granite porphyry intrusion has a zircon U–Pb age of 245.1 ± 4.4 Ma (Zeng et al. 2012), and occurs as an irregular stock that has variable compositions. It is the source of the porphyry mineralization. Mineralization took place during the Indosinian orogenic phase, when the crust in this region was subjected to NW-SE compression (Sun and Liu 2014).

The main metallic minerals at Chehugou are pyrite, molybdenite and chalcopyrite. Molybdenite occurs as veinlets, disseminations and as breccia cement, and as a minor component in quartz veins. Chalcopyrite and pyrite occur as irregular massive aggregates in quartz veins and cemented breccias.

The main Cu-Mo mineralized zone has a very complex shape. Several branches of the main zone occur as parallel subzones in Figure 1. Because Cu-Mo mineralization is unevenly distributed in this deposit, it is difficult to determine the boundary of the ore bodies using the constraints from common geological features. The shape and scale of the ore bodies depend on the cut-off grade (Sun and Liu 2014).

Fig.1. Surface map and typical cross section of the Chehugou Cu-Mo deposit

The distinctive feature of the deposit is the extensive magmatic-hydrothermal brecciation associated with the ore bodies (Fig. 1). The breccias have a clast-supported texture, with Cu- and Mo-sulfides cement. The irregular fragments of wall rocks (granite and metamorphic rocks) in the breccias show obvious jigsaw-fit to mosaic textures. These features are consistent with hydrofracturing driven by
over-pressured fluids. Cu-Mo mineralization was associated genetically with brecciation, with decompression during Mo and Cu precipitation.

Fluid inclusion conclusions support this hypothesis. Petrographic and microthermometric analyses of fluid inclusions by Chu et al. (2010) indicates that the fluids had high temperatures, high salinities, and were CO₂-bearing. They provided evidence on phase separation, with fluid pressures varying from 160 MPa to 0.45 MPa during mineralization. The sharp drop of pressure was mostly caused by decompression of over-pressured fluids through hydrofracturing or magmatic-hydrothermal explosion.

2.2 Fenghuangshan skarn Fe-Cu deposit

The Fenghuangshan skarn Fe-Cu deposit is located in the Tongling district, southern China. It is a major deposit in the Yangtze metallogenic belt, which is located along the northern margin of the Yangtze Craton. The deposit is hosted by Paleozoic carbonates and felsic intrusive rocks. The ore bodies are irregular to tabular in shape, and are located along the contacts of the Xingwuli intrusion (Fig.2). The Xingwuli intrusion mainly consists of calc-alkaline granodiorite and quartz monzodiorite. U–Pb age of zircon from the granodiorite is 143.1 ± 1.6 Ma, and the Re-Os isochron age of molybdenite from ores is 141.7 ± 0.8 Ma (Li et al. 2014). This is consistent with the transition from compression to extension in the region (Deng et al. 2011).

Ore is dominated by Cu sulfide-bearing magnetite and siderite. There is also minor disseminated-Cu sulfides in the quartz monzodiorite, granite, skarn and Cu sulfide-bearing breccias.

Brecciation is extensive at Fenghuangshan, both in the ore bodies and host rocks, and was closely associated with copper mineralization (Figs. 2 and 3). From ore bodies to more distant wall rocks, brecciation systematically varies from matrix-supported breccias, to clast-supported breccias, and then to crackle breccias (Fig. 3). According to the criteria described by Jébrak (1997), the morphological and compositional features of the breccias, especially the jigsaw-fit textures consisting of angular wall rock fragments in hydrothermal cement of sulfides and carbonates (Fig. 3e), suggest that the breccias formed from over-pressured hydrothermal fluids. Failure and brecciation of the rocks induced by the over-pressured fluids would have resulted in sharp drop of fluid pressure. From microthermometric analyses of fluid inclusions, Lai et al. (2007) concluded that pressures varied from > 131 MPa to 12 MPa during mineralization.

3 Computational modeling of coupled MTH process

3.1 Model construction and conditions

Based on geological field data and geometric modeling, we constructed a 3D dynamic model of Chehugou and a 2D dynamic model of Fenghuangshan deposit (Fig. 4), using FLAC3D and FLAC2D respectively. The dimension of the Chehugou FLAC3D model is X (NE) × Y (NW) × Z (depth) = 1,500m × 1,100m × 1,500 m, with 42444 tetrahedron elements. The model consists of two rock units, granite porphyry and metamorphic rocks (Fig. 4a). The dimension of the Fenghuangshan FLAC2D model is X (NE) × Z (depth) = 1100m × 1400m, with 3850 tetragonum elements.
The model consists of two rock units, carbonate and granodiorite (Fig. 4b).

The initial and boundary conditions of the numerical modeling experiments are determined according to the inferences about the geodynamic setting and evolution of the deposits. We used FLAC3D model (Fig. 4a) to simulate syn-compressional cooling of the hot intrusion in the Chehugou area. The initial temperature of the granite porphyry intrusion was set to 750°C, while the wall rocks were set with a temperature gradient of 30°C/km from the surface, which has a constant temperature of 25°C. The granite porphyry intrusion is also set to have lithostatic initial pore fluid pressure, while the wall rocks were assigned hydrostatic initial pore fluid pressure. We used FLAC2D (Fig. 4b) to simulate the syn-stretching cooling of a hot intrusion at Fenghuangshan. The initial temperature of the intrusion was set to 600°C, while the wall rocks were set with a temperature gradient of 20°C/km from 45°C at the top of the model, which is not the palaeosurface of the mineralization system. The granite porphyry intrusion was assigned lithostatic initial pore fluid pressure, whereas the wall rocks were assigned hydrostatic initial pore fluid pressure.

3.2. Results and implication

By controlling time-step, the FLAC3D model (Fig. 4a) and FLAC2D model (Fig. 4b) were run to simulate the syntectonic cooling and thermal evolution of the intrusion-centered dynamic systems at Chehugou and Fenghuangshan. The results provide useful information for analyzing the role of decompression of over-pressured fluids in mineralization.

Dilatant deformation produced in the modeling experiments was distributed unevenly along the contact zones of the intrusions (Figs. 5b, 5c and 6d). In the Chehugou model, most of the high dilatant zones occurred in the SW wall of the intrusion (Figs. 5b and 5c). This is where intensive brecciation is distributed in the field. The high dilatant zones produced in the Fenghuangshan model also showed a positive relationship between the space of location of brecciation and ore bodies (Fig. 6d). These modeling results suggest that brecciation was a direct result of dilatant deformation caused by the coupled MTH processes during cooling of the intrusions.

Figure 5. Modelling results for Chehugout. a Locations of sections A-A', B-B' and C-C' in the model. b and C Volume strain in sections A-A' and B-B' respectively when model reach at about 1% bulk shortening. d and e Mechanical state of the section A-A' at time t1 and t2 respectively (see Fig. f for the time t1 and t2. P is the location of the monitored element). f Evolution curve of the pore pressure varying with volume strain in the monitored element P.

Complex relationships between the pore fluid pressure and the volume strain in the contact zones of these two models indicates overpressure at the beginning and decompression later (Fig. 5f and 6a). The two models display different patterns of deformation, varying with fluid pressure before the monitoring elements (P in Fig. 5b and M in Fig. 6b) reached peak pore pressure. After peak pressure, the two models show dramatic dilation and decompression accompanied by centralized tensile failure along the contact zones (compare Fig. 5d with 5c and 6c with 6b). Tensile failure of blocks in the two models show a positive spatial association with the locations of ore
bodies and breccias. In the natural systems, these features suggest that the sharp increase in volume strain was possibly the result of hydraulic fracturing caused by overpressured fluids and tectonic stress. Hydrofracturing caused the rapid decrease of fluid pressure, which could cause phase separation, an important depositional mechanism. Fracturing can produce dilatant space for mineralization and focusing of fluids (e.g., Frikken et al. 2005). So that, decompression of over-pressured fluids can play an important role in localization of intrusion-related orebodies.

**4. Conclusion and discussion**

Hydrous hot intrusions emplaced under lithostatic load can exsolve over-pressured fluids that will be localized at their root and in contact zones. This can occur in compressive regimes (as at Chehugou) or in extensional setting (Fenghuangshan deposit). High fluid pressure can cause fracturing and consequent decompression of over-pressured fluids to facilitate brecciation, deposition of ores and localization of ore bodies.

Due to difficulties in determining pressures in hydrothermal systems, fluid pressure fluctuation and its role in hydrothermal mineralization is undervalued (Roedder and Bodnar 1981). Our computational modelling method is able to provide an analogue approach to study such problems.

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**Figure 6.** Modeling results for Fenghuangshan. a Evolution curve of the pore pressure varying with volume strain in the monitored element M (see Fig. b for the M location). b and (c) Mechanical states at time t1 and t2 respectively (see Fig. a for time t1 and t2). d Volume strain distribution at time t2.
Abstract. Skarn deposits are the most important in Peru; occurring in the last 12 to 9 m.y, the area of study is located in San Marcos- Ancash, 20 km south of Antamina; exactly in the Canrash lagoon, where there is an overthrust of the Oyon group on the limestones from Jumasha, which present an average orientation of E56S and subdivisions towards the west. The fault that controls the overthrust of Oyon group on the limestones from Jumasha is of Andean orientation and it will allow the ascent of material generated from the Eocene to the Miocene. The location of granular rocks on the generation of a skarn type system, the prograde phases in the Canrash lagoon present brown garnets, green garnets, clinopyroxenes, wollastonite and magnetite, the retrograde phases is evidenced by brown garnets, epidote, chlorite, hematite, chalcopyrite and Calcite, the latter predominating in distal areas; Finally they have minerals of supergene environment, such as malachite, azurite, limonites and clays. The main minerals are bornite and chalcopyrite, which has values of 0.5% in the skarn of wollastonite and 2 to 3% in areas of endoskarn.

1 Introduction

Peru has mineral deposits like WordClass, such as Yanacocha, Antamina, La Granja among others; Magmatism and tectonics are the main dominant factors. Petrogeochemistry is a tool for exploration, it comprises magmatic processes, beginning with the assimilation of magma, location, cortical contamination to hydrothermal activity; allowing for discriminating the fertile and sterile magmas, the favorable contents for the generation of mineral deposits, corresponding to cortical thicknesses of 46 to 54 km are Ce / Y = 5.8 to 9.8, Sr / Y = 60 to 109, Sm / Yb = 4.3 to 8 and La / Yb = 31 to 56, on the other hand the Eu / Eu * ratio defines if the magmas present a significant degree of humidity, the area studied is composed of wet magmas; the thickening of the crust (amphibolite composition) alters its stability and is transformed into garnets, this generates a release of water which will rehydrate the magmas, and later in the late magmatic phases will be of relevance for the generation of a hydrothermalism rich in metals. The stratigraphy is a fundamental tool, the reaction generated between the box rock and the fluid is determinant in the zone, to know and understand the stratigraphy will define the preservation of a mineralized system, and on the other hand the tectonic-structural aspect determines the control of the magmatic emplacement to the distribution of mineralization. The present research proposes to review the stratigraphic, structural and petrogeochemical controls that generate a propitious condition to host the skarn mineralization of Canrash, the application of this knowledge was made in the location of a target, 15 km south of Antamina, north of Huanzalá, where the contents of chalcopyrite up to 3% are identified in the endoskarn, described and with anomalous values of As = 252 ppm, Zn = 2780 ppm, Pb = 2970 ppm, Cu = 0.05 and Mo = 2.5 ppm.

2 Regional geology

Figure 1. Canrash lagoon-San Marcos-Ancash dominated by Chonta fault.
The survey area is comprised by sedimentary rocks of the Mesozoic, shallow marine environments and silico-clastic sequences.

The Mesozoic was dominated by subduction, where the carbonate and clastic sequences were deposited in the after-arc, from the Valanginian to the Aptian (Bissig et al. 2008), after the fragmentation and expansion of the Atlantic, began a compression regime and ceased the extension of the after-arc (Mochica Phase, Megard et al. 1984).

3 Stratigraphy

The stratigraphy of the Andes of central Peru presents mainly three great sequences of Cretaceous. In the base of the sequences of the Oyon Formation, on these and in discordance is the sequence of lower Valanginian to upper Aptian, are siliciclastic deposits of deltaic type denominated Group Goyllarisquizga (Megard et al. 1978).

4 Structural geology

Structurally the belt is controlled, to west by the fault system and to east by the system of folds and faults of Marañón, which forms a single set with direction NW-SE and forms a folded and running belt, with convergence to the NE, is the Result of the greater deformation of the Eocene (Mourier, et al. 1988). The NE-SW structure was mainly due to the changes of directions of the folds and faults, especially to the location of igneous bodies from Miocene.

5 Mineralization and alteration

The distal zone forms an exoskarn mineralogically conformed by Epidote + Calcite and smaller amount of garnets, then there is an exoskarn zonation where predominants Garnets + Calcite and Epidote almost null, within the alteration inside the sample with the texture of the army's exsolution, with an altered matrix in presence of fractures and the disseminations of Chalcopyrite.
Radiated wollastonite in contact with intrusive, presence of quartz and calcite (an edge sector of the metasomatism zone). Brown garnet anhedral to subhedral, with presence of calcite (Endoskarn zone).

Figure 5. Photomicrographs of samples

Figure 6. a and b PGls and alterations of clays with presence of opaque (Cpy) 20x. c GRNs, Cac, Px 5x. d Cac.

6 Petrogeochemistry Peru central

In the study area the cortical range of mineralization has been established from 46 to 54km, corresponding to values Ce/Y =5.8 to 9.8, Sr/Y=60 to 109, Sm/Yb=4.3 to 8 and La/Yb=31 to 56, these being typical petrogenetic characteristics of miocene magmatism. (Mpodozis, et al. 2013).

Figure 7. The ratios of Fe2O3 / FeO showing the oxidation of the magma where the mineralized generation in Cu or Mo will be determine, we can observe notoriously in the districts of Uchuchacua, Raura, Palca where the less oxidized and differentiated tendencies will prefer Cu generation.

Figure 8. The proportion Al2O3/Na2O+K2O+CaO showing saturation of alumina, so the majority of analized samples standing for a field peraluminous highly.

Conclusions

- The main metallotecs are Santa and Jumasha, being the Santa formation mineralized by replacement, due to the low potential to generate skarns and it’s potential to generate intrusives, it emplacement in a way concordant. For example, the Huanzala mine.
- The magmatism in the mineral deposits of the center are of series Calco-alkalic to shoshonitic, typical of a transitional after arc.
- It has high potassium content and a peraluminous saturation.

Figure 9.

-The evolution of the arc depends on the ratios of Sr/Y and Sm/Yb. The first shows an evolution of subalkaline arc to adakitic that according to J.P. Richards are the generators of mineralizations of WorldClass.

-The values of Sm/Yb show mineralogical variation in the crust from amphiboles to garnets, beginning from the mineralogical instability that generates detachment of water molecules (amphibole), so this generate to magmatic rehydration.

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References


Characteristics of a Se-rich low-intermediate sulphidation epithermal deposit in the River Reef zone, the Poboya prospect, central Sulawesi, Indonesia

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Abstract. Gold mineralisation in the River Reef Zone of the Poboya prospect, Central Sulawesi, Indonesia is hosted within metamorphic and igneous rocks. Hydrothermal alteration is zoned from inner, high-temperature, to outer low-temperature propylitic zones. Alteration resulting from fluid-rock interaction during waxing and waning stages of the hydrothermal system. Veins host electrum, naumannite-aguilarite, argyrodite, pyrargyrite, selenopolybasite, freibergite, chalcopyrite, sphalerite, galena, stibnite, pyrite, marcasite, pyrrhotite, and hematite. These ore minerals can be further subdivided into early and late sub-stages. Fluid inclusion microthermometry shows that the mineralising fluids is characterised by formation temperature of 250°C and salinity of 0.3 NaCl wt % eq. Mineral assemblages, chemical composition, and formation temperature are consistent with Se-bearing Au-Ag epithermal deposits. The River Reef Zone is classified as a low-intermediate sulphidation epithermal deposit.

1 Introduction

The Poboya prospect is located approximately 12 km northeast of Palu City, Central Sulawesi, Indonesia (Fig. 1a). Gold mineralisation has been outlined in three vein zones: River Reef Zone, Hill Reef 1 Zone, and Hill Reef 2 Zone (Fig. 1b). Due to technical, economic, and legal limitations, exploration conducted from 1993 to 2012 was concentrated on the River Reef Zone. This abstract describes the characteristics of the River Reef Zone, including host rocks, hydrothermal alteration, vein textures, ore and gangue mineralogy, as well as fluid chemistry. These characteristics provide an insight into the classification and origin of the gold deposit.

2 Geologic background

The Poboya prospect is hosted by the Western Sulawesi Province which has a metamorphic core complex as its basement (Van Leeuwen et al. 2016). This basement is unconformably overlain by the Tertiary Tinombo Formation and was intruded by a Late Cenozoic granitic intrusion. The Quaternary Celebes Molasse and alluvium deposits cover the older rock units (Fig. 1a; Van Leeuwen and Muhardjo 2005).

Geological structures in the Palu area are prominently controlled by the NNW-trend Palu Koro Fault Zone (PKFZ; Katili 1970). PKFZ extends from the end of the Matano Fault to the western end of the North Sulawesi Trench. Around the Palu area, the PKFZ formed a pull-apart basin, where the Poboya prospect is situated on the eastern margin of the basin (Wajdi et al. 2012).

At the northeastern portion of the Poboya prospect, the exposed metamorphic core complex consists of biotite gneiss and schist. These rocks were intruded by granite. Due to rapid uplift of the metamorphic core complex, biotite gneiss, schist unit, and granite were eroded, transported, and deposited as the Celebes Molasse which crops out in the southwestern portion of the prospect. Recent alluvium can be found along the Poboya riverbank (Fig. 1b; Wajdi et al. 2012).

3 Methodology

Several methods were employed to characterise the River Reef Zone. Petrography was used to identify host rocks, alteration mineral assemblages, vein textures, and ore-gangue mineralogy. Clays were identified through X-ray diffractometry (XRD). Scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) was used to determine the chemical composition of several ore minerals in order to deduce the ore-forming fluid characteristics. Fluid inclusion microthermometry was used to obtain information regarding the temperature and the salinity of mineralising fluids.

4 Host rocks

Gold mineralisation is hosted within the granite, biotite gneiss, and schist. The granite is composed mainly of quartz, orthoclase, and plagioclase. The biotite gneiss comprises quartz, orthoclase, and plagioclase-rich light bands and biotite-rich dark bands. These bands determine
gneissose layering. Myrmekitic textures were also observed implying granite as a protolith of this rock.

The biotite schist is intercalated with feldspar amphibolitic schist. The biotite schist has similar rock-forming minerals to the biotite gneiss. A stronger schistosity is the main difference between these schist and gneiss. Feldspar porphyroblasts in the biotite schist are characterised by a deflected biotite schistosity around the feldspar porphyroblasts. In contrast, the amphibolitic schist is composed predominantly of quartz, plagioclase, and hornblende.

5 Hydrothermal alteration

Zonation of hydrothermal alteration assemblages has been delineated in the River Reef Zone. The alteration zone proximal to the veins is an inner propylitic zone consisting of illite, chlorite, chlorite/smectite, illite/smectite, and calcite. Within this zone, feldspar that is in direct contact with the veins was partly altered to quartz. The inner propylitic zone extends to a high-T propylitic zone composed of chlorite, epidote, calcite, illite/smectite, and smectite. The outermost alteration zones comprises an assemblage of chlorite, illite/smectite, and smectite (Fig. 2).

6 Vein textures

Vein textures in the River Reef Zone can be classified into three groups according to the texture scheme of Morrison et al. (1995): primary growth, replacement, and recrystallization textural groups. The primary growth textural group is represented by massive, micro-comb, banded, colloform and lattice textures reflecting initial open-space fillings. Massive texture is composed predominantly of quartz and minor calcite. This texture was deposited after micro-comb texture. Calcite is more abundant in veins with banded texture compared to these with massive texture. Massive coarse calcite alternates with bands of microcrystalline quartz, micro-comb quartz, and chaledony. Toward the centre of the veins, there is a repetition of colloform and micro-comb textures with minor calcite. Lattice texture is characterised as an aggregate of platy calcite with considerable interstices which results from boiling (Simmons and Christenson

Figure 1. a Regional geologic (after Sukamoto et al. 1985) and b local geologic map of the Poboya prospect

Figure 2. Zoned hydrothermal alteration

This zoned hydrothermal alteration formed due to fluid-rock interaction (e.g., Robb 2005). The hydrothermal fluid reacted with feldspar and biotite to form illite and chlorite, respectively. These reactions also resulted in residue silica appearing as feldspar replacement. The high temperature of the hydrothermal fluid promoted feldspar replacement by epidote in the high-T propylitic zone (Fournier 1985). Lastly, as the distance from the fluid conduit increased, the fluid temperature decreased resulting in smectite and illite/smectite.
1994). Replacement platy calcite by quartz occurs locally. Recrystallization in the veins is represented by moss texture. This texture is characterised as individual spheres with a chalcedony centre and a crystalline quartz rim.

7 Ore-gangue mineralogy

Ore minerals in the River Reef Zone consist of electrum (el), naumannite-argentite (nm-agu), argyrodite (arg), pyrrargyrite (pyra), selenopopylsite (spo), freibergite (fre), chalcopyrite (cp), sphalerite (sph), galena (gn), stibnite (sb), pyrite (py), marcasite (mc), pyrrhotite (po), and hematite (hem). These minerals are embedded within quartz and calcite as gangue minerals. Paragenetically, the ore minerals were precipitated in two stages: main and weathered stages. The main stage can be further subdivided into early and late sub-stages. The early stage is marked by an ore mineral assemblage of el + nm-agu + cp + py ± mc ± sph ± po. Meanwhile, the late stage is characterised by more various ore minerals comprising an assemblage of el + nm-agu + spo + fre + sph + py + mc ± arg ± pyra ± cp ± gn ± sb ± hem. In the main stage, most of Ag-bearing minerals appear to have precipitated after electrum and pyrite. The weathered hematite and goethite are recent oxidation products of pyrite in the shallow portion of the veins.

In terms of chemical compositions, several ore minerals show compositional variations. From the early to late stages, Ag content in electrum changes from 70 at % to 60 at %. Likewise, Ag-S-Se minerals in the late stage have a higher S content compared to those in the early stage. A trend could also be identified in freibergite compositions. In the shallower portion, freibergite has higher Ag contents than in the deeper portion.

8 Ore-forming fluid

The ore-forming fluid of the late stage is characterised by formation temperature of 250°C and salinity of 0.3 NaCl wt % eq. The temperature of the early stage is higher (290°C) as deduced from ore mineral assemblages and chemical compositions. The change on mineral assemblages reflects slight decreases in ore fugacity of sulphur and selenium. These characteristics lie on the general trend of Se-bearing Au-Ag epithermal deposits with the ore-forming fluid path follows the equilibrium of naumannite-argentite (Fig. 3a; Simon et al. 1997). In terms of sulphidation states, these characteristics reflect low-intermediate sulphidation states (Fig. 3b; Einaudi et al. 2003).

9 Conclusions

The gold deposit in the River Reef Zone is hosted within granite, biotite gneiss, and schist. Hydrothermal alteration around the mineralized structures comprises inner, high-T, and low-T propylitic zones. Veins show several textures such as massive, micro-comb, banded (primary growth), lattice (primary growth and replacement), and moss (recrystallization) textures. Within the veins, ore minerals were precipitated in main and weathered stages. Ore minerals were deposited in the main stage which can be further subdivided into early and late stages. All of these characteristics suggest that this deposit can be classified as a Se-rich low-intermediate epithermal sulphidation deposit.
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References


Porphyry copper and high-sulfidation epithermal Au (Ag) mineralization, igneous Peñas Blancas complex of Jasimaná (Miocene), Salta, NW Argentina

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Abstract. This article describes Cu-Au mineralization associated with Porphyry and high-sulfidation Au (silver) epithermal systems in the Igneous Peñas Blancas Complex (CIPB) of Jasimaná (middle Miocene), Salta province, NW Argentina. The area is part of the Central Andes, located in a zone of intersection between regional structural lineaments of NW-SE trend and NE-SW trend. The following vein-hosted mineralization was identified: quartz-pyrite, chalcopyrite, hematite-magnetite with gold (up to 3 g/t Au). Field studies and petrographic and geochemical studies enabled us to recognize areas with seritization, silicification, and propylitic alteration, associated with Au, Ag, Cu, Mo, Pb, Zn and As anomalies. This new area adds up to the already known mineralization of subvolcanic bodies of the Central Andes of Argentina, such as Pan De Azucar, Cerro Redondo, Chinchillas, Orosmayo, Pancho Arias, Inca Viejo, Diablillos, among others.

1 Introduction

The study area is located in the SW of Salta province, near the border with Catamarca province, NW Argentina, between 25° and 26° (Fig. 1), surrounded by Puna, Cordillera Oriental and Sierras Pampeanas geological provinces. The mineral occurrences of Cu and Au are contained in the Igneous Peñas Blancas Complex (CIPB). This NNO orientated lithological unit is part of a series of Middle and Superior Miocene calc-alkaline magmatic bodies situated in a transition zone between the geological provinces of Puna Austral and NW Sierras Pampeanas.

Few studies were carried out previously in the area, among them the mappings by the Fabricaciones Militares (Plan NOA I, 1979) and the Argentinian Geological Service (1998) stand out. The intrusive igneous host rocks described in the present paper were not identified in either of the studies, since they were included as part of the Oire Eruptive Complex or Eastern Puna Eruptive Belt (Ordovician) (Mendez et al. 1973). In this context, Castillo’s (1999, 2001) studies constitute the first petrographic and mineralogical research about the CIPB.

Figure 1. Location map.

The present work offers detailed field observations, geochemical analysis and metallogenic interpretations which enable to connect the CIPB mineralization with the porphyry copper and the high-sulfidation epithermal Au (silver) systems with superimposed hydrothermal and supergene processes.

2 Geological regional setting

2.1 Generalities

The study area belongs to the following geological provinces: Cordillera Oriental (Southern segment), West of the Cumbres Calchaquíes; Puna Austral, South of the Calama-Olacapato-Toro lineament; and Sierras Pampeanas. It shares more stratigraphic, tectonic and geomorphological affinities with the Puna Austral and the Sierras Pampeanas Septentrionales.

The basement corresponds to a group of magmatic, metamorphic, migmatite and mylonite rocks which are part of the metamorphic Precambrian basement as well as the Ordovician Eastern Puna Eruptive Belt. We can also notice the presence of granites and tourmaline pegmatites in an upper Paleozoic-lower Triassic, circular, caldera
shaped body. In the Peñas Blancas area, the Eastern Puna Eruptive Belt shows intrusive igneous rocks such as Tertiary (Miocene) granites, rhyolites and pegmatites, of calc-alkaline composition, forming the so called Igneous Peñas Blancas Complex (CIPB). Associated to those rocks are also Paleogene sediments of the Payogastilla group, pyroclastic rocks, Miocene ignimbrites and recent Quaternary sediments (Fig. 2).

2.2 Structural Setting
The dominant tectonic style consists of block faulting with high-angle reverse faults that form a terraced relief with heights growing towards the SW between 2600 and 4800 meters above sea level. The principal faults follow a sub-meridian trend, and minor faults generally have a NNE-SSW trend. The metamorphic basement lithological units and the eruptive block, as well as the posterior intrusive granites, behave as rigid blocks before the deformation processes, showing cataclastic and mylonitization zones.

3 Geology of the igneous Peñas Blancas Complex (CIPB)
The group of granitic intrusions and volcanic rocks (rhyolitoids) named CIPB of Jasimaná (Castillo 1999, 2001) covers an area of 56 square km, it has a NNW orientation and a morphology of gentle slopes in the periphery sectors. In the field, no lithological contact was observed between granitoids and rhyolitoids, so they probably correspond to co-magmatic pulses in different sequential occurrences, although all part of the same geological phenomenon.

The CIPB is located in an area of tectonic distension and it intrudes biotite gneiss belonging to the Eastern Puna Eruptive Belt. It contains coarse- and fine-grained facies which match granites and rhyolites respectively. From the geochemical point of view, they are of subalkaline nature with a distinct calc-alkaline peraluminous tendency.

The intrusive bodies are located in an area of block faulting, delimited by high-angle reverse faults following a sub-meridian trend. On the Eastern flank, the tectonic control of the intrusion with the Eastern Puna Eruptive Belt is distinct, with the characteristics of a deformed fault, with fluxion textures, where the orthoclase and biotite follow the NNW trend of the regional lineament.

The volcanic phenomenon generates thick accumulations such as pyroclastical fluids, principally ignimbrites, which cover various sectors of the study area.

The age of the igneous complex was obtained with whole-rock radiometric data with values of 13+1Ma, potassium content of 3.5% and 7.4+0.3Ma with potassium content of 2.8% corresponding to rocks of PBCI (Miocene Middle) and Ignimbrites (Miocene-Pliocene) of pyroclastic flows from the Western sector of Jasimaná, respectively.

4 Alteration
Field studies established that the most interesting zone is the Luingo zone (Fig. 2), where alteration processes were identified, including pyritization with gold anomalies, silicification, sericitization with quartz veinlets and supergene alteration (ferruginous oxidation).

Sertization zones with quartz veinlets, stockwork structures and copper mineralization were identified. The silicification zone shows crystalline quartz and A- and B-type quartz veinlets. In the pyritization and propylitic alteration area, chlorite-epidote with gold anomalies is common. An area with supergene alteration, predominated by ferruginous oxidation (hematite-limonite) was located, indicating interaction between rain water and hydrothermal solutions.
5 Cu and Au mineralization

Field observations and posterior geochemical studies established the presence of quartz-pyrite-chalcopyrite vein-hosted mineralization and hematite-magnetite with gold anomalies, located in granitoids and rhyolitoids of the CIPB.

The granitoids have magnetite and hematite fracture fillings, and euhedral crystalline quartz veinlets associated with oligisto and pyrite which showed Au 0.1 and 0.9 g/t. The disseminated pyrite mineralization appears in subcircular concentrations, and is distributed irregularly in the intrusive body. The thickness of the mineralized veins attains 0.6m for a strike length of 200 meters, following a 340° trend with a 25° SW dip, and they have a coating of oxidation.

The rhyolite bodies contain pyrite in breccia and veins, with Au anomalies of 0.1 and 0.12 g/t and ferruginous oxidations (oligisto-hematite) of average thickness 0.4 m. This kind of mineral paragenesis also appears in smaller veinlets, filling joints and faults in the host-rock.

An area of pyritization can be seen in a fault zone with clay and associated hematitic and limonitic oxides and boulder of magnetite (Figure 4). Samplings based on old adits show Au anomalies with 2-3 g/t Au and Ag 60ppm.

Geochemical analysis revealed Cu, Mo, Au, Pb, Ag, Zn and As anomalies.

6 Conclusions

The presence of vein-hosted disseminated Cu-Au mineralization was established in Igneous Peñas Blancas Complex of Jasimaná, NW Argentina. Au anomalies are associated with quartz veins from border areas and copper mineralization in quartz veinlets in silicification and sericitization areas.

The host rocks related to the neogene calc-alkaline volcanism, the geo tectonic position, the geochemical alteration along with the alteration observed in the study area enable to identify a mineralization system of Porphyry Cu-Mo type and high-sulfidation epithermal Au.

The precambrian-paleozoic shear zones (Ordovician) were reactivated during the Mesozoic and Cenozoic eras, allowing the upward migration of magma and hydrothermal fluids, and of metalliferous brine.

The Au anomalies of the superficial sampling show a considerable potential for the discovery of deep mineralization. More detailed studies are necessary in order to locate the economic mineralized occurrences of this important deposit typology.

This study should be considered the starting point for future detailed studies on the Jasimaná area in order to establish economical ore body.

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Geological characteristics of the Tielongnan Cu (Au-Ag) porphyry-epithermal deposit, Tibet

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Abstract. The Tielongnan deposit, located in north-central Duolong district, has an estimated Cu resource of more than 11 Mt. The 110 Ma Meiriqiecuo Formation of intermediate-basic volcanic rocks is significant to ore preservation. Isotopic data, ore minerals and fluid inclusions data show features of high sulfidation-state epithermal and porphyry mineralization. The upper part of the epithermal Au orebodies have been eroded, because depth estimation results indicate that the upper orebodies exposed at surface formed at the depths of about 1.2 km. Geophysical and other exploration works indicate that there is huge potential for more Cu to be discovered.

1 Introduction

The Duolong district is located in Gerze county, Ngari region, Tibet, western Bangongcuo - Nujiang metallogenic belt. The Bangongcuo-Nujiang metallogenic belt is a world-class porphyry belt in the eastern Tethyan metallogenic domain. Strata in the Duolong district consist of Paleozoic - Mesozoic marine sedimentary formations, fore-arc flysch sediments, local continental volcanic, and molasse. The strata include the early middle Jurassic Sewa group, the late Cretaceous Meiriqiecuo group and the Late Cretaceous Abushan group (Xu et al. 2015). NE and EW trending buried fault sets developed in Duolong district. Previous study (Duan et al. 2013) shows that the late northeast faults are the major ore-controlling structure. The northeast faults have steep angle with left-lateral strike-slip and thrust fault characteristics. Magmatism was dominated by small volume Cretaceous diorite-granodiorite intrusions. These rocks are overlaid by the Meiriqiecuo Group medium-basic volcanic rocks.

2 Deposit types and characteristics

2.1 Morphologies, occurrences and scale

Six Cu (Au, Ag) orebodies have been discovered in this field, including one main orebody (I) and five smaller orebodies (II, III, IV, V, VI). The main orebody elongates along a northeast direction and is 1.8 km long and 1.4 km wide, and extends to 960m below surface with a moderate dip to the SE. Besides, the orebody shaped like an inverted bell in the middle. The copper resource is more than 1000 t at 0.53%, and accounts for more than 99% of the total resource. Mineralization is hosted mainly in the diorite porphyry, granodiorite porphyry, and their host rocks, both as porphyry and epithermal mineralization. The porphyry Cu (Au, Ag) mineralization mainly occurred at deep and the epithermal mineralization superimposed on the porphyry type Cu (Au, Ag) mineralization. The II, III, IV, V, VI orebodies trend along northeast, elongate 400 m, 100 ~ 200 m wide, about 50 ~ 90 m thick, shaped lenticular, and occur at the top of the main orebody.

2.2 Ore textures and components

Disseminated ores and a small amount of brecciated, massive, banded, crusty and patchy structures ores (Fig. 1) are the typical ore types in Tielongnan. The main metallic minerals include pyrite, bornite, enargite, digenite, covellite, chalcopyrite, chalcocite, tetrahedrite, tennantite, molybdenite, limonite, and hematite (Fig. 1). Minor metallic minerals include galena, sphalerite, native copper, magnetite, malachite, and azurite.

These superposed mineral assemblages also reflect the porphyry-epithermal mineralization. Early porphyry mineralization is characterized by a combination of chalcopyrite-bornite-pyrite (± molybdenite). During the late epithermal mineralization stage, minerals such as covellite, digenite, chalocite, and enargite formed. These minerals always replace the early formed chalcopyrite, and bornite.

Advanced argillic alteration is characterized by mineral assemblage of quartz, dickite, kaolinite, alunite, pyrophyllite, and diaspore. Sericitic alteration hosts quartz, plagioclase, biotite, sericite assemblage. Chlorite, epidote, and calcite are typical minerals in propylitic alteration zone.
Figure 1. Characteristics of metallic minerals in Tiegelongnan deposit. a) RN1604-149.0 m Metasomatism of pyrite with chalcopyrite, bornite, enargite and digenite. b) ZK2404-693.2 m Pyrite replaced by bornite and covellite, bornite replaced by covellite. c) ZK2404-816.0 m Pyrite replaced by chalcopyrite, covellite and digenite, chalcopyrite replaced by digenite and covellite. d) ZK2404-712.8 m chalcopyrite-bornite exsolution texture; Chalcopyrite and bornite were replaced by covellite, and chalcopyrite was replaced by digenite and covellite. e) ZK1604-502.3 m Zonal pyrite coexists with bornite which was replaced by chalcopyrite and covellite. f) ZK2404-722.4 m Fracture quartz filled with pyrite, chalcopyrite and bornite. g) ZK2404-729.1 m Disseminated fine-grained chalcopyrite and pyrite.

3 Metallogenic characteristics

The Duolong district is characterized by large resources, and a variety of deposit. There are porphyry copper (gold, silver) deposits such as Bolong and Duobuza, porphyry-epithermal copper (gold, silver) deposits, such as Tiegelongnan, and breccia hosted Naruo and Nadun copper (gold, silver) deposits. These deposits are all related to the early Cretaceous intermediate-silicic granodiorite porphyry.

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References


Paleoproterozoic porphyry-related Au ± Cu (± Mo) systems in the Alta Floresta gold province, southern Amazonian Craton, Brazil: the case of the X1 and Paraíba deposits

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Abstract. The Alta Floresta Gold Province (AFGP) consists of Paleooproterozoic plutono-volcanic sequences (1.98 - 1.75 Ga) originated from a series of successive magmatic arcs that accreted to the southwestern margin of the Central Amazonian Province. The province contains a significant number of intrusion-hosted gold systems, some of which are temporally and spatially associated with 1.8 - 1.7 Ga quartz-feldspar porphyries. Among these, X1 and Paraíba deposits are two important examples in which the Au ± Cu (± Mo) mineralizations, both disseminated or in quartz veins, are partially hosted, respectively, by ca. 1.80 Ga and ca. 1.78 Ga quartz-feldspar porphyries of tonalite and syenogranite composition. In both deposits, the gold (Ag = 5 - 30%)-bearing pyrite ±chalcopyrite ± molybdenite zones are contained within phengitic muscovite-chlorite-rich zones with distal propylitic and potassic alteration with K-feldspar. Molybdenite Re-Os and pyrite Pb-Pb systematics constrain the mineralization age to 1.84 - 1.78 Ga, which overlaps with the host porphyry ages. Hence, the X1 and Paraíba deposits represent magmatic-hydrothermal systems that bear broad similarities to porphyry gold-rich systems, but that have formed at deeper crustal levels with a significant involvement of magmatic CO₂-rich fluids.

1 Introduction

The Alta Floresta Gold Province (AFGP) is located in the southern sector of the Amazonian Craton, between the Venturi - Tapajós (2.0 – 1.8 Ga) and Rio Negro - Juruena (1.80 – 1.55 Ga) geochronological provinces (Tassinari and Macambira 1999) in the Mato Grosso state, Brazil. The province outlines a NW-SE to E-W-striking belt of 500 km extension and 30 km wide containing plutonic-vulcanic sequences generated in continental arc settings during the Paleooproterozoic (1.95 – 1.75 Ga; Souza et al. 2005). A significant number of high grade, low tonnage (< 5 t) gold systems occur throughout the province which on the basis of mineralization style and metallic association, are grouped into: (1) disseminated and structurally-controlled vein-type Au ± Cu (± Mo) deposits (e.g. Luizão, Pê Quente, X1, Serrinha and Paraíba deposits); (2) structurally-controlled vein-type Au + Zn + Pb ± Cu deposits (e.g. Francisco, Bigode and Luiz deposits); and (3) disseminated Cu + Mo ± Au deposits (e.g. Ana and Jaca deposits). These deposits are commonly hosted by relatively oxidized I-type, calc-alkaline to sub-alkaline, medium to high potassium, metaluminous to slightly peraluminous granitic intrusions of tonalite to syenogranite compositions and quartz-feldspar porphyries representative of A2-type post-orogenic alkaline granites of ages from 1.98 to 1.78 Ga (Paes de Barros 2007; Assis 2011, 2015).

Group (1) is by far and large the most abundant in the province and from which gold has been exploited by artisanal mining since the 1980s. These intrusion-hosted deposits have been interpreted as orogenic gold systems (Santos et al. 2001), intrusion-related gold systems (Paes de Barros 2007), or similar to gold-rich porphyry systems (Moura et al. 2006). In this work we use the porphyry-related X1 and Paraíba Au - (Cu - Mo) deposits to argue on the basis of wall-rock alteration, ore associations, fluid regimes, and U-Pb, Pb-Pb and Re-Os geochronology, that these deposits may be deep crustal level analogues of gold-rich, copper and molybdenium-poor, porphyry systems.

2 Host rocks and hydrothermal alteration

The X1 Au ± Cu (± Mo) deposit is hosted by an equigranular to porphyritic biotite granodiorite and a quartz-feldspar porphyry of tonalitic composition (Rodrigues 2012). The porphyry is devoid of mafic phases and contains 5 - 10% quartz and plagioclase phenocrysts in an aphanitic to very-fine-grained groundmass composed of quartz (60 - 75%), plagioclase (15 - 30%) and K-feldspar (1 - 8%), with apatite, zircon and rutile as accessory phases (Fig. 1A). Its geochemical composition is consistent with a highly evolved, calc-alkaline, high K, sub-alkaline and slightly peraluminous magma formed in within a continental arc onset. Both the biotite granodiorite and the quartz-feldspar porphyry at the X1 deposit have been variably affected by the following hydrothermal alteration.
types: (1) strong potassic alteration with orthoclase ± hematite, usually distal to the mineralized zones; (2) phyllic alteration zones with coarse-grained muscovite + quartz + sulfides that partially or completely replace that potassic alteration within either the core of the granitic host as alteration halos around quartz-rich veins (3) propylitic alteration with chlorite + epidote + calcite ± apatite ± rutile ± hematite ± pyrite distal to the ore zones; (4) distal and restricted chloritic alteration; and (5) pervasive to late calcite-rich veinlets, locally with bladed calcite (Rodrigues 2012).

The host rocks of the Paraíba Au - (Cu - Mo) deposit include fine-grained equigranular biotite gneiss with an alkali-feldspar granitic composition, medium to coarse-grained equigranular biotite tonalite, and quartz-feldspar porphyry of syenogranitic composition (Trevisan 2015; Batolomeu 2016). The quartz-feldspar porphyry forms meter-wide dikes that cut the tonalite and gneiss. It consists of about 20% phenocrysts of microcline (40%), quartz (40%) and orthoclase (20%) in a medium to fine-grained groundmass containing microcline (35%), quartz (40%), plagioclase (20%), orthoclase (3%) and biotite (2%) (Bartolomeu 2016; Fig. 1B).

**Figure 1.** a X1 quartz-feldspar porphyry with pyramidal quartz phenocrysts. b Paraíba quartz-feldspar porphyry with microcline, quartz and orthoclase phenocrysts immersed in a matrix affected by strong potassic alteration with K-feldspar.

Potassic alteration with K-feldspar (orthoclase + quartz + hematite ± microcline ± pyrite ± molybdenite) and propylitic alteration (epidote + clinozoisite + chlorite + carbonate ± quartz ± magnetite) predominate outwards to the mineralizing zones. Phyllic alteration zones defined by sericite and/or coarse-grained muscovite + quartz ± carbonate ± magnetite ± sulfides are proximal to the gold ± copper ± molybdenum vein zones within the tonalite and quartz-feldspar porphyry, together with more subordinate silicic alteration represented by fronts of replacement or aggregates and related veins exemplified by quartz veins, stockwork zones, fractures or hydrothermal breccias. Particular in shear zone hosted gold-sulfide veins, potassic alteration with biotite + quartz + magnetite + carbonate +

sulfides is replaced by chloritic alteration (chlorite + quartz + carbonate ± magnetite ± rutile ± titanate ± zircon ± sulfides). Additionally, also occur late veinlets of variable composition (carbonate, quartz, quartz + carbonate, epidote, sericite and chlorite) (Trevisan 2015; Batolomeu 2016).

### 3 Gold ± copper (± molybdenium) ore zones

The gold mineralization at the X1 deposit is mainly disseminated within the phyllic alteration zones and to a lesser extent in the quartz veins. The ore assemblage consists of pyrite ± chalcopyrite ± gold ± molybdenite ± rutile ± hematite, and gold grades range from 0.5 to 10 g/t. Quartz veins usually exhibit a centimeter to meter-wide phyllic alteration halo and contain the same sulfide mineral assemblage, but lower gold contents (< 0.2 ppm). Within the phyllic zone, chalcopyrite and molybdenite have generally filled pyrite, quartz and muscovite interstices, or occur as small inclusions within pyrite. Gold (Ag = 20 - 30 wt.%) appears as small inclusions (~ 20 µm) in pyrite together with tsumoite (BiTe), hessite (Ag2Te), galena, monazite, sphalerite, apatite and molybdenite (Figs. 2A-B; Rodrigues 2012).

Gold ± copper (± molybdenium) mineralization at Paraíba is mainly associated with meter-wide gold lode veins controlled by a N05W / 65-70NE dextral strike-slip shear zone, as well as with a set of 5 to 20 cm wide veins. To a lesser extent, disseminated mineralization also occurs at Paraíba, particularly in the quartz-feldspar porphyry within the silicic, phyllic and potassic (with K-feldspar) alteration halos. The ore zones mainly comprise pyrite ± chalcopyrite ± molybdenite and minor magnetite. Covellite and hematite have commonly replaced chalcopyrite. Galena, sphalerite, scheelite, barite, monazite, xenotime, Bi-Te rich phases, bismuth, aikinite (PbCuBiS3), oxyallanite, hessite (Ag2Te), stutzite (Ag5-xTe3) and thorite occur in subordinate concentrations, typically as inclusions within pyrite. Gold (Ag = 5 - 24 wt.%) occurs as inclusions (2 - 20 µm) in pyrite and chalcopyrite (Fig. 2C-D; Trevisan 2015; Batolomeu 2016).
Fluid inclusions in muscovite-sulfide-quartz veins from the Paraíba mineralized vein quartz and display degree of fill in the 0.10 - 0.80 range. Salinity is generally low (up to 8.7 wt.% NaCl eq.) and homogenization temperatures vary from 160°C to 316°C, with higher concentrations at 285°C (Trevisan 2015). Previous microthermometry investigations (Silva and Abram 2008) have shown that type 4 inclusions consist essentially of a CO₂-liquid phase.

5 Temporal relationships between granitic hosts and the Au ± Cu (± Mo) ore

Zircon U-Pb dating using SHRIMP IJe gave a crystallization age of 1.901 ± 13 (MSWD = 1.3) and 1.784 ± 10 Ma (MSWD = 0.54) for the biotite granodiorite and quartz-feldspar porphyry, respectively, at the X1 deposit. The X1 quartz-feldspar porphyry exhibits TDM ages of 2.18 to 2.12 Ga and εNd(t) values ranging from -1.7 to -1.39 suggesting a mixing between a metasomatized mantle and crust (Assis 2015). Re-Os age obtained in molybdenite separates yielded a weighted average model age at 1.786 ± 5 Ma (MSWD = 0.16) (Assis 2015).

At the Paraíba deposit, zircon U-Pb dating also by SHRIMP IJe provided a crystallization age of 2.014 ± 5.1 Ma (MSWD = 2.0; Trevisan 2015) and 1.820 ± 17 Ma (MSWD = 0.4; unpublished data) for the biotite tonalite and quartz-feldspar porphyry, respectively. The geochemical investigation of the Paraíba quartz-feldspar porphyry is still under progress. A Pb-Pb age obtained in pyrite separates provided a geochronometry independently of age of 1.841 ± 22 Ma (MSWD = 1.6; Santos 2011) for the Paraíba Au-(Cu-Mo) mineralization.

6 Conclusions

The continental arc setting attributed to the AFGP plutono-volcanic sequences, the close spatial relationship between the Au ± Cu (± Mo) mineralizations and granitic plutons, and the types and distribution of the hydrothermal alteration, collectively suggest that the X1 and Paraíba deposits may be genetically linked to the emplacement of magmatic-hydrothermal systems. This is further corroborated by the pyrite Pb-Pb and molybdenite Re-Os ages of 1.841 ± 22 and 1.786 ± 5 Ma that remarkably overlap the crystallization ages of the porphyries at the Paraíba (1.820 ± 17 Ma) and X1 (1.784 ± 10 Ma) deposits, respectively. Similar age interval has also been obtained for other intrusion-hosted gold deposits of the province: Re-Os model ages of pyrite are in the range of 1.790 ± 9.4 Ma to 1.782 ± 8.9 for the Luizão and of 1.792 ± 9.0 to 1.784 ± 11 Ma for the Pé Quente deposits (Assis, 2015); Re-Os model age of 1805 ± 7 Ma in ore-related molybdenite at the Juruna gold district in the northern
sector of the province (Acevedo 2014). Nevertheless, porphyry outcrops or interception of porphyries by drill cores have not been reported so far at the Luizão and Pé Quente deposits. This age interval is further confirmed by the sericite $^{40}$Ar/$^{39}$Ar ages between 1.779 ± 6.5 and 1.777 ± 6.3 Ma from the sericitic alteration halo of the Francisco gold-base metal deposit, which are in agreement to the 1.774 ± 7.5 Ma União do Norte porphyry (Assis 2015). Hence, the interval of 1.841 Ma - 1.782 Ma seems to mark an important regional gold metallogeny episode in the AFGP. The regional felsic magmatism in the province that displays a broad temporal association with this 1.84 -1.78 Ga gold event includes volcanics and granitic intrusions that belong to the Colédor group (1.82 - 1.77 Ga), the Paranaíta (1.81 - 1.79 Ga) and Teles Pires intrusive suites (1.78 - 1.75 Ga). These units show no evidence of regional metamorphism, but have been extensively affected by regional E to NW-striking brittle-ductile shear zones. The first two units show affinities to relatively oxidized I-type, calc-alkaline, medium to high K, metaluminous to slightly peraluminous plutonic-volcanic sequences from continental arc settings and that commonly contain intrusion-hosted deposits/occurrences (e.g., Juruena gold district; Acevedo 2014). The latter suite, on the other hand, represents post-orogenic to anorogenic felsic magmatism and hitherto shows no evidence of hosting gold deposits. Despite the lack of consensus regarding the regional tectonic framework of the AFGP, the Colédor group and Paranaíta intrusive suites have been interpreted as part of the evolution of the Juruena magmatic arc (~1815 to 1780 Ma; Silva and Abram 2008; Duarte 2015). Within this framework, the X1 and Paraíba porphyries and the accompanying Au - (Cu - Mo) mineralizations were likely emplaced either during late accretionary orogeny or post-orogenic extensional stages (Assis 2015; Duarte 2015).

At the deposit scale, exsolution of H$_2$O-CO$_2$ fluids from the crystallizing porphyries may have triggered the magmatic-hydrothermal system. The CO$_2$-rich nature of these magmatic fluids suggest that emplacement of the causative porphyries likely occurred at deep crustal levels, since the solubility of volatiles in magma is controlled dominantly by pressure (Lowenstern 2001). Fluid phase separation accompanied by progressive mixing with externally-derived fluids (meteoric?) causing dilution, cooling (400°C - 350°C) and increase in fO$_2$, may have caused the solubility of Au and other metals to decrease and ore to precipitate.

On the basis of the geotectonic setting, combined with the geological characteristics of the mineralizations and their temporal relationship with the porphyries, we argue that the ore-forming processes at the X1 and Paraíba Au- (Cu - Mo) deposits were similar to those observed in porphyry Cu ± Mo ± Au, but at deeper crustal levels. In a similar scenario, Paleoproterozoic Cu - Au and Cu - Mo ± Au porphyry-type mineralization associated with sub-volcanic felsic rocks formed in continental magmatic arc settings, together with calc-alkaline volcanic rock hosting epithermal Au and base metal mineralization have also been reported in the Tapajós Gold Province in the southern Amazonian Craton (Juliani et al. 2005).

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